DEPOSITION OF COLLOIDAL SPHERES UNDER QUIESCENT CONDITIONS

by

CHAI GEOK TAN

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Department of Chemical Engineering

The University of British Columbia
1956 Main Mall
Vancouver, Canada
V6T 1Y3

Date October 10, 1987
ABSTRACT

The phenomenon of deposition (or release) of fine particles or other microscopic species, suspended in a liquid, onto (or from) a foreign substrate surface plays a critical role in many natural and industrial processes. Traditionally, the analysis of this phenomenon has been conceptually divided into two steps — the transport step and the adhesion step. Attempts to understand the role of the adhesion step on the overall deposition process under most practical situations are complicated by the presence of a large number of interdependent parameters such as double layer thickness, particle and wall zeta-potential, particle size and flow, amongst others. Thus, as a first step towards gaining a better understanding of the phenomenon, an experimental study of a very simple deposition system, where only the random nature of the deposition process and the double layer interactions between deposited particles are important, was undertaken.

In this idealized system, a stable suspension of monodispersed, negatively charged colloidal silica spheres one micron in diameter, suspended in an aqueous medium in a specially constructed deposition cell, were allowed to settle by gravity and be deposited permanently onto a cationic polymer-coated glass cover slip. The magnitude of surface potential was altered by adjusting the pH of the suspension using NaOH and HCl, while the electrical double layer thickness was varied by dissolving different predetermined quantities of KCl into the suspension.

The results showed that the trends in the experimental surface coverages
obtained were in accordance with expectation in that as the double layer thickness, $1/\kappa$, or the particle zeta potential, $\zeta_p$, increased (leading to an increase in the interaction energy between the particles), the surface coverage decreased. Furthermore, the extent of surface coverages obtained when both $1/\kappa$ and $\zeta_p$ were changed was found to be greater than that when $1/\kappa$ alone was used as the controlling variable. A separate series of studies examining the effect of substrate double layer thickness on surface coverage was also performed by dissolving different predetermined quantities of $\mathrm{K}_3\mathrm{PO}_4$ into the suspension so that the substrate and the particles could differ in their respective double layer thicknesses. The results of surface coverages obtained in this study showed that the influence exerted by the substrate double layer was negligible. Besides these findings, the presence of geometric exclusion due to the random nature of the deposition process was also noted, although its effect was difficult to quantify.

Besides the systematic experimental study of colloidal deposition, attempts were made to develop two computer simulation models to generate deposition prediction which could be compared with results measured experimentally. The first scheme involved a two-dimensional simple rejection model where only non-overlapping particles were deposited, while the second scheme consisted of a three-dimensional model where the rolling of sedimenting particles over the surfaces of previously-deposited particles as well as the stacking of particles were allowed. Comparison of experimental results with those obtained using the two-dimensional model revealed that for all cases, the simulated results consistently underpredicted the experimental results due to the oversimplifying nature of the simulation. The trends in the experimentally obtained results,
however, were approximated by the simulated results. Owing to its very complex nature, successful completion of the three-dimensional model simulation did not materialize. It is expected, however, that when such a model is successfully completed, it will yield predicted results which are in better quantitative agreement with those measured experimentally.

Besides the above, a separate study examining the effects of reaction temperature and the types of alcoholic solvent used on the properties of silica particles produced was also performed. This study led to the development of a novel method in which dispersed, uniform-sized, spherical silica particles in the size range of 0.2 to 2.0 μm can be produced by simply varying the reaction temperature and the type of alcoholic solvent used.
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1. INTRODUCTION

Judging from the number of publications in the literature, it can easily be concluded that a great deal of research effort has been devoted towards understanding the phenomenon of deposition (or release) of fine particles or other microscopic species, suspended in a liquid, onto (or from) a foreign substrate surface. This phenomenon plays a critical role in many natural and industrial processes and a knowledge of it is of paramount importance in the design and operation of the processes involved.

Examples of applications or processes involving this phenomenon are: physical separation processes such as the removal of suspended particles in a packed bed filtration unit and froth flotation of mineral fines; biomedical and physiological processes such as metastasis where malignant cells are carried in the bloodstream from the primary tumor to other locations in the body forming secondary tumors, atherosclerosis where cholesterols are deposited on the interior walls of the arteries, and thrombosis where blood cells adhere to injured vessels thereby occluding the flow of blood during injuries; biological processes such as the attachment of microbes onto other surfaces in their search for nutrients, stabilization and establishment of intermicrobial relationships; industrial processes such as chemical and thermal fouling of surfaces; and deposition of sizing materials onto cellulose fibers during paper making.

The analysis of the deposition of colloidal species onto a substrate is usually accomplished by conceptually dividing the process into two steps:
1. a transport step in which the particles are transferred from the bulk of the solution to the interface region, and

2. an adhesion step in which the particles in the interface region are attached to the substrate by overcoming various surface interaction forces which arise at short distances of separation.

The forces relevant to these two steps can in turn be classified into three categories:

1. forces related to the motion of the fluid and the motion of the particles relative to the fluid and forces causing the Brownian motion of the particles; the hydrodynamic drag forces and the convection-diffusion effects fall under this category;

2. external forces such as those due to electric, magnetic and gravitational fields; and

3. chemical and colloidal forces which result from the interactions of substrates and particles with molecules and ions in the suspending medium; these include the van der Waals, electrical double layer, Born repulsion and structural forces.

The transport step is usually controlled by those in the first two categories which are responsible for bringing the particles to the interfacial region while the adhesion step is dominated by the forces in the third category, which decide if a particle will be deposited onto the substrate.

Thus, it can be seen that this classification is useful in defining clearly the specific role played by each step and hence each type of force in the overall deposition process. Although this separation of the process into two steps is largely conceptual, studies by some investigators have actually confirmed the validity of this concept under certain conditions.
The transport step has traditionally been a popular field with chemical engineers and fluid dynamicists. Accordingly, theoretical and experimental studies in this area are abundant and the subject is well understood for a great variety of flow situations. Recently, an excellent review paper in this area has been presented by Papavergos and Hedley (4).

In the present investigation, the primary objective is to gain a better understanding of the role played by the forces in the adhesion step of the particle deposition process, and hence this chapter will mainly focus on a review of those theoretical and experimental studies that explore the role of colloidal forces on deposition and resuspension.

It is anticipated that the rate of deposition of a colloidal species onto a substrate is critically influenced by the physicochemical interactions between the colloidal species and the substrate. Despite the diversity of the applications listed above, the underlying physical and chemical phenomena relevant to the deposition of the particles remain the same. The most important of these interactions are the London-van der Waals and the electrical double layer interactions.

Attempts to understand the role of physicochemical phenomena on the deposition process are complicated by the presence of a large number of
interdependent parameters and sometimes by the practical difficulties in quantifying some of these parameters sufficiently accurately. In view of the above, many experimental studies have been carried out over the years to investigate separately or jointly the role of the relevant parameters on colloidal deposition. Examples of parameters studied include types and strength of electrolytes in the dispersion medium (5,6,7,8,9), pH of suspension (10), size and concentration of particles (11), polydispersity of particles (12), and types and characteristics of substrates (6,13,14,15), amongst others.

Owing to the enormous amount of published information about this subject, this chapter is not intended to provide a comprehensive review of all the literature on the deposition of colloidal species. Only the theoretical and experimental studies which are the most relevant to the present thesis will be briefly discussed.

Although there have been some studies conducted on the deposition of colloidal particles onto spheres in packed beds (16,17,18,19), the results do not yield any direct information on local deposition rates due to the method used for obtaining experimental data, which was merely a comparison of inlet and outlet suspended particle concentrations. The first systematic study of particle deposition under well-defined conditions was reported in 1966 by Marshall and Kitchener (13), who introduced a rotating disc technique to investigate the deposition of carbon black particles, suspended in an aqueous medium, onto the disc surface as a function of
the particle and substrate zeta potentials and the thickness of the double
layer. The surface characteristics of the disc were altered by coating
different types of plastics onto it while the thickness of the double layer
was changed through the addition of KCl to the suspension. The
concentration of accumulated particles was measured as a function of time
by rinsing the disc, drying it in a dessicator, and counting the particles
under a microscope. Their results showed that the deposition was greatest
when the electrical double layer interaction between particles and solids was
attractive. However, when the double layer interaction was repulsive,
particularly when the double layer thickness increased, a great reduction in
deposition was observed. Similar experiments employing the same technique
were later performed by Hull and Kitchener (14) who, instead of carbon
particles, used a stable colloid of monodisperse polystyrene spheres. Similar
trends in results, as compared with the results of Marshall and Kitchener,
were observed.

This rotating disc technique of studying particle deposition proved
successful and has been used by several other investigators in the field
(20,21,22). Besides the rotating disc collector, collectors of other geometries
have also been employed. These include cylindrical (23), spherical (24) and
parallel-plate channel (25) collectors.

As mentioned earlier, deposition or adhesion of cells on surfaces
plays an important role in many biological and biomedical processes.
Ruckenstein, Marmur and co-workers have long been involved in
systematically investigating the effects of various forces on the static deposition of cells onto surfaces (26,27,28,29). Besides thermal and surface interaction forces, the effect of gravity on cell deposition on either horizontal or inclined surfaces has also been investigated recently by these researchers and by others (30,31). These results indicated that gravity plays a significant role in the deposition process.

Recently, Tamai, Suzawa and co-workers (6,15,32) have studied the effects of pH, types and quantities of electrolytes and surface characteristics on both the deposition rate and the surface coverage by depositing anionic and cationic latex particles onto various plastic fibers that exhibit different surface properties. The method involved the immersion of a rectangular (1x2 cm) piece of preweighed plastic fabric into a 200 ml latex dispersion of known solids concentration. The electrolyte concentration was adjusted using either sodium chloride or sodium sulfate. The pH was varied using hydrochloric acid or sodium hydroxide. The rate of deposition was determined through turbidity measurements of the dispersion at regular intervals using a spectrophotometer. At the end of a 12-hour period, the immersed cloth was withdrawn and rinsed with a particle-free solution of the same composition to remove undeposited free particles. The sample was then dried in air, coated with gold and photographed using a scanning electron microscope.

Their results showed that the rate of deposition increased as the concentration of electrolytes increased. Different electrolytes at the same
ionic strength gave similar results. Increasing the pH of the suspension increased the magnitude of the zeta potentials of both the particles and the fibres, thus raising the repulsive energy barrier and reducing the rate of particle deposition. One peculiar finding observed was that despite potential energy maxima exceeding 500 kT, measurable deposition still occurred. The authors suggested that the observed deposition, which is many orders-of-magnitude greater than predicted theoretically, must be due to surface heterogeneity.

In many experimental studies (e.g., 33,34,35,36) of colloidal deposition involving fluid flow, it is commonly observed that initially the rate of deposition is linear with time. However, as surface coverage increases, the rate of deposition decreases asymptotically with time and usually much less than a monolayer coverage is obtained when the substrate is "saturated". For example, Bowen (33) reported in his thesis that the maximum surface coverage attained never exceeded 10%. In view of this, several possible causes of incomplete coverage have been postulated to rationalize this behaviour. The first is that of a change in the surface chemical state or the charge of the substrate as the substrate surface becomes covered with particles. In an attempt to predict the effect of surface coverage on the rate of particle deposition in packed beds, Wnek et al. (37) have proposed a model based on this argument. In their model, they suggested that the deposition of each particle alters the average charge density of the entire surface by a fixed amount such that, when the surface is completely covered with particles, a new plane surface is created which has the same
charge density as the particles. Thus, because the charge density and the $\zeta$-potential (Stern potential) are closely related, the deposition of negatively charged particles onto a positively charged substrate effectively decreases the $\zeta$-potential of the substrate. With sufficient deposition, the substrate $\zeta$-potential becomes negatively charged. This gives rise to a repulsive potential energy barrier and hence, a reduced rate of deposition. This model, although it predicted qualitatively the correct shape of the accumulation curve and the general observed influence of the wall $\zeta$-potential, failed to yield good quantitative agreement with the experimental results (33). Furthermore, it is deemed to be fundamentally incorrect for the reason outlined below.

Besides energy heterogeneity mentioned above, the observed behaviour may also be due to surface heterogeneity, i.e., due to a change in the geometry of the substrate surface and a reduction in surface area available for deposition introduced by the deposited particles. This explanation was first put forward by Ruckenstein et al. (27) in their development of a model aimed at explaining the coverage-dependent rate of cell deposition through a stagnant fluid onto a horizontal plane by sedimentation and diffusion. Although the approach taken by this model is fundamentally sound, it yields complete surface coverage as time becomes very large under all circumstances. This result will never be true for most, if not all, experimental conditions. Thus, to improve upon this model, Bowen (33) replaced the particle radius by an effective particle radius on the recognition of the fact that because of the finite thickness of the electrical double layer
surrounding each sphere, there exists a minimum distance of separation below which two particles cannot approach each other. The resulting final surface coverage thus obtained is approached asymptotically and will always be less than complete coverage.

It was further recognised that, because deposition is a random process and hence there exists finite probability that one particle would approach to within any distance (greater than twice the effective particle radius) of a second particle, a correct accounting for the finite size of the deposited particles would therefore lead to the possibility of some areas of the uncovered surface being totally excluded from further deposition, and hence an even smaller value of the final surface coverage will be obtained. Based on this reasoning, Bowen has derived an equation representing the coverage at which the maximum possible geometric exclusion can occur. Manifestations of this effect on further particle deposition have been observed experimentally by other investigators (34,35,36,38).

However, despite these two relationships representing the two extremes of surface coverage, Bowen found that the measured surface coverage for most runs was well below the envelope of possible results predicted by the two relationships. Thus, besides the effects mentioned above, some other effects must be present. He suggested that an additional contributing factor arises from the fact that the suspension is flowing. That is, when a particle carried by a fluid in laminar flow deposits on a surface, the fluid streamlines are forced to move over and around the
particle. At very low surface coverages, when the randomly deposited particles are relatively far apart, the distribution of streamlines over the bare portion of the wall is probably little affected. However, when this distance becomes a few particle diameters, the distribution of streamlines over the bare wall is influenced by the presence of deposited particles; the closer these particles are to each other, the more the streamlines are pushed away from the wall. Thus, it is hypothesized that, as the spacing between deposited particles decreases, the probability of a particle diffusing the increased distance to the wall will be greatly reduced, and hence there will be a reduction in deposition.

Thus, it can be seen that the relationship between subsequent particle deposition and surface coverage is not a simple one, but is influenced by a variety of experimental parameters such as double layer thickness, particle and wall $\xi$-potentials, particle size and flow, among others. Therefore, in order to gain a better understanding of deposition behaviour, it will be necessary in the present investigation to begin by studying very simple deposition situations under stagnant conditions, so that only the random nature of the deposition process and the double layer interactions between deposited particles are important.

Once randomness is included, it is no longer possible to model the process analytically. Several numerical studies have been carried out in the past which use random number generators to help simulate random deposition or flocculation processes. One of the earliest models in this area
was developed by Marjorie J. Vold (39,40,41,42), who studied the volume of a sediment formed by the settling of spherical particles that cohere permanently on first contact. The physical situation envisaged is a suspension of randomly distributed particles which are allowed to fall vertically under gravity. In the simulation, this was represented by a Monte Carlo model in which N particles are dropped one by one into a container and each particle is allowed to come to rest when it strikes either the bottom (i.e. no previously dropped particle on its way down) or the first previously dropped particle it contacted on its way down. The x- and y- starting coordinates were generated using a random number generator. The simulation did not actually involve motion of the particle through successive points; instead, the path and resting place of the particle were determined by methods of analytic geometry. Similar studies on cluster formation were performed later by Sutherland (43,44) and, more recently, by Meakin (45).

Although greater in number than the published literature on three-dimensional random deposition, studies of two-dimensional random deposition have generally focussed on finding the final maximum random packing density, i.e., the so-called "jamming limit" (46,47), although studies about other aspects of this problem have also been conducted. Some of these include: the geometry of depositing species (48), the monolayer structure formed and the packing fraction obtained through contraction of the coordinate system (49), and the relationship between one- and two-dimensional random packing (50).
Feder and Giaever (47,48) have performed the computer simulation of two-dimensional random sequential deposition of discs onto a planar surface in an attempt to verify the results of the experimental study of deposition of ferrition molecules, a visible, nearly spherical, rigid, iron-storage protein found in horse spleen, onto Lexan polycarbonate and carbon surfaces. In their experimental studies, although the dependence of surface coverage on many physicochemical properties of the surfaces were acknowledged, no attempts were made to quantify these properties and only a couple of attempts, in a non-systematic manner, were made to study the effects of variations in pH and added electrolytes on deposition. Furthermore, the deposited surface was rinsed and dried before micrographs were taken. These procedures create the possibility of resuspension and rearrangement of deposited particles. Thus, extremely poor agreement, both in terms of quantity and pattern of surface coverage, between experimental and simulated results were obtained. The only useful conclusion that can be drawn from their study is that the computer simulated maximum surface coverage was found to be 54.73%, a figure which has also been reported by others (51).

In the present investigation, besides the systematic experimental study of colloidal deposition under stagnant conditions, two computer simulation models have been developed to generate predicted deposition results which can be compared with those measured experimentally. The first, similar to the one employed by Feder and Giaever, uses a two-dimensional approximation in which disc-like particles are simply placed
at random coordinates on a plane surface. Only those particles that do not overlap previously deposited particles are assumed to remain on the surface. The second model involves random deposition in a three-dimensional environment where particles are allowed to sediment under gravity towards the deposition surface. When they reach the vicinity of the surface they are permitted to roll over previously deposited particles to eventually contact the surface or to become "nested" within the other particles. Only those that ultimately contact the surface are considered to be part of the final deposit.

For both models, the final fraction of the total area occupied by all the deposited particles is determined. Calculations of the new fraction of total area occupied by deposited particles on the substrate area are also performed by successively reducing the particle diameter. This manipulation of the data enables the determination of surface coverage as a function of $\kappa a$, where double layer thickness $(1/\kappa)$ is deemed to be the difference between the reduced and the original particle radius and $a$ is the reduced particle radius.

In Chapter 2 of the present study, the relevant theoretical background pertaining to the thesis is presented. This includes discussions in Section 2.1 on the initial development of the Gouy-Chapman electrical double layer theory, the simplifying approximation by Debye-Hückel, the definition of double layer thickness, and further refinements on the electrical double layer model by Stern and Grahame. This section is followed by a brief
review (in Section 2.2) on electrokinetic phenomena, with its resulting emergence of \( \xi \)-potential and the techniques by which this parameter can be quantified. In Section 2.3, a short qualitative discussion is presented on the effects of electrolytes on the \( \xi \)-potential and double layer thickness, and this is followed in Section 2.4 by a brief review of the theory of the various surface interaction forces involved in the deposition process, particularly the electrical double layer and the London-van der Waals interaction forces.

Chapter 3 discusses in detail the experimental requirements such as the production and preparation of various experimental materials, the design of the experimental apparatus, and the techniques used in the acquisition of experimental data. In particular, a novel method exploiting the effect of temperature control in the preparation of monodisperse silica spheres in the colloidal range is presented in detail in Section 3.2.2.

Mathematical details for the formulation of the computer algorithm necessary for the simulation of particle deposition are presented in Chapter 4. The results of the experiments are discussed in Chapter 5 while the summary and conclusions are presented in Chapter 6.
2. THEORETICAL BACKGROUND

2.1. THE ELECTRICAL DOUBLE LAYER

In general, most substances acquire a surface electric charge when brought into contact with an aqueous medium. This acquisition of an electrical charge occurs either as a result of the ionization of slightly soluble surface groups or as a result of the preferential adsorption of specific ions from solution. This surface charge influences the distribution of nearby ions in the aqueous medium in order to maintain electro-neutrality. As a consequence, ions of opposite charge (counter-ions) are attracted towards the surface and ions of like charge (co-ions) are repelled away from the surface. This, together with the mixing tendency of random molecular (thermal) motion, leads to the formation of an electric double layer made up of the charged surface and a neutralising excess of counter-ions over co-ions near the surface. This excess charge is distributed in a diffuse manner in the aqueous medium such that its concentration falls from a maximum at the interface to zero at distances sufficiently removed from the surface (bulk of solution). This system of two charge layers, a fixed charge on the surface of the solid and a smeared-out or diffuse layer in the liquid next to the solid, is the Gouy-Chapman model of the electrical double layer.

2.1.1. The Gouy-Chapman Model

The mathematical development of this model has been treated in standard texts and hence only a simplified version of the treatment will be given here.
In essence, the model is based on the following assumptions:

1. The surface is assumed to be flat, of infinite extent and uniformly charged.

2. The ions in the diffuse part of the double layer are assumed to be point charges.

3. The solvent is assumed to influence the double layer only through its dielectric constant or permittivity, which is assumed to be constant throughout the diffuse part.

4. The electrolyte is assumed to consist of a single cationic and anionic species, both having the same charge number \( z \).

By using the Boltzmann distribution to describe ionic concentration, and Poisson's equation to relate charge density and electric potential, expressions which describe the decay of potential with distance from the charged surface are derived.

Let the electric potential be \( \psi_0 \) at a flat surface and \( \psi \) at a distance \( x \) from the surface in the electrolyte solution. By applying the Boltzmann distribution, the probability of finding an ion at the position \( x \) is:

\[
n_{\pm} = n_0 \exp \left[ \frac{\mp ze_0 \psi}{kT} \right] \tag{2.1}\]

where \( n_+ \) and \( n_- \) are the respective numbers of positive and negative ions per unit volume at points where the potential is \( \psi \) (i.e. where the electric potential energy is \( +ze_0 \psi \) and \( -ze_0 \psi \), respectively), \( z \) is the valency of the ions, \( e_0 \) the electron charge, \( k \) the Boltzmann constant, \( T \) the absolute temperature and \( n_0 \) the identical bulk concentration of both ionic species where the potential \( \psi = 0 \).

The net volume charge density \( \rho \) at points where the potential is \( \psi \) is
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related to the ion concentration as follows:

\[ \rho = z e_0 (n_+ - n_-) \]  

[2.2]

Substituting Equation [2.1] into Equation [2.2] yields

\[ \rho = z e_0 n_0 \left[ \exp\left( \frac{-z e_0 \psi}{kT} \right) - \exp\left( \frac{+z e_0 \psi}{kT} \right) \right] \]  

[2.3]

Since \( e^x - e^{-x} = 2 \sinh(x) \), therefore Equation [2.3] can be rewritten as

\[ \rho = -2 z e_0 n_0 \sinh \left( \frac{z e_0 \psi}{kT} \right) \]  

[2.4]

The variation of potential with distance from a charged surface is described by Poisson’s equation

\[ \nabla^2 \psi = -\frac{4 \pi \rho}{\epsilon} \]  

[2.5]

which, for an infinite planar surface, takes the form

\[ \frac{d^2 \psi}{dx^2} = -\frac{4 \pi \rho}{\epsilon} \]  

[2.6]

where \( \epsilon \) is the dielectric constant of the aqueous medium.

Combination of Equations [2.4] and [2.6] gives rise to what is known as the Poisson-Boltzmann equation
\[
\frac{d^2\psi}{dx^2} = \frac{8\pi ze_0n_0}{\epsilon} \sinh \left[ \frac{ze_0\psi}{kT} \right] \tag{2.7}
\]

The solution (52) of this expression, with the boundary conditions \( \psi = \psi_0 \) when \( x = 0 \); and \( \psi = 0 \), \( d\psi/dx = 0 \) when \( x = \infty \) can be written in the form

\[
\psi = \frac{2kT}{ze_0} \ln \left[ \frac{1 + \gamma \exp(-\kappa x)}{1 - \gamma \exp(-\kappa x)} \right] \tag{2.8}
\]

where

\[
\gamma = \frac{\exp[(ze_0\psi_0)/(2kT)] - 1}{\exp[(ze_0\psi_0)/(2kT)] + 1} \tag{2.9}
\]

and

\[
\kappa = \left[ \frac{8\pi e_0^2 n_0 z^2}{1000 \epsilon kT} \right]^{0.5} = \left[ \frac{8\pi e_0^2 N_A C z^2}{1000 \epsilon kT} \right]^{0.5} \tag{2.10}
\]

where \( N_A \) is Avogadro’s constant and \( C \) is the concentration of electrolyte.

The assumption that the potential in the diffuse part of the double layer can be reasonably well-represented by the solution of the Poisson-Boltzmann equation is generally considered to be valid below electrolyte concentrations of the order of \( 10^{-2} \text{M} \) for 1-1 electrolytes (53). Studies by Krylov and Levich (54) for concentrations in the range of 0.1 - 0.5M seem to indicate that the potential drop is sharper at these concentrations than would be predicted by the Gouy-Chapman theory. Furthermore, one must account for all relevant effects, such as volume of ions and variation of permittivity, which are neglected in the above model.
2.1.2. The Debye-Hückel Approximation

For the case where the potential is less than approximately 25.6 mV at 25°C \((kT/e_o = 25.6 \text{ mV at } 25^\circ\text{C})\), the Poisson-Boltzmann equation can be linearized through a power series expansion of the exponential term \(e^x = 1 + x + x^2/2! + \ldots\) in Equation [2.9], and by retaining only the terms through first-order, Equation [2.8] reduces to

\[
\psi = \psi_0 \exp(-\kappa x) \quad [2.11]
\]

This linearization of the Poisson-Boltzmann equation is known as the Debye-Hückel approximation. Equation [2.11] shows that at low potentials the potential decreases exponentially with distance from the charged surface. However, for very small distances from the charged surface, the potential is likely to be relatively high, so that the Debye-Hückel approximation becomes inapplicable and the rate of decay of the potential given by Equation [2.8] is predicted to be greater than an exponential rate.

The Poisson-Boltzmann equation for a spherical interface takes the form

\[
\nabla^2 \psi = \frac{1}{r^2} \frac{d}{dr} \left[ r^2 \frac{d\psi}{dr} \right] = \frac{8\pi z e_o n_o}{\epsilon} \sinh \frac{z e_o \psi}{kT} \quad [2.12]
\]

where \(r\) is the distance from the centre of the sphere. This expression cannot be integrated analytically without approximation of the exponential terms. If the Debye-Hückel approximation is made, then the equation reduces to
\[ \nabla^2 \psi = \kappa^2 \psi \quad [2.13] \]

which, on integration (with the boundary conditions, \( \psi = \psi_0 \) at \( r = a \) and \( \psi = 0 \), \( d\psi/dr = 0 \) at \( r = \infty \)) gives

\[ \psi = \psi_0 - \frac{a}{r} \exp\{-\kappa(r-a)\} \quad [2.14] \]

where \( a \) is the particle radius.

Unfortunately, the Debye-Hückel approximation \( (z\psi \leq 25 \text{ mV}) \) is often too limiting for the treatment of many colloid and surface phenomena. Unapproximated solutions of Equation \([2.12]\) have been obtained numerically with a computer by Loeb et al. (55).

2.1.3. Surface Charge Density, \( \sigma_0 \)

The condition of electro-neutrality at a charged interface requires that the density of charge at the two faces be equal. This implies that when one of the phases contains a diffuse layer, the total charge contained in a volume element of the solution of unit cross section extending from the wall to infinity must contain the same amount of charge, although of opposite sign, as a unit area of wall contains. In mathematical form, this statement may be written as

\[ \sigma_0 = - \int_{0}^{\infty} \rho(x) \, dx \quad [2.15] \]
Combining Equations \([2.6]\) and \([2.15]\) therefore yields

\[
\sigma_0 = \frac{\varepsilon}{4\pi} \int_0^\infty \frac{d^2\psi}{dx^2} \, dx
\]  

\[\text{[2.16]}\]

which upon integration gives

\[
\sigma_0 = \frac{\varepsilon}{4\pi} \left[ \frac{d\psi}{dx} \right]_0^\infty
\]  

\[\text{[2.17]}\]

As \(x\) approaches \(\infty\) (bulk of solution), it is envisaged that both \(\psi\) and \(d\psi/dx\) approach zero. Therefore, Equation \([2.17]\) becomes

\[
\sigma_0 = \frac{\varepsilon \kappa \psi_0}{4\pi}
\]  

\[\text{[2.18]}\]

From Equation \([2.18]\), it can thus be seen that the surface charge density \(\sigma_0\) depends on both the surface potential \(\psi_0\) and (through \(\kappa\)) on the ionic composition of the medium. If the double layer is compressed (i.e. \(\kappa\) increased), then \(\sigma_0\) must increase.

2.1.4. The Electric Double Layer Thickness \(1/\kappa\)

The inverse of \(\kappa\) which is defined in Equation \([2.10]\) is commonly referred to as the thickness of the double layer. This is due to the fact that this quantity represents the separation between the plates of a parallel plate capacitor having the same surface potential and charge density as the electric double layer. All distances within the double layer are determined relative to this quantity.
However, in the diffuse double layer model, although $1/\kappa$ is still customarily referred to as the double layer thickness, it is a misnomer. This can be seen from Equation [2.11] which, upon substitution of $1/\kappa$ for $x$, predicts that the potential falls to $1/e$ of its surface value as opposed to the value of zero expected in the bulk solution.

2.1.5. The Stern Layer

As stated in Section 2.1.1, the development of the Gouy-Chapman theory of the diffuse layer assumes point charges in the electrolyte medium. However, ions have finite sizes and the finite size of ions will limit the inner boundary of the diffuse part of the double layer, since the centre of an ion can only approach the surface to within its hydrated radius without becoming specifically adsorbed. The assumption that the ions have no volume is acceptable at low electrolyte concentrations but will break down as ionic concentration increases. When the electrolyte concentration and potentials are very high, the Gouy-Chapman theory predicts an unacceptably high counter-ion concentrations at the surface, with an impossibly small value for the double layer thickness.

In light of this shortcoming, Stern proposed a model to include the finite size of ions by considering the double layer to be divided into two parts by a plane known as the Stern plane located at a distance $\delta$ (about a hydrated ion radius) from the surface. Within this plane, the possibility was considered of specific ion adsorption giving a compact layer of counter-ions attached to the surface by electrostatic and van der Waals forces strong enough to overcome
Grahame (56) further distinguishes within the Stern layer an "inner Helmholtz plane" and an "outer Helmholtz plane". The former is the plane through the centers of specifically adsorbed ions, which are usually dehydrated upon adsorption, while the latter corresponds to the Stern plane.

Outside the Stern plane, the double layer continues to be described by Gouy-Chapman's model. The only modifications of the analysis of the diffuse double layer required by the introduction of the Stern plane are that $x$ is now measured from $\delta$ rather than from the wall and that the Stern potential $\psi_\delta$ is used instead of the surface potential $\psi_0$ as the potential at the inner boundary of the diffuse layer.

**2.2. ELECTROKINETIC PHENOMENA**

Electrokinetic phenomena is the term assigned to the four phenomena that arise when attempts are made to separate the mobile part of the electric double layer from the charged surface. This separation of the two parts of the double layer can be achieved by directing an externally applied electric field along the phase boundary (resulting in a relative movement between the phases) or by mechanically initiating a relative movement between the phases (resulting in an induced electric field and a transport of electricity).
The four electrokinetic phenomena are:

1. **Electrophoresis** — which involves the movement of a charged surface relative to a stationary electrolyte due to an applied electric field.

2. **Electro-osmosis** — which is complementary to electrophoresis and involves the movement of an electrolyte relative to a stationary charged surface due to an applied electric field.

3. **Streaming Potential** — which is the opposite of electro-osmosis and refers to the electric field which is created when an electrolyte is made to flow next to a stationary charged surface.

4. **Sedimentation Potential** — which is the opposite of electrophoresis and refers to the electric field which is created when charged particles are allowed to sediment relative to a stationary electrolyte.

Specifically, when electrophoresis occurs, several forces are present. Firstly, there is the force exerted by the applied potential as a consequence of the charge carried by the particle. Secondly, there is a viscous retarding force due to the flow of liquid past the particle which, for isolated spherical particles in creeping flow, is given by Stokes’ Law. Thirdly, since the diffuse layer contains a net excess of counter-ions, there will be a net force acting on the liquid due to the interaction of the ion charges with the electric field. The resulting flow of liquid (electro-osmosis) causes a retarding force on the particle. This effect is called the electrophoretic retardation. Fourthly, the distribution of ions in the vicinity of the particle is deformed as the particle moves away from the centre of its ionic atmosphere. The Coulombic attraction between the ions tends to rebuild the ionic atmosphere, a process which takes a finite time called the relaxation time. Thus in the steady state the charge centre of the diffuse layer constantly lags behind the centre of the particle. Consequently a dipole is formed which results in an electric force that acts on the particle. This force is usually
a retarding one and is called the relaxation effect. The latter two effects are complicated functions of the zeta potential, the particle size, the thickness of the double layer and the valence and mobility of the specific ions in the solution.

2.2.1. Electrokinetic (Zeta) Potential \( \xi \)

When an electrokinetic phenomenon occurs, the potential that is at the surface of shear between the charged surface and the electrolyte solution is called the electrokinetic potential or, more commonly, the zeta potential, due to the usage of the Greek letter \( \xi \) as the symbol. This potential is an important parameter in the study of colloidal stability because it has been customarily assumed to be identical with the Stern potential, \( \psi_\delta \), introduced in the Stern theory, which cannot be evaluated experimentally. The assumption of the identity of \( \psi_\delta \) and \( \xi \) stems from the following arguments and findings.

Although the exact location of the shear plane is not known, it is generally conceived to be located either on \((57,58,59)\) or slightly outside \((60)\) the Stern plane, the latter being the more widely accepted choice. This is because in addition to the immobilized ions in the Stern layer, a certain amount of solvent will probably also be bound to the charged surface for the following reasons. Firstly, because of the microscopic roughness of all solid surfaces \((61)\), the moving liquid will not penetrate the depressions but will glide across them, thereby effectively pushing the shear plane further away from the surface. Secondly, there exists an anomalously high viscosity in the vicinity of the surface \((62)\) created by the interaction of polar solvent molecules with the high electric
field strength in this region. This high viscosity effectively moves the shear plane further out into the solution. Furthermore, the experimental results of various researchers (63,60,57,64) indicate that the distance between the Stern plane and the shear plane is only a few Angstroms. Thus, at low and intermediate electrolyte concentrations, where $1/\kappa \geq 100\text{Å}$, the double layer thickness greatly exceeds the distance between the Stern plane and the shear plane and the assumption of identical $\psi_\delta$ and $\xi$ would, for practical purposes, appear to be justified. Figure 2.1 is a schematic representation of a charged surface and its double layer, together with other relevant parameters mentioned above.

2.2.2. Determination of Zeta Potential

Although the zeta potential may be determined by any one of the electrokinetic techniques outlined in Section 2.2, the most commonly used technique is that of electrophoresis. Theoretical expressions relating the zeta potential to the measured electrophoretic mobility under various specific conditions have been established by Smoluchowski (65), Henry (66), Hückel (67), Overbeek (68), Booth (69) and Wiersema et al. (70).

Of the above, the theory of Wiersema et al. is conceivably the most inclusive as it not only accounts for the effects of retardation, relaxation and surface conductance, it also can be used for zeta potentials as high as 150 mV. The main assumptions of this model are:

1. The particle is a rigid, non-conducting sphere with its charge uniformly distributed over the surface.
Figure 2.1 A schematic representation of a charge surface and its double layer, together with other parameters as shown.
2. The electrophoretic behaviour of the particle is not influenced by other particles in the dispersion.

3. Permittivity and viscosity are constant throughout the mobile part of the double layer, which is described by the Gouy-Chapman theory.

4. Only one type each of positive and negative ions are present in the mobile part of the double layer.

Wiersema et al. simultaneously solve the Poisson-Boltzmann equation which governs the distribution of electrical potential, the Navier-Stokes' equation which describes the fluid motion, and the transport equations which control the movement of ions in the solution. The solution is obtained by the method of successive approximations using a computer. Their results are given in tabulated form in terms of dimensionless variables.

2.3. EFFECT OF ELECTROLYTE ON SURFACE POTENTIAL, ZETA POTENTIAL AND DOUBLE LAYER THICKNESS

If ionic strength remains constant in an electrolyte solution, the addition of potential determining ions will cause changes in the magnitude of surface potential which, in turn, produce changes in the zeta potential. For example, the OH\(^-\) ion is a potential determining ion for silica surfaces in an aqueous medium. Thus, under conditions of relatively high electrolyte concentrations where the addition of OH\(^-\) ions causes insignificant changes in the ionic strength of the solution, any increase of OH\(^-\) ions increases the specific adsorption of OH\(^-\) ions on (or release of H\(^+\) ions from) the surface and hence changes the magnitude of the surface and zeta potentials. In solutions of low electrolyte concentrations,
addition of any ions into the solution will affect the equilibrium adsorption of counter-ions into the Stern layer. As a result, the surface potential remains unchanged but the potential at the Stern plane and hence the zeta potential is affected. This addition in effect causes the double layer thickness to be reduced according to Equation [2.10]. The effects of pH and ionic strength on zeta potential, surface potential and double layer thickness are shown schematically in Figure 2.2.

2.4. PARTICLE-PARTICLE AND PARTICLE-SURFACE INTERACTIONS

2.4.1. Double Layer Interaction Energies

When two double layers overlap, for example when two particles dispersed in a polar medium approach each other, an electrostatic interaction of the ions in the diffuse layers occurs. The electrostatic potential energy thus created by the two interacting surfaces can be determined through either force (71) or free energy (72) considerations from a knowledge of the distribution of space charge (or electrical potential) between the two interacting bodies, and from the electrostatic boundary conditions at their surfaces. The calculation of the interaction energy, $\phi_{edl}$, is complex. No exact analytical expression can be given and recourse must be made to numerical solutions or to various approximations.

All utilizable solutions for the determination of interaction energy assume (i) that the distribution is described by the Poisson-Boltzmann equation whose shortcomings have been outlined in Section 2.1.1 and (ii) that either a constant
Figure 2.2 The effects of (a) ionic strength and (b) pH on zeta potential, surface potential and double layer thickness.
surface potential or a constant surface charge density boundary condition applies. However, which boundary condition best applies in real situations remains unclear. It has been suggested that if the time taken for the re-establishment of electrochemical equilibrium between the surface and the bulk solution is negligible compared to the time taken for a Brownian collision to occur and if the surface charge is the result of the adsorption of potential-determining ions, then it can be assumed that the surface potential will remain constant during the interaction and the surface charge density will adjust accordingly (see Equation [2.18]). Conversely, if the equilibrating process takes much longer than the Brownian collision, then a constant charge density during interaction is the correct assumption. This problem has been studied by Overbeek (73), who concluded that the rate of double-layer overlap in a typical Brownian motion encounter between particles is too fast for adsorption equilibrium to be maintained and that the true situation will, in general, lie somewhere between constant potential and constant charge density.

By adopting the linearized form of the Poisson-Boltzmann equation and Derjaguin's approximation (71) at small separations, Hogg et al. (74) have derived an expression for the case of constant-potential double-layer interaction energy $\phi_{edl}$ between two dissimilar spheres, namely

$$\phi_{edl} = \frac{\varepsilon a_1 a_2 (\psi_{\delta_1}^2 + \psi_{\delta_2}^2)}{4(a_1 + a_2)} \left[ \frac{2\psi_{\delta_1} \psi_{\delta_2}}{\psi_{\delta_1}^2 + \psi_{\delta_2}^2} \ln \left( \frac{1 + e^{-\kappa H}}{1 - e^{-\kappa H}} \right) + \ln \left( 1 - e^{-2\kappa H} \right) \right]$$

[2.19]

where $a_1$ and $a_2$ are the radii of the spherical particles, $\psi_{\delta_1}$ and $\psi_{\delta_2}$ are their respective Stern potentials, $H$ is the shortest distance between their Stern
layers, $\varepsilon$ is the permittivity of the dispersion medium and $\kappa$ is defined in Equation [2.10].

For equal spheres, with $a_1 = a_2 = a$ and $\psi_\delta_1 = \psi_\delta_2 = \psi_\delta$, Equation [2.19] reduces to

$$\phi_{\text{edl}} = \frac{\varepsilon a \psi_\delta^2}{2} \ln (1 + e^{-\kappa H}) \quad [2.20]$$

When one of the particle radii becomes infinite, a situation corresponding to the interaction between a sphere and a plate, the expression for the interaction energy, $\phi_{\text{edl}}$, reduces to

$$\phi_{\text{edl}} = \frac{\varepsilon a}{4} \left[ 2 \psi_\delta_1 \psi_\delta_2 \ln \left( \frac{1 + e^{-\kappa H}}{1 - e^{-\kappa H}} \right) + (\psi_\delta_1^2 + \psi_\delta_2^2) \ln (1 - e^{-2\kappa H}) \right] \quad [2.21]$$

For the case where the charge densities at both surfaces remain constant during the interaction, Wiese and Healy (75) give the following expression for the interaction between two dissimilar spherical particles:

$$\phi_{\text{edl}} = \frac{\varepsilon a_1 a_2 (\psi_\delta_1^2 + \psi_\delta_2^2)}{4(a_1 + a_2)} \left[ \frac{2 \psi_\delta_1 \psi_\delta_2}{\psi_\delta_1^2 + \psi_\delta_2^2} \ln \left( \frac{1 + e^{-\kappa H}}{1 - e^{-\kappa H}} \right) - \ln (1 - e^{-2\kappa H}) \right] \quad [2.22]$$

For the case of equal particle size and equal Stern potentials, Equation [2.22] reduces to:

$$\phi_{\text{edl}} = -\frac{\varepsilon a \psi_\delta^2}{2} \ln (1 - e^{-\kappa H}) \quad [2.23]$$
For particle-plate interactions, Equation [2.22] can be rewritten as

\[
\phi_{\text{edl}}^\sigma = \frac{\varepsilon a}{4} \left[ 2 \psi_1 \psi_2 \ln \left( \frac{1+e^{-\kappa H}}{1-e^{-\kappa H}} \right) - (\psi_1^2 + \psi_2^2) \ln (1-e^{-2\kappa H}) \right]
\]

[2.24]

For the mixed case, where the interaction is between one surface at constant potential and a second surface at constant charge density, Kar et al. (76) obtained for the general particle-particle interaction

\[
\phi_{\text{edl}}^{\sigma-\psi} = \frac{\varepsilon a_1 a_2}{4(a_1+a_2)} \left[ 2 \psi_1 \psi_2 \left( \frac{\pi}{2} - \tan^{-1}(\sinh\kappa H) \right) - (\psi_2^2 - \psi_1^2) \ln (1+e^{-2\kappa H}) \right]
\]

[2.25]

which, for the case of equal particle size and equal Stern potentials, reduces to

\[
\phi_{\text{edl}}^{\sigma-\psi} = \frac{\varepsilon a}{4} \psi_2 \left( \frac{\pi}{2} - \tan^{-1}(\sinh\kappa H) \right)
\]

[2.26]

For particle-plate interaction, Equation [2.25] becomes

\[
\phi_{\text{edl}}^{\psi-\sigma} = \frac{\varepsilon a}{4} \left[ 2 \psi_1 \psi_2 \left( \frac{\pi}{2} - \tan^{-1}(\sinh\kappa H) \right) - (\psi_2^2 - \psi_1^2) \ln (1+e^{-2\kappa H}) \right]
\]

[2.27]

when the particle surface (surface 1) remains at constant potential and

\[
\phi_{\text{edl}}^{\sigma-\psi} = \frac{\varepsilon a}{4} \left[ 2 \psi_1 \psi_2 \left( \frac{\pi}{2} - \tan^{-1}(\sinh\kappa H) \right) + (\psi_2^2 - \psi_1^2) \ln (1+e^{-2\kappa H}) \right]
\]

[2.28]

when the plane surface (surface 2) remains at constant potential.
At separations large compared to the double layer thickness \((\kappa H \geq 5)\) such that \(e^{-\kappa H} \ll 1\), Equations [2.21], [2.24], [2.27] and [2.28] all reduce to

\[
\phi_{\text{edl}} = \frac{e}{2} \psi_1 \psi_2 e^{-\kappa H}
\]  

[2.29]

This expression is identical to that obtained by Bell et al. (77), who used the linear superposition approximation to arrive at Equation [2.29]. This suggests that the expressions obtained using Derjaguin's approximation may be used here to represent the sphere-plate interaction energy at all separation distances. A general prediction of the interaction energy based on the above expressions is that \(\phi_{\text{edl}}\) should decrease in an approximately exponential fashion with increasing \(H\) and that the range of \(\phi_{\text{edl}}\) should be decreased by increasing \(\kappa\) (i.e. by increasing electrolyte concentration and/or counter-ion valency).

It should be noted here that all the equations derived above for the calculation of double layer interaction energies are applicable only when two double layers are involved. If a third double layer is present, for example, as in the case of two negatively charged spheres depositing on a positively charged planar substrate, these equations will be inapplicable. This is because the potential distribution between two spheres situated on a planar substrate will be distorted by the presence of the additional surface. Except for the deposition that takes place on a surface whose macroscopic dimensions approach those of the particles, the presence of a third double layer is, in fact, commonplace in all processes where deposition takes place on an extended surface. However, despite its frequent occurrence in many deposition processes and its obvious effect on the double layer interaction energy and hence the surface coverage, no published
theory for the potential distribution between three interacting double layers is currently available. Thus, until an analysis of this situation becomes available, the equations discussed above will be assumed to be approximately applicable.

2.4.2. London-van der Waals Interaction

In 1873, van der Waals first introduced the idea of the existence of an attractive force present between two neutral atoms to explain the behaviour of non-ideal gases and liquids. This force of attraction between neutral, chemically saturated molecules may originate from any of the following electrical interactions:

1. Two molecules with permanent dipoles mutually orientate each other in such a way that, on average, attraction results.

2. Dipolar molecules induce dipoles in other molecules so that attraction results.

3. Attractive forces can also exist between non-polar molecules. These universal attractive forces, known as dispersion forces, were first explained by London (1930) and are due to the rapidly fluctuating dipole moment generated in a neutral atom A by the motion of electrons around its nuclei. The electric field of this instantaneous dipole polarizes a nearby neutral atom B and the returning field of the induced dipole from atom B then interacts with atom A resulting in an attractive force between them.

With the exception of highly polar materials, London dispersion forces account for nearly all of the van der Waals attraction. London showed that the energy of attraction between two atoms varies inversely as the sixth power of their distance of separation and is, to a first approximation, independent of the interaction with other atoms. Thus, for an assembly of molecules, dispersion forces are, to a first approximation, additive and the van der Waals interaction
energy between two particles can be computed by summing the attractions between all interparticle molecule pairs. The results of such summations predict that the van der Waals interaction energy between collections of molecules decays much less rapidly than that between individual molecules.

Using the above assumptions, Hamaker (78) obtained the van der Waals attraction energy, $\phi_{vdw}$, for the interaction of a number of geometrically simple bodies. For the case of two spherical particles of radii $a_1$ and $a_2$, separated in vacuum by a shortest distance $H$, Hamaker derived the following expression for the interaction energy, $\phi_{vdw}$:

$$\phi_{vdw} = -\frac{A}{12} \left[ \frac{y}{x^2+xy+x} + \frac{y}{x^2+xy+x+y} + 2 \cdot \ln \left[ \frac{x^2+xy+x}{x^2+xy+x+y} \right] \right]$$

where

$$x = \frac{H}{a_1+a_2}, \quad y = \frac{a_1}{a_2}$$

$A$ is a constant, known as the Hamaker constant.

For equal spheres, with $a_1=a_2=a$ (i.e. $x=H/2a$), Equation [2.30] takes the form

$$\phi_{vdw} = -\frac{A}{12} \left[ \frac{1}{x(x+2)} + \frac{1}{(x+1)^2} + 2 \cdot \ln \left[ \frac{x(x+2)}{(x+1)^2} \right] \right]$$

[2.31]
If a small interparticle separation is assumed, such that $H < a$ (i.e. $x << 1$), Equation [2.31] simplifies to

$$\phi_{vdw} = -\frac{Aa}{12H} \quad [2.32]$$

For the sphere-plate system:

$$\phi_{vdw} = -A\left[\frac{2a(H+a)}{H(H+2a)} + \ln\left[\frac{H}{H+2a}\right]\right] \quad [2.33]$$

It should be noted that the above equations only apply at very small distances of separation ($H \leq 10$ nm) and even then only as a first approximation for bodies whose thicknesses exceed molecular dimensions.

Values of $\phi_{vdw}$ calculated from any of the above equations will be overestimated at large distances ($H > c. 10$ nm). This is because if two atoms are further apart than a certain distance, by the time the electric field from one dipole has reached and polarised the other, the electron configuration of the first atom will have changed. This will result in a poor correlation between the two dipoles and the two atoms then experience what is known as "retarded" van der Waals forces. This finite time required for the propagation of electromagnetic radiation between the particles results in a weakening of $\phi_{vdw}$ and hence the attractive force is less than that predicted by the above equations.

The effect of retardation has been worked out by Casimir and Polder (79), who obtained an expression for the retarded energy, $\phi_{r}^{\text{ret}}$, between a pair of atoms by correlating it with the unretarded energy, $\phi_{r}^{a-a}$ and a correction
function, \( f(p) \), as shown below:

\[
\phi_{a-a}^{\text{ret}} = \phi_{a-a} \cdot f(p)
\]  \[2.34\]

where \( p = 2\pi H/\lambda \) and \( \lambda \) is the wavelength characteristic of the atom dipole fluctuations.

Approximate expressions for \( f(p) \) has been obtained by Overbeek (80) as follows:

\[
f(p) = 1.01 - 0.14p \quad \text{if} \quad p < 3
\]  \[2.35\]

\[
= \frac{2.45}{p} - \frac{2.04}{p^2} \quad \text{if} \quad p \geq 3
\]

Expressions for the retarded van der Waals interactions between macroscopic bodies have been obtained by Clayfield et al. (81), who repeated Hamaker's calculation using Equation [2.34], with Equation [2.35] to represent the atom-pair interaction. They derived the following expression for the sphere-plate interaction:

\[
\phi_{vdw}^{\text{ret}} = -2\Lambda_{132} \cdot I_{sp}
\]  \[2.36\]

where

(i) For \( H > \rho \)

\[
I_{sp} = I_1 = \frac{Ca^3}{15H^2(H+2a)^2} - \frac{2Da^3(H+a)}{45H^3(H+2a)^3}
\]
(ii) For $H+2a > \rho > H$

\[ I_{sp} = I_2 \]
\[ = I_1 + \frac{\rho' \rho^3}{12} (4a-\rho') \left[ -\frac{A}{4\rho^4} + \frac{B}{3\rho^3} + \frac{C}{5\rho^5} - \frac{D}{6\rho^6} \right] \]
\[ + \rho' \left( a - \frac{\rho'}{3} \right) \left[ -\frac{A}{12\rho^3} + \frac{B}{6\rho^2} + \frac{C}{20\rho^4} - \frac{D}{30\rho^5} \right] \]
\[ + \frac{A}{12} \left[ -\ln \frac{\rho}{H} + \frac{\rho'}{H\rho^2} \left[ H^2 + \frac{3H\rho'}{2} + a\rho' \right] \right] \]
\[ + \frac{B}{6} \left[ 2(a+H)\ln \frac{\rho}{H} + \rho' + \frac{(2a+H)\rho'}{\rho} \right] \]
\[ + \frac{C}{60H^2\rho^3} \left[ H(\rho'-3a) - a\rho' \right] \]
\[ + \frac{D\rho'^2}{360H^3\rho^4} \left[ H^2(12a-4\rho') + H\rho'(8a-\rho') + 2a\rho'^2 \right] \]

(iii) For $\rho > H+2a$

\[ I_{sp} = I_3 \]
\[ = 4a^3(\rho'-a) \left[ -\frac{A}{4\rho^4} + \frac{B}{3\rho^3} + \frac{C}{5\rho^5} - \frac{D}{6\rho^6} \right] \]
\[ + \frac{4a}{3} \left[ -\frac{A}{12\rho^3} + \frac{B}{6\rho^2} + \frac{C}{20\rho^4} - \frac{D}{30\rho^5} \right] \]
\[ + \frac{A}{12} \left[ -\ln \frac{H+2a}{H} + \frac{2a(a+H)}{H(2a+H)} \right] + \frac{B}{3} \left[ 2a - (a+H)\ln \frac{H+2a}{H} \right] \]
where \( \rho = \frac{3\lambda}{2\pi} \)

\( \rho' = \rho - H \)

\( A = 1.01 \)

\( B = 0.14 \cdot 2\pi/\lambda \)

\( C = 2.45/(\pi/\lambda) \)

\( D = 2.14/(2\pi/\lambda)^2 \).

For the interaction between two spheres having equal radii \( a \), Clayfield et al. gave the following expression for the retarded van der Waals energy:

\[
\phi_{\text{vdw}}^{\text{ret}} = -\frac{A_{132}}{H+2a} I_{\text{ss}} \tag{2.37}
\]

where

(i) \( \text{For } \rho \leq H \)

\[
I_{\text{ss}} = I_{s1}
\]

\[
= \frac{C}{30} \left[ \ln \frac{(H+2a)^2}{H(H+4a)} + 2a \left[ \frac{1}{H+4a} - \frac{1}{H} \right] + a^2 \left[ \frac{1}{H^2} + \frac{2}{(H+2a)^2} + \frac{1}{(H+4a)^2} \right] \right]
\]

\[
- \frac{D}{180} \left[ \frac{1}{H} - \frac{2}{H+2a} + \frac{1}{H+4a} + 2a \left[ \frac{1}{(H+4a)^2} - \frac{1}{H^2} \right] + 2a^2 \left[ \frac{1}{H^3} + \frac{2}{(H+4a)^3} + \frac{1}{(H+4a)^3} \right] \right]
\]
(ii) For $H+2a \geq \rho > H$

\[ I_{ss} = I_{s2} \]
\[ = I_{s1} + a\rho'^2 \left[ a - \frac{\rho'}{3} \right] + \beta \left[ \rho'^2 a(a+H) + \frac{\rho'^3(a-H)}{3} - \frac{\rho'^4}{4} \right] \]
\[ + \gamma \left[ \rho'^2 Ha(2a+H) + \frac{\rho'^3}{3} \left[ 4a(H+a) - H(2a+H) \right] + \frac{\rho'^4}{2} H - \frac{\rho'^5}{5} \right] \]
\[ + \frac{A}{12} \left[ \rho' - 2(2a+H)ln \frac{\rho}{H} + H(2a+H) \left( \frac{1}{H} - \frac{1}{\rho} \right) \right] \]
\[ + 2a \left[ 2(a+H)(\frac{1}{H} - \frac{1}{\rho}) - H(2a+H) \left( \frac{1}{H^2} - \frac{1}{\rho^2} \right) \right] \]
\[ - \frac{B}{3} \left[ \frac{\rho^2 - H^2}{2} - 2(a+H)\rho' + (H^2+4aH+2a^2)ln \frac{\rho}{H} \right] \]
\[ + a \left[ -\rho' - H(2a+H) \left( \frac{1}{H} - \frac{1}{\rho} \right) \right] \]
\[ - \frac{C}{30} \left[ ln \frac{\rho}{H} - 2(a+H)(\frac{1}{H} - \frac{1}{\rho}) + \frac{H(2a+H)}{2} \left( \frac{1}{H^2} - \frac{1}{\rho^2} \right) \right] \]
\[ + 3a \left[ -\left( \frac{1}{H} - \frac{1}{\rho} \right) + (a+H) \left( \frac{1}{H^2} - \frac{1}{\rho^2} \right) - \frac{H(2a+H)}{3} \left( \frac{1}{H^3} - \frac{1}{\rho^3} \right) \right] \]
\[ + \frac{D}{60} \left[ \left( \frac{1}{H} - \frac{1}{\rho} \right) - (a+H) \left( \frac{1}{H^2} - \frac{1}{\rho^2} \right) + \frac{H(2a+H)}{3} \left( \frac{1}{H^3} - \frac{1}{\rho^3} \right) \right] \]
\[ - 4a \left[ \frac{1}{2} \left( \frac{1}{H^2} - \frac{1}{\rho^2} \right) - \frac{2(a+H)}{3} \left( \frac{1}{H^3} - \frac{1}{\rho^3} \right) - \frac{H(2a+H)}{4} \left( \frac{1}{H^4} - \frac{1}{\rho^4} \right) \right] \]
(iii) For \( \rho \geq H + 4a \)

\[
I_{ss} = I_{s3} \\
= \frac{A}{6} \left[ (2a+H) \ln \frac{H(H+4a)}{(H+2a)^2} + a^2 \left[ \frac{1}{H} + \frac{2}{H+2a} + \frac{1}{H+4a} \right] \right] \\
- \frac{B}{3} \left[ (H^2+4aH+2a^2) \ln \frac{(H+2a)^2}{H(H+4a)} - 4a^2 \right]
\]

(iv) For \( H + 4a \geq \rho > H + 2a \)

\[
I_{ss} = I_{s4} \\
= I_{s3} + a \left[ \frac{4a^3}{3} - (\rho'-2a)^2 \left[ a - \frac{\rho'-2a}{3} \right] \right] \\
+ \beta \left[ \frac{4a^3}{3} (2a+H) + \frac{(\rho'-2a)^4}{4} \\
- \frac{(\rho'-2a)^3}{3} (a-H) - (\rho'-2a)^2(a+H) \right] \\
+ \gamma \left[ \frac{4a^3}{3} \left[ H^2+4aH+2a^2+ \frac{6a^2}{5} \right] - (\rho'-2a)^2H(a+2a) \\
- \frac{(\rho'-2a)^3}{3} \left[ 4a(H+a)-H(2a+H) \right] - \frac{(\rho'-2a)^4}{2} H + \frac{(\rho'-2a)^5}{5} \right] \\
+ \frac{A}{12} \left[ -2(2a+H) \ln \frac{H+4a}{\rho} + H + 4a - \rho + R \left( \frac{1}{\rho} - \frac{1}{H+4a} \right) \\
+ 2a \left[ -Q \left( \frac{1}{\rho} - \frac{1}{H+4a} \right) \right] + \frac{R}{2} \left( \frac{1}{\rho^2} - \frac{1}{(H+4a)^2} \right) \right]
\]
\[-\frac{B}{3} \left[ \frac{(H+4a)^2 - \rho^2}{2} - Q(H+4a - \rho) \right] \]
\[+ (H^2 + 4aH + 2a^2) \ln \frac{H+4a}{\rho} + a \left[ H+4a - \rho + R \left( \frac{1}{\rho} - \frac{1}{H+4a} \right) \right] \]
\[- \frac{C}{30} \left[ \ln \left(\frac{H+4a}{\rho}\right) - Q \left( \frac{1}{\rho} - \frac{1}{H+4a} \right) + R \left( \frac{1}{\rho^2} - \frac{1}{(H+4a)^2} \right) \right] \]
\[+ 3a \left[ \frac{1}{\rho} - \frac{1}{H+4a} - Q \left( \frac{1}{\rho^2} - \frac{1}{(H+4a)^2} \right) + \frac{R}{2} \left( \frac{1}{\rho^3} - \frac{1}{(H+4a)^3} \right) \right] \]
\[+ \frac{D}{60} \left[ \frac{1}{\rho} - \frac{1}{H+4a} - \frac{Q}{2} \left( \frac{1}{\rho^2} - \frac{1}{(H+4a)^2} \right) + \frac{R}{3} \left( \frac{1}{\rho^3} - \frac{1}{(H+4a)^3} \right) \right] \]
\[+ 4a \left[ \frac{1}{2} \left( \frac{1}{\rho^2} - \frac{1}{(H+4a)^2} \right) \right] \]
\[- \frac{Q}{3} \left( \frac{1}{\rho^3} - \frac{1}{(H+4a)^3} \right) + \frac{R}{4} \left( \frac{1}{\rho^4} - \frac{1}{(H+4a)^4} \right) \]

where \( Q = 2(3a + h) \)
\( R = (h + a)(h + 4a) \)
\( a = \left[ \frac{A}{2\rho^2} - \frac{B}{\rho} - \frac{C}{3\rho^3} + \frac{D}{4\rho^4} \right] \)
\( \beta = \left[ -\frac{2A}{3\rho^3} + \frac{B}{\rho^2} + \frac{C}{2\rho^4} - \frac{D}{5\rho^5} \right] \)
\( \gamma = \left[ \frac{A}{4\rho^4} - \frac{B}{3\rho^3} - \frac{C}{5\rho^5} + \frac{D}{6\rho^6} \right] \)

Since the frequency of electronic fluctuations in atoms is of the order of \(10^{15}\) to \(10^{16}\) per second, the value of the wavelength, \(\lambda\), may range from 300
to 3000 Å. However, to simplify calculations, Overbeek (81) recommends a value of 1000 Å for λ to be applicable for most materials.

If the above equations can be considered correct, i.e., the assumption that the interactions between individual molecules embedded in macroscopic bodies are additive, then the remaining problem in calculating the van der Waals interaction between colloidal solids is that of evaluating the Hamaker constant, A. Two methods are available for this calculation. The first of these methods is the London-Hamaker microscopic approach, in which the Hamaker constant is evaluated from the individual atomic polarisabilities and the atomic densities of the materials involved. The second method is the macroscopic approach of Lifshitz (82), who assumed that the attraction force between two interacting bodies was due to a fluctuating electromagnetic field in the gap, arising from all electric and magnetic polarizations within the two surfaces. In this way, the interacting bodies and the intervening medium can be treated as continuous phases and hence the van der Waals interaction energy and the retardation effects could be determined just from the bulk properties of the materials concerned. However, the calculations are complex, and require the availability of bulk optical/dielectric properties of the interacting materials over a sufficiently wide frequency range.

The various methods of calculating the Hamaker constant, A, from optical dispersion data have been reviewed by Gregory (83) and Visser (84). In general, values of Hamaker constants for single materials have been reported to vary between $10^{-20}$ and $10^{-19}$ J. Some examples are given in Table 2.1 (84). Where a range of values is quoted for a given material, it reflects different
methods of calculation within the basic microscopic or macroscopic method.

Table 2.1

<table>
<thead>
<tr>
<th>Material</th>
<th>A(microscopic) x 10⁻²⁰J</th>
<th>A(macroscopic) x 10⁻²⁰J</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>3.3–6.4</td>
<td>3.0–6.1</td>
</tr>
<tr>
<td>Ionic crystals</td>
<td>15.8–41.8</td>
<td>5.8–11.8</td>
</tr>
<tr>
<td>Metals</td>
<td>7.6–15.9</td>
<td>22.1</td>
</tr>
<tr>
<td>Silica</td>
<td>50.0</td>
<td>8.6</td>
</tr>
<tr>
<td>Quartz</td>
<td>11.0–18.6</td>
<td>8.0–8.8</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>4.6–10.0</td>
<td>6.3</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>6.2–16.8</td>
<td>5.6–6.4</td>
</tr>
</tbody>
</table>

In the presence of a liquid dispersion medium, rather than in a vacuum or in air, the Hamaker constant A must be replaced by an effective Hamaker constant. For example, for the interaction between two solids 1 and 2 in a dispersion medium 3, the effective Hamaker constant is given by

\[ A_{132} = A_{12} + A_{33} - A_{13} - A_{23} \]  

where \( A_{ij} \) is the Hamaker constant for the interaction of material i with material j in a vacuum.

If the attractions between unlike phases is taken to be the geometric mean of the attractions of each phase to itself, i.e., if

\[ A_{ij} = (A_{ii} \cdot A_{jj})^{0.5} \]
then Equation [2.38] becomes

\[ A_{132} = (A_{11}^{0.5} - A_{33}^{0.5}) (A_{22}^{0.5} - A_{33}^{0.5}) \]  \[2.39\]

If the two interacting solids are of the same material, the above expression becomes

\[ A_{131} = (A_{11}^{0.5} - A_{33}^{0.5})^2 \]  \[2.40\]

\(A_{132}\) will usually be positive (attraction), i.e., when \(A_{11}\) and \(A_{22}\) are either both greater or both less than \(A_{33}\). However, in the unusual situation where \(A_{33}\) has a value intermediate between those of \(A_{11}\) and \(A_{22}\), then \(A_{132}\) is negative, i.e., a repulsive van der Waals interaction occurs between the solids. However, for the interaction of solids of the same material, \(A_{131}\) is always positive, indicating an attraction between them. The interaction will be weakest when the solids and the dispersion medium are chemically similar, since \(A_{11}\) and \(A_{33}\) will be of similar magnitude and the value of \(A_{131}\) will therefore be low.

The method of pair-wise addition due to Hamaker has fallen on strong criticism. Firstly, it is evident that if atom 1 in A exerts a force on atom 1 in B, the presence of neighbouring atoms in A and B is bound to influence the interaction between A1 and B1. Secondly, it is not obvious whether the electric field propagated by an instantaneous dipole some distance from the free surface ought to take into account the finite dielectric properties of the material that lies between it and the atoms in the other body. Thirdly, it is not clear how the addition needs to be modified if the space between bodies A and B is not air or vacuum but another dielectric medium. These difficulties have been eliminated in the Lifshitz approach by treating the interacting bodies and the intervening
medium in terms of their bulk properties, specifically their dielectric constants. This approach is able to deal with bodies made of layers of different dielectric properties and is also able to cope with the problem of solids separated by a liquid medium (85).

Despite the superiority of the Lifshitz approach, it is extremely difficult to apply in practice. Furthermore, results for many body shapes are not easy to obtain due to the complexity in mathematical treatment of the continuum theory. Even then, the evaluation of the interaction energy still requires a knowledge of the complete optical spectra over all wavelengths for all the materials of interest, of which few are available. In light of the foregoing, the retarded Hamaker Equation [2.40] will be used here for the calculation of London-van der Waals interaction energy.

2.4.3. Other Relevant Forces

Besides the above-mentioned electric double layer and van der Waals forces, other forces which are important in the deposition process include

1. **Viscous interaction force**, which is due to the increased resistance to movement experienced by a particle near a foreign surface. This force reduces the mobility of a particle and hence tends to retard deposition.

2. **Born repulsion force**, which is a short-range molecular interaction force resulting from the overlap of the electron clouds surrounding individual molecules on the two approaching surfaces.

3. **Structural force**, which arises as a result of changes in the solvent structure (i.e. changes in the local ordering of molecules) in the vicinity of a surface or interface due to packing constraints.
2.4.4. Overall Interaction Energy

The total energy of interaction between two solids is obtained by summation of the electric double layer and van der Waals energies. Potential energies due to Born and structural forces could be similarly superimposed to provide a more complete picture of the overall interaction, if the expressions were available.

Figure 2.3 is a qualitative sketch of two general types of potential energy curves which are possible. It should be noted that as the separation distance \( H \to 0 \), \( \phi_{\text{edl}} \to \) constant and \( \phi_{\text{vdw}} \to -\infty \) and as \( H \to \infty \), both \( \phi_{\text{edl}} \) and \( \phi_{\text{vdw}} \to 0 \) with \( \phi_{\text{edl}} \) decreasing more rapidly. The two curves show that attraction predominates at very small and very large separations. At intermediate separations, the effects of the two contributions must be considered in more detail. In general, the potential energy curve consists of a maximum and two minima as sketched, although some of these features may be masked if one contribution greatly exceeds the other. The height of the maximum above \( \psi=0 \) is the energy barrier. The deeper minimum is called the primary minimum, and it is due to the repulsion caused by the Born force which predominates at very small distances when the two surfaces come into contact. The more shallow one is called the secondary minimum and it is due to the fact that the van der Waals energy falls off more slowly (approximately as \( 1/H \)) at large separations than does the electrical double layer interaction (approximately as \( e^{-kH} \)). Their depth is measured from \( \psi=0 \) also. Although attraction predominates at large distances, that is, the secondary minimum is generally present, it may be quite
Figure 2.3 Qualitative sketch of two general types of overall interaction energy ($\phi_n$) which are possible.
shallow, especially in view of the effects of retardation and the medium on attraction.

When two particles approach one another or when a particle approaches a surface due to diffusion, either of the following will occur. When no barrier is present or when the height of the barrier is negligible compared to the thermal energy of a particle (as shown in curve $\phi_{T2}$), then the net attractive force will pull the two bodies together into the primary minimum. As a result, flocculation or deposition occurs. On the other hand, if the height of the potential energy barrier is appreciable compared to the average Brownian energy (refer to curve $\phi_{T1}$), the surfaces will repel each other and thus flocculation or deposition is prevented. This system, represented by curve $\phi_{T1}$, is stable with respect to primary minimum flocculation or deposition. Nevertheless, flocculation or deposition could still occur into the secondary minimum. However, the process in this case will be much more reversible than in the primary minimum case due to the finite depth of the energy well.

The general character of the potential energy-distance curve can be deduced from the parameters that appear in the repulsive and attractive interaction energy expressions. These parameters are: sign and magnitude of the Stern potentials of each surface; double layer thickness, which is in turn controlled by the concentration and valence of the electrolyte (Equation [2.10]); the system Hamaker constant, which depends on the materials of the two interacting solids and on the medium separating them (Equation [2.39]); and the particular pair of boundary conditions assumed during the double layer interaction,
that is, either constant surface potential or constant surface charge density, or both.

For Stern potentials of equal sign, the potential energy is repulsive everywhere except at very small distances of separation where it is dominated by the London-van der Waals force. In this case, the effect of variations in the value of $\psi_\delta$ on the total interaction potential energy, with $\kappa$ and $A$ constant, is that the height of the potential energy barrier will increase with increasing values of $\psi_\delta$ as would be expected in view of the increase in repulsion with this quantity. The effect of variations in the value of $\kappa$ is that as $\kappa$ increases (through increasing either the concentration of electrolyte or valence of the counter-ions), the height and thickness of the energy barrier decrease until the barrier disappears altogether at very large values of $\kappa$. When the Stern potentials of the two surfaces are of opposite sign, the overall interaction energy is everywhere attractive, regardless of the values of $\kappa$ and $A$. Of the parameters mentioned, the Hamaker constant $A$ is the one which can be least controlled because its value is determined by the chemical nature of the dispersed and continuous phases involved. The effect of the variations in the value of $A$ on the total interaction energy is that the height of the potential energy barrier decreases and the depth of the secondary minimum increases with increasing values of $A$. Qualitative sketches of the effects of $\psi_\delta$, $\kappa$, and $A$ on the total interaction energy for both like and unlike charged surfaces are demonstrated in Figures 2.4, 2.5 and 2.6, respectively.
Figure 2.4 Effect of Stern (or zeta) potential on overall interaction energy as a function of separation distance between two charged surfaces.
Figure 2.5 Effect of double layer thickness ($1/\kappa$) on overall interaction energy as a function of separation distance between two charged surfaces of same polarity.
Figure 2.6 Effect of Hamaker constant $A$ on overall interaction energy as a function of separation distance between two charged surfaces of same polarity.
3. EXPERIMENT

3.1. INTRODUCTION

The main object of the experimental work was to investigate the effects of surface potential and electrical double layer thickness on surface coverage of charged colloidal silica spheres deposited by gravity onto an oppositely-charged planar substrate. The magnitudes of the two surface potentials were altered by adjusting the pH of the suspension while the electrical double layer thicknesses were varied by dissolving different pre-determined quantities of a neutral electrolyte into the suspension.

3.2. COLLOIDAL PARTICLES

In accordance with the conditions implicit in the theory, a model colloidal suspension of dispersed, uniformly-sized, spherical particles was mandatory. A review of the literature showed that the procedures for the preparation of several organic and inorganic materials (86,87,88,89,90,91) in the size-range of interest are available. In the present study, silica was chosen as the model colloid due to the fact that, besides meeting the above requirements, silica suspensions are notably stable over a wide range of electrolyte conditions (92) and that the surface chemistry of silica has been extensively studied and well documented (93,94).
3.2.1. Production of Amorphous Silica Spheres

Several methods are available for the production of amorphous silica particles (93). The most common method is to hydrolyze silicon halides in a hydrogen-oxygen flame. Another method for the production of amorphous silica is that of chemical precipitation by reacting tetra-esters of silicic acid (tetra-alkyl silicates) with water, a technique developed by Stöber et al. (90). This reaction is carried out in a mutual solvent due to the immiscibility of water with alkyl silicates. The reaction is catalysed by either acid or base solutions. According to Aelion et al. (95), the overall production takes place via two steps, namely, (i) the hydrolysis of ester to silicic acid (ii) followed by the dehydration of silicic acid forming amorphous silica, i.e.,

\[
\begin{align*}
(i) \quad & \text{Si(OC}_2\text{H}_5)_4 + 4\text{H}_2\text{O} = \text{Si(OH)}_4 + 4\text{C}_2\text{H}_5\text{OH} \\
(ii) \quad & \text{Si(OH)}_4 = \text{SiO}_2 + 2\text{H}_2\text{O}
\end{align*}
\]

In the presence of a hydroxyl ion catalyst and an excess of water, both the hydrolysis and the dehydration reactions are fast and complete. The hydrolysis reaction is rate-controlling and is first order with respect to the tetra-ethyl-ortho-silicate (TEOS) concentration. Stöber et al. (90) found that when the mutual solvent is an alcohol and the catalyst is ammonium hydroxide, the reaction produces silica spheres of fairly narrow size distribution in the size range of 0.05 to 2.0 μm, depending on the type of alkyl group of the silicate and on the mutual solvent. The longer the alkyl chain, the larger the particles.
3.2.2. Production of Large Uniform Silica Spheres

Owing to the inherent limitations in resolution of an optical microscope, it is essential that a model colloid of size in the vicinity of one micron be used. Although Stöber et al. were able to produce silica spheres in the 0.05 to 2.0 μm range, the method still has two notable drawbacks. Firstly, it produces larger particles (>1.0 μm) which are occasionally non-spherical and often unacceptably non-uniform. Secondly, to achieve a range of sizes requires the use of alkyl silicates other than TEOS, which is the only tetra-ester of silicic acid commercially available in a pure form. Therefore, in the present investigation, an attempt was made to produce monodisperse silica spheres with a suitable range of sizes by reacting only TEOS and water. In this case, the reaction rate was altered by varying the temperature (−20°C to 60°C) and the alcoholic solvent (methanol, ethanol, n-propanol and n-butanol).

The materials used were as follows. Methanol, n-propanol and n-butanol (AnalaR grade, BDH), as well as absolute ethanol (Stanchem), were used as solvents. Distilled water was deionized just prior to use. TEOS (Reagent grade, Fisher) was twice vacuum distilled before use in the experiments to ensure maximum sphericity and monodispersity as reported by Bowen (33). Anhydrous ammonia (99.9%, Union Carbide) was employed as the catalyst/stabilizer. The general sequence of steps was similar to that employed by Bowen (33) and is described below.

Measured volumes of alcohol and freshly distilled and deionized water were
pipetted into a 120 ml glass bottle with a teflon-lined screw-on cap. The bottle was then positioned in a specially constructed plexiglass jacket. An ethylene glycol-water mixture was circulated through the insulated jacket from a refrigerated constant temperature bath (NESLAB Endocal RTE-9) to maintain the reaction temperature to within ±0.1°C of the desired value. The contents of the bottle were agitated continuously by a magnetic stirrer. After thermal equilibrium was attained, anhydrous ammonia gas from a cylinder was bubbled into the water-alcohol mixture through a glass capillary until saturation was reached (indicated by no further increase in volume). At this juncture, the TEOS, which had been maintained at the same temperature, was injected into the bottle using a glass syringe. The bottle was then capped tightly to prevent ammonia from escaping. For all experiments, the volume ratio of TEOS:water:alcohol was 1:5:25, a ratio found by Bowen (33) to yield optimal results for the TEOS, water and n-propanol system.

After an invisible hydrolysis reaction in which silicic acid was formed, the mixture suddenly became opalescent signifying the onset of silica precipitation. The precipitate appeared almost instantaneously at 60°C but only after a lapse of about 15 minutes at -20°C, indicating that the rate of the hydrolysis reaction was considerably reduced as the temperature was lowered. As a consequence, the contents of the reaction bottle were sampled at 1, 2, 3, 5 and 9 hours for reaction temperatures of 60, 40, 20, 0 and -20°C, respectively, preliminary experiments in which average sizes were measured at times shorter than these having indicated that the reactions had already reached completion in all cases. Clean glass capillaries were used to transfer a droplet of the
suspension to carbon-coated electron microscope carrier grids. The samples were allowed to dry and then micrographs were taken at a number of random locations on the grid using a Hitachi HU-11A transmission electron microscope. The photographs, along with those of a calibration standard (54864 lines/in., Ladd Research Industries), were then analyzed automatically by means of a Leitz TAS-PLUS image analyzer. Between 100 to 400 particles were measured in order to determine the average size and standard deviation of each sample.

Figure 3.1 shows an electron micrograph of one of the batches of larger silica particles, obtained in this case using the solvent ethanol and a temperature of 0°C. Figure 3.2 gives the cumulative size distribution curve of the same sample plotted in terms of normal-probability co-ordinates. The two figures demonstrate that the particles are normally distributed, reasonably spherical and have a relatively narrow range of sizes. This sample has an average diameter of 1.37 µm and a standard deviation of 0.05 µm, indicating that only 5% of the particles differ from the median size by more than 3%. Similar results were realized with the other large particle batches; generally speaking, the smaller particles were even more monodisperse and spherical.

The number average particle sizes obtained as a function of temperature and type of solvent are listed in Table 3.1 and plotted as Figure 3.3. Several runs were repeated on different days under otherwise identical experimental conditions. These showed excellent reproducibility. Because of water miscibility considerations, the alcohols used as solvents in the present study were restricted to those having low molecular weights and straight hydrocarbon chains. Even so,
it was not possible to employ n-butanol below 0°C. Also, excessive evaporation prevented particle production with methanol and ethanol at temperatures exceeding 40°C.

The most dominant feature of Figure 3.3 is that, regardless of which alcoholic solvent is used, the average size of the produced particles varied inversely with temperature. One possible explanation is that this trend is related to the saturation concentration of ammonia, which decreases with increasing temperature. This hypothesis was tested by conducting two experiments (one with

![Figure 3.1 Electron micrograph of silica particles obtained using ethanol as the solvent and at a temperature of 0°C](image)

Figure 3.1 Electron micrograph of silica particles obtained using ethanol as the solvent and at a temperature of 0°C
Figure 3.2 Normal-probability plot of the cumulative size distribution curve of the particle batch shown in Figure 3.1
TABLE 3.1

Average diameter (μm) and standard deviation of silica spheres obtained using different temperatures and solvents

<table>
<thead>
<tr>
<th>SOLVENT</th>
<th>TEMPERATURE (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-20</td>
</tr>
<tr>
<td>Methanol</td>
<td>1.01±0.04</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.87±0.11</td>
</tr>
<tr>
<td>n-Propanol</td>
<td>1.67±0.05</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>0.88±0.03</td>
</tr>
</tbody>
</table>

* replicate experiment
** water-alcohol mixture saturated with ammonia at 40°C.

ethanol and one with n-propanol) in which the alcohol/water mixtures were saturated at 40°C and then cooled to 20°C before injecting the TEOS. As can be seen from Table 3.1 and Figure 3.3, the results of both tests were virtually the same as those obtained in corresponding solutions saturated at 20°C, indicating that the ammonia concentration near saturation levels does not significantly influence particle size.

A more plausible explanation is that the trend is associated with the hydrolysis reaction rate, which was observed to decrease significantly at lower
Figure 3.3 Average diameters of silica particles as a function of temperature and type of solvent used. The two filled-in symbols represent cases where the water-alcohol mixture was saturated with ammonia at 40°C before the reaction was carried out at 20°C.
temperature. This relationship between particle size and reaction rate is in accord with the earlier observations of Stöber et al. (90) and can be interpreted in terms of the limited self-nucleation model of monodisperse particle production first proposed by LaMer and Dinegar (96). The model hypothesizes the existence of a critical concentration, $C_{\text{sat}}^*$, above which nucleation proceeds at an appreciable rate and below which nucleation is negligible. $C_{\text{sat}}^*$ is significantly greater than the saturation concentration, $C_{\text{sat}}$ above which spontaneous growth will occur providing that nuclei are already available. A schematic representation of this model is depicted in Figure 3.4. Thus, as the hydrolysis of TEOS proceeds, silica nuclei begin to form only after the silicic acid concentration exceeds $C_{\text{sat}}^*$. As soon as a sufficient number of nuclei are present, particle growth permanently reduces the super-saturation of Si(OH)$_4$ below $C_{\text{sat}}^*$. From this point onwards, only particle growth can occur and, providing that the self-nucleation period is limited to a very short initial outburst, the final sol will be monodisperse. If the reaction rate is markedly reduced, it thus seems reasonable that a much smaller number of nuclei will be required to relieve the high supersaturation of silicic acid. As a consequence, since the same amount of TEOS is reacted in each experiment, the average size of the particles must increase as the temperature is diminished.

The relationship between particle size and the different alcohols employed is far more complicated. In general, particles produced in ethanol and n-propanol exhibited the strongest temperature dependence, especially at low temperatures. At elevated temperatures, the particle size varied directly with the chain length of the alcohol, but under cooler conditions, this tendency appeared to reverse itself.
Figure 3.4 Schematic diagram showing how a nucleation and a growth period may be separated resulting in a monodisperse sol except in the case of methanol. This complex behaviour is not easily explained but it is probably related to the different effects temperature has on such solution properties as solubility and viscosity.

The most important result demonstrated by this study is that, by using a single alkyl silicate (commercially available TEOS) along with a short-chain alcoholic solvent (ethanol or n-propanol), and by simply varying the reaction temperature, it is possible to produce uniform silica spheres over a wide range of
sizes (0.2 - 2.0 \( \mu m \)). The particles made in this fashion are relatively monodisperse, with the size distribution becoming wider as the temperature is increased. The best results are obtained when the apparatus is maintained as clean as possible and reagents of maximum purity are employed.

Thus, in order to fulfill the implicit requirement that a model colloid in the size range of around one micron be used in the experiment, a batch of monodispersed silica spheres exhibiting similar qualities as those mentioned above was produced by reacting TEOS (2 ml) with water (10 ml) in n-propanol (50 ml) at a reaction temperature of approximately 0°C. The number average particle size obtained in this case was 1.00 ± 0.04 \( \mu m \).

3.3. CLEANING OF PARTICLES

The particles which are produced by the above method are not in a utilizable form due to the presence of various contaminants residing in the solution. These include the mutual alcohol solvent, the alcohol produced by the hydrolysis of alkyl silicate, and ammonia. Therefore, in order to yield a highly dispersed suspension of silica particles in water with minimum carry-over of contaminants from the production solution, a suitable cleaning method had to be developed.

A method that was initially pursued rather substantially was that due to Bowen (33). In his thesis, Bowen reported a washing technique whereby the treated silica particles could be easily redispersed in aqueous solution having
conductivity values in the range of 1 - 2 μmho/cm. The procedures necessary for this technique are described below. A batch of freshly produced particles was filtered almost to dryness and the wet filter cake was placed in a water-cooled beaker containing the wash solution and a magnetic stirring bar. The contents of the beaker were then stirred and treated ultrasonically in a Branson 5200 ultrasonic bath for ten minutes after which the contents of the beaker were refiltered and the dispersion process repeated. After the filtration step, the particles were dried at 100°C for 48 hours in a vacuum oven. The addition of heat during the drying process is required to improve the desorption of ammonia. When water was used as the wash solution, it was found that the final hydrosol was always far less disperse than the initial suspension. However, when two or three washings in either n-propanol or n-butanol were used, the resultant silica suspensions were found to be as well dispersed as the original production suspension. According to Bowen, the reason why alcohol pretreatment is effective in promoting dispersion is due to the difference in the solubilities of silica in water and in alcohol, the former being rather substantial while the latter is negligible. It is suggested that as the water in the filter cake evaporates upon drying, the dissolved silicic acid precipitates on the available surface, thereby cementing together those particles in contact. Since the solubility of concave silica surfaces is less than that of convex surfaces (94), these bridges tend to grow rather than dissolve upon subsequent redispersal. Thus, many particles remain chemically bound together after resuspension. Furthermore, silica surfaces strongly adsorb many layers of water. Consecutive washing of particles in alcohol greatly increases the removal of these adsorbed water layers. Because the solubility of silica in alcohols is very small, a negligible amount of precipitation takes place
during the drying process. Thus, alcohol-treated silica particles can be dried to produce an easily dispersed powder.

Although the above method produces silica particles which can be easily redispersed, it still suffers from the formation of small quantities of agglomerates which are undesirable for the deposition experiments. Thus, to avoid this problem, a revised method based on the above was developed. In this method, the drying step for the removal of ammonium ions was eliminated. This elimination takes care of particle agglomeration. However, it results in silica suspensions with unacceptably high values of conductivity due to the presence of ammonium ions in the solution. One way of removing these ions is to repeat the filtration and dispersion process using clean, distilled and deionized water as the wash solution until the conductivity of the filtrate reaches the desired value. This process, however, is rather arduous as it requires considerable repetition before the conductivity of the solution becomes acceptable. As an alternative, a cross-flow filter was devised to handle this task. A schematic diagram of this cleaning device is depicted in Figure 3.5. The filter, which was constructed of thick-walled plexiglass, was made up of two parts. The top portion consisted of a cylindrical chamber 7 cm in height and 6.2 cm in diameter with an 'O'-ring sealed screw-on cap. The bottom part housed a 55 mm perforated stainless steel disc, a 55 mm porous polyethylene disc, a 47 mm filter membrane, and a 55 mm stainless steel annular ring. The filter membrane was sputter-coated with a thin layer (400 Å) of gold-palladium alloy that enabled the membrane surface to be charged when a potential difference was applied across the membrane at the top and the stainless steel disc at the bottom. The porous disc of polyethylene was
Figure 3.5 Schematic diagram of the cross-flow filter (cross-sectional view)
used as a support for the flimsy filter membrane as well as to act as an insulator preventing the two charged surfaces from contacting. The filter was assembled by slipping the top portion into the bottom portion and fastened with six sets of bolts and nuts. The filter was designed to withstand pressures of up to 20 p.s.i.g.

The general procedures for the cleaning of silica suspensions were as follows. A portion of previously produced silica suspension was filtered and redispersed twice using n-propanol as the wash solution to remove the majority of ammonium ions in the solution. These filtered silica particles were then washed with water, dispersed and transferred into the filter chamber. A magnetic stirring bar was introduced into the chamber to create a tangential motion which swept particles clear of the membrane surface. A potential difference was created across the filter membrane and the stainless steel disc by a regulated power supply (Anatek Model 50-1.0S). Since it is known that the silica particles will exhibit a negatively charged surface under the prescribed experimental conditions, the membrane surface was negatively charged to maintain a repulsion between the particles and this surface. Distilled and deionized water, which was kept in a specially constructed pressure vessel, was forced through a filtration unit equipped with a filter membrane 0.2 μm in pore size to remove any dust that may have been present in the system. Nitrogen gas from a cylinder was used as the pressure source to maintain the pressure in the vessel at 10 p.s.i.g.. This filtered water was then allowed to be added dropwise into the chamber. The conductivity of the outflow from the filter was continuously monitored with a Seibold (model LTA) conductivity meter. The cleaning process was terminated
when the desired conductivity value was attained. It was found that for an initial conductivity value of 3 μmho/cm, a washing time of less than 30 minutes was sufficient to reach a final value of 1 μmho/cm.

This method of cleaning would thus seem ideal for the present purpose. However, in the course of cleaning, it was discovered that some particles managed to deposit on the alloy-coated membrane surface, although they seemed to be rather loosely attached to this surface. Possible causes include the flow through the membrane, which may force particles to the surface; and the conducting coating on the membrane surface, which may not be electrically continuous, thus creating patches that do not repel the particles. Although this defect may be quite easily corrected, it was not pursued further due to time constraints. Since the loss of particles to the surface is very undesirable in the experiments, subsequent cleanings were done using the tedious revised method mentioned above, with filtration replaced by centrifugation for solid-liquid separation.

3.4. THE DEPOSITION CELL

The deposition of colloidal silica spheres onto a planar substrate was carried out in a specially constructed deposition cell. The cell, built of plexiglass, has a cylindrical configuration and dimensions 15 mm I.D., 26 mm O.D., and 10 mm height. The inner wall of the cell was made very smooth to minimize mechanical entrapment of particles. Both cell ends were fitted with an 'O'-ring and sealed with a 0.17 mm thick glass cover slip 25 mm in diameter. It should
be noted here that only the bottom surface acted as the deposition surface and hence was coated with plastic. The other was not. The cover slip was held firmly in place by screwing threaded aluminum end-cups onto the threaded outer wall. The aluminum cup was designed with a concentric circular opening of 15 mm, which enabled the transmission of light through the cell when it was placed under an optical microscope. A schematic diagram of the deposition cell is depicted in Figure 3.6.

![Schematic diagram of the deposition cell](image)

Figure 3.6 Schematic diagram of the deposition cell

3.5. PREPARATION OF DEPOSITION SURFACE

In the deposition experiments, circular cover slips 25 mm in diameter and 0.17 mm in thickness were used as the deposition substrate. The experiments were to be carried out under conditions where the silica sols are stable and negatively charged to prevent coagulation. This occurs in the pH range of about 4 to 11. The iso-electric point of the silica surface is approximately pH 3 and
hence the sol is positively charged below this value. Above pH 11, the high counter-ion concentration thins the double layer to the extent that the sol becomes unstable. Unfortunately, in the pH range where the particles are stable, the glass cover slip will also exhibit a negatively charged surface. Thus, to ensure adherence of silica spheres onto the glass surface upon contact, the surface characteristics of the glass have to be altered to one exhibiting a positive charge. This was accomplished by coating the clean cover slip with a very thin layer of a cationic copolymer of 80% 2-vinyl pyridine and 20% styrene (2VP/S).

3.5.1. Production of 2-Vinyl Pyridine/Styrene

Unfortunately, the copolymer 2VP/S was not available commercially and hence a method of manufacturing this copolymer had to be found. A literature search revealed that Utsumi et al. (97) had reported a method whereby this copolymer can be prepared by solution polymerization. A modified version of this method has been adopted and the procedures necessary are detailed below.

4 ml of methanol (AnalaR grade, BDH), 4 ml of styrene (99%, Mallinckrodt) and 15 ml of 2-vinyl pyridine (97%, Aldrich) were injected using clean glass syringes into a 100 ml test tube equipped with a sealable screw-on cap and was tightly wrapped with aluminum foil to exclude light. Both styrene and 2-vinyl pyridine were freshly vacuum distilled prior to use as each contained a higher boiling point inhibitor added to prolong shelf-life. Nitrogen gas (Union Carbide), deoxygenated in a pyrogallol solution (5 g pyrogallol, 50 g KOH, and 100 ml H₂O) and dried in a packed bed of anhydrous calcium sulphate
(DRIERITE) was allowed to bubble through the mixture via a glass capillary. At the end of one hour, 0.2 g of benzoyl peroxide (AnalaR grade, BDH) was added through a glass funnel to initiate the polymerization reaction and the bubbling was continued. The bubbling of nitrogen was terminated when the viscosity of the solution had increased to such an extent that the passage of nitrogen was no longer possible. At this juncture, the glass capillary was removed from the solution and the test tube was tightly sealed and stored in a dark location for two days at room temperature. The resultant polymer was a clear golden brown solid residing at the bottom of the test tube.

After the glass test tube was carefully broken away from the polymer mass, the solid polymer was broken down into small pellets of plastic which were then dissolved in 500 ml of chloroform (Reagent grade, Fisher). When dissolved, the polymer solution was filtered to remove glass debris present in the solution due to the breakage of the test tube. The filtered polymer solution was then placed in a 500 ml separatory funnel and added dropwise to 1600 ml of petroleum ether (Reagent grade, Fisher) in a well-stirred 2000 ml beaker. On contact with the petroleum ether, the polymer formed a white fibrous precipitate which could be continuously removed from the beaker using a glass rod. This fibrous precipitate was further purified by repeating the process once. The final precipitate was washed in 400 ml of fresh petroleum ether and then dried under vacuum for one day. Approximately 15.6 g of 2VP/S were obtained.
3.5.2. Coating of Deposition Surface

Plastic coated surfaces were prepared by coating the cover slips with solutions of 2-vinyl pyridine/styrene in chloroform (AnalaR grade, BDH) using the falling level method that has been employed for preparing support films for electron microscopy. A schematic diagram of the coating apparatus used is shown in Figure 3.7. It consists of a thick-walled glass funnel 10 cm in diameter and 18 cm in height. Attached to it was a 4 ft length of 2 mm I.D. glass capillary tubing equipped with a 2 mm bore teflon stop-cock at the bottom to control the discharge of solution. The apparatus and its dimensions have been designed to give similar results to those used by Revell and Agar (98). They suggested that the final film thickness and uniformity of the coated film are proportional to the concentration of plastic in the solution and to the constant drainage rate. The latter can be effected by having the dimensions of the effective head of the liquid be very much larger than that of the specimen. The concentration of plastic solution used was 0.5 w% which, according to Marshall (99), yields an optimal thickness of 200 Å.

The procedures for coating were as follows. Circular cover slips were cleaned with hot chromic acid (concentrated sulphuric acid saturated with sodium dichromate) and thoroughly washed to remove all traces of residual acid. They were then contacted with methanol for one hour and dried under vacuum for an additional hour to remove layers of adsorbed water in order to improve the strength of the bond between the plastic film and the glass substrate. The cover slip was then fitted to a simple spring clip which gripped the sides of the upper
Figure 3.7 Schematic diagram of the coating apparatus
edge of the specimen and the surface on which the film was to be coated was held vertically in the solution. Care was taken to ensure that the specimen was immersed to a level where the solution was just beneath the edge of the clip. This is necessary to create a steady and non-disturbed flow which would otherwise affect the thickness and uniformity of the coated film. When the solution in the funnel had come to rest, it was allowed to drain by carefully opening the stop-cock. When finished, the film was allowed to dry in situ for approximately five minutes before the specimen was removed. The coating apparatus was then washed with chloroform to remove any traces of plastic which might alter subsequent solution concentrations or block the capillary tube.

3.6. PARTICLE DEPOSITION

It can be anticipated from theory that the extent of surface coverage depends on both the electric double layer thickness and the surface potential of the particles. The double layer thickness is dependent upon the quantity and valency of neutral electrolytes present in the system while the surface potential is dependent upon the pH of the suspension. Thus, in the present investigation, the experiment was divided into two portions.

1. the study of the effect of surface potential on surface coverage of silica spheres, and

2. the study of the effect of double layer thickness on surface coverage of silica spheres.

The surface potential of the particles was varied by altering the pH of the dispersion using either HCl or NaOH while KCl was used as the neutral electrolyte in achieving various predetermined electrolyte concentrations.
Although the experiment was divided into two parts, the procedures necessary for both were similar and hence only the general sequence of steps are outlined below. A portion (approximately 66.7 mg) of freshly prepared silica spheres in suspension, enough for several experiments, was cleaned by the process described earlier (Section 3.3). The cleaned suspension was then divided into eight equal lots and these were placed in eight 50 ml volumetric flasks. When the effect of pH on surface coverage was to be studied, distilled, deionized and filtered water was used to make up the volume of the suspension and the pH was adjusted to the desired value using either NaOH or HCl. On the other hand, when the effect of double layer thickness on surface coverage was to be studied, a predetermined amount of KCl was added to achieve the desired electrolyte concentration and again distilled, deionized and filtered water was used to make up the volume. In either case, both the pH and the conductivity of the suspensions were measured. The ambient temperature of the room was also recorded. The suspensions were then dispersed for 30 minutes in a Branson 5200 ultrasonic bath, after which they were transferred into the deposition cells using clean disposable pipettes. The suspension concentration was such as to provide up to 30 layers of spheres on the deposition surface. Care was taken to ensure that the trapping of air bubbles inside the cell was avoided. This was achieved by filling the cell with the suspension up to the rim at which a convex meniscus was formed. A clean cover slip was then placed carefully over the meniscus in such a way that the excess suspension was squeezed out, leaving a tightly sealed, air bubble-free cell. The cover slip was then held firmly in place by screwing the aluminum cap onto the cell. The particles in the cell were allowed to settle by gravity and be deposited onto the polymer-coated substrate
for a day, although a simple calculation using Stokes' equation showed that a few hours were sufficient. After settling, the unattached particles were removed by rinsing the suspension with distilled, deionized and filtered water until the suspension became almost particle-free, leaving only a single layer of spheres on the substrate surface. This rinsing step was necessary to ensure that the best possible optical observation was obtained.

3.7. MEASUREMENT OF SURFACE COVERAGE

The determination of surface coverage of silica particles on the polymer-coated glass substrate was performed by using a Zeiss Universal optical microscope with a 100x oil immersion objective and a Kontron IPS image analysis system. The two pieces of equipment were "linked" together so that the particles seen at random positions under the microscope could be "transferred" to the image analyser and processed into sharp contrast black and white images. These images were then superimposed onto a measuring frame whose area had previously been calibrated. For the present analysis, the measuring frame was a 30 μm by 30 μm square. To properly account for particles overlapping the edges of the frame, those touching the top and right edges were eliminated, while those touching the left and bottom edges were included and made into complete spheres. It is assumed that the number of particles in the measuring frame after the adjustment will not deviate significantly from the true number before adjustment, as the inclusion and exclusion of particles overlapping opposing edges will have a cancelling effect. The adjusted number of particles within the measuring frame was then counted. For each cell substrate, the total number -of
particles at various randomly chosen locations under the microscope were counted. The total projected area of the particles within the measuring frame was obtained by multiplying the number of particles within the frame by the projected area of one particle, the average diameter of which had been determined earlier using a transmission electron microscope. The fractional area occupied by the spheres was then obtained by dividing the total projected area of spheres by the area of the measuring frame. Figure 3.8 shows a photograph of a polymer-coated substrate with a single layer of deposited silica spheres.

Figure 3.8 Photograph of polymer-coated substrate with a single layer of deposited silica spheres
3.8. MEASUREMENT OF ZETA POTENTIAL

3.8.1. Particle Zeta Potential - Micro-electrophoresis

The zeta potential of the particles, $\zeta_p$, was determined using a Rank Brothers Mark II micro-electrophoresis apparatus, which basically consists of a transparent cell of either rectangular or cylindrical cross-section, a pair of electrodes, and a microscope. The cell is used for containing a sample of the particle suspension, the system of electrodes for applying a potential gradient within the suspension, and the microscope for observing the resulting motion of the particles. The determination of zeta potential involves the measurement of particle electrophoretic mobility ($\mu$m/sec.)/(volt/cm), which was obtained by measuring the time taken for a targeted particle to traverse a prechosen distance (as determined by a calibrated grid in the microscope eyepiece) in a known potential gradient. In general, about 20 such measurements were made, after which the average electrophoretic mobility was converted into zeta potential using the numerical results of Wiersema et al. (70). A sample calculation based on their technique is shown in Appendix A.2.

Although the Rank Brothers instrument was designed to accommodate both types of cells, in the present study, a rectangular cell approximately 0.1 x 1.0 cm in cross-section and 7.0 cm in length was employed for all mobility measurements. This preference of the rectangular cell over the cylindrical one is due to the fact that the former had the advantage of permitting electro-osmotic measurements (see Section 3.8.2), which are taken at the mid-plane between the
top and the bottom of the cell, without interference from sediments resulting from the action of gravity on the particles during mobility measurements. If the cylindrical configuration were used, the sediment would disturb the electro-osmotic velocity distribution and hence result in substantial measurement errors. Furthermore, the plastic coating (Section 3.5.2) required for the electro-osmosis measurements could be applied more easily to the rectangular cell than to the cylindrical one.

During the electrophoresis measurements, samples of the suspensions used in the deposition experiments were transferred to the cell using a clean glass syringe. The cell was rinsed twice with the same suspension, refilled and then clamped within a constant temperature bath maintained at 25.0 ± 0.2°C, equivalent to the operating temperature of the deposition runs.

Once the sample was in position, blackened platinum electrodes, constructed of a 13 x 20 x 0.013 mm sheet of bright platinum rolled into a cylinder and sealed into standard-taper glass fittings, were placed in mating electrode compartments at either end of the cell. The electrodes were used to apply a d.c. potential gradient along the length of the cell. The glass fittings served to seal the ends of the cell in order to prevent evaporation that might cause unwanted convective currents within the cell. After each electrophoresis measurement the blackened electrodes were thoroughly washed with distilled water and stored in distilled water until required for the next measurement.

Direct illumination was provided by a 12 V, 100-watt quartz iodine lamp.
The light beam could be focussed at any position within the cell by means of an adjusting screw on the illuminating condenser. The condenser was of the dark-field type, which allowed the particles to be seen as points of light against a black background.

The movement of the particles within the cell was observed with a microscope employing a 10x objective and a 10x eyepiece. The microscope was attached to a micrometer stage and hence could be focussed at any position along the line normal to, and passing through the centre of, the large face of the cell across its entire smaller width. To register the mobility of the particles, the eyepiece contained a graticule with a square grid. The graticule was calibrated against a "stage micrometer" (see Appendix B, Section B.1.2) and was found to have an average grid spacing of $119 \pm 0.09 \mu\text{m}$.

The potential gradient was applied using a d.c. supply and the overall voltage drop between the two electrodes was read from a voltmeter. In order to determine the potential gradient (applied voltage/interelectrode distance) from the measured voltage drop, it was necessary to determine the effective interelectrode distance, $l$, which can be found based on a knowledge of the solution conductivity, $\lambda$, the cross-sectional area of the cell at the plane of viewing, $A$, and the measured resistance between the two electrodes, $R$. The relationship between these parameters is

$$ l = R\lambda A \quad [3.1] $$

The procedures required for measuring these quantities are given in Appendix B, Section B.1.1. The effective interelectrode distance, $l$, for the rectangular cell used
in the present study was determined to be 7.085 cm.

When a potential difference is applied to the cell, both the particles (electrophoresis) and the solution (electro-osmosis) are set in motion. Since the cell is closed, this electro-osmotic movement, which manifests itself as a constant velocity flow at the four walls of the channel, generates a difference in pressure between the extremities of the cell. As a consequence of this pressure difference, a return flow down the centre of the channel occurs. Thus, there exists within the cell cross-section a region where the fluid velocity is zero. The location of these "stationary levels" in a closed rectangular cell can be determined from the solution of the equation of hydrodynamic motion describing the steady-state flow in the channel subject to the constant electro-osmotic slip velocity at the walls (33). Komagata (100) showed that for a rectangular cell of half-width $a$ and half-thickness $b$ ($a/b \geq 2$), and for measurements taken at the centre of the cell width, the stationary levels are symmetric about the mid-plane of the channel and are located at

$$\frac{y}{b} = \pm \left[ \frac{1}{3} + \frac{128b}{\pi^5 a} \right]^{0.5} \quad [3.2]$$

where $y$ is the distance from the mid-point. For the cell used in the present experiments, $a=0.4922$ cm, $b=0.05605$ cm (see Appendix B, Section B.1.1), and hence $y/b=\pm 0.6172$.

The true electrophoretic velocities of the particles were measured with the microscope focussed at either of the two stationary levels. The stationary levels
were located by moving the microscope focus a distance of 0.3828b and 1.6172b from the front inside face of the cell. To eliminate polarization effects, each particle was timed over the same distance in both directions. The necessary field reversal was attained by means of a simple switching circuit provided with the instrument. Random errors due to Brownian motion and depth-of-field effects were minimized by measuring the velocity of at least ten different particles. In some experiments, 20 separate determinations were made. The same number of measurements were taken at both stationary levels to assure that their positions had been properly located. The average velocity was converted to an mobility by dividing by the applied potential gradient.

3.8.2. Substrate Zeta Potential - Electro-osmosis

The zeta potential of the plastic used to coat the deposition substrate, $\xi_w$, was measured by the method of electro-osmosis. These measurements were performed simultaneously with the $\xi_p$ measurements in the rectangular cell. Thus, prior to the measurements, the rectangular cell was cleaned and coated with a layer of 2VP/S. The coating procedures were similar to those described in Section 3.5.2. for creating plastic films on the glass cover slips used in the deposition experiments.

As mentioned in the previous section, the wall zeta-potential is responsible for the electro-osmotic flow which occurs when a potential gradient is applied along the length of the cell. Although an expression for the electro-osmotic velocity distribution is available in terms of the wall zeta-potential, the motion -of
the liquid cannot be measured directly. However, since the electrophoretic velocity
do the particles relative to the liquid is everywhere constant, if the particle
velocity relative to the walls is measured at one other location in the cell as
well as at the stationary levels, then the electro-osmotic velocity can be
determined by difference. The location for this additional measurement of particle
velocity was chosen to be the centre of the channel because the gradient of the
electro-osmotic velocity profile at this location is zero and hence, the depth-of-field
error is minimal. Except for the location of the measurement, the procedure for
electrophoretic measurements was identical to that for the determination of
particle zeta potential. At least 10 particles were timed at the centre of the
channel in either direction. For a cell with a/b ≥ 2, the wall zeta-potential, \( \xi_w \),
was determined using the relationship derived by Bowen (33)

\[
\xi_w = \frac{8 \pi \mu}{\epsilon \chi} \left[ \frac{1 - (192b)/(\pi^5 a)}{1 + (384b)/(\pi^5 a)} \right] \left[ U_E - U_o \right]
\]

[3.3]

where \( U_E \) is the true electrophoretic velocity (measured at the stationary level),
\( U_o \) the apparent velocity at the mid-plane, \( \mu \) the solution viscosity, \( \epsilon \) the
solution dielectric constant, and \( \chi \) the applied potential gradient.
4. COMPUTER SIMULATION OF RANDOM PARTICLE DEPOSITION

In the present study, the random deposition of monodispersed spherical particles onto a planar surface under quiescent conditions has been numerically simulated using two different schemes. The first scheme involved a two-dimensional simple rejection model where only non-overlapping particles were deposited while the second scheme consisted of a three-dimensional model where the rolling of sedimenting particles over the surfaces of previously-deposited particles as well as the stacking of particles were allowed.

4.1. TWO-DIMENSIONAL RANDOM PARTICLE DEPOSITION MODEL

In this model, particles 0.5 unit in diameter were dropped at randomly chosen x- and y- coordinate positions one at a time onto a planar surface 10 x 10 units square divided evenly into 100 identical square lots of 1 x 1 unit. The random position of the centre of the falling particle was generated using the UBC Computer Centre random number generator (RAND). If it was found that the value of either one of the (x,y) coordinates generated fell outside the prescribed range (i.e., outside the substrate area), the generated (x,y) coordinates were discarded and a new set of random (x,y) coordinates generated. This process was repeated until a satisfactory set of (x,y) values was obtained. When a particle was dropped, the projected distance in the (x,y) plane between this particle and each of the previously deposited particles in the neighbouring lots, including the lot of the falling particle, was computed.
If this distance were bigger than the sum of the particle radii (or in this case, the particle diameter, since all particles were assumed to be of equal size), i.e., the falling particle did not overlap with the particles already in place, then it was considered permanently fixed at this position. The x and y coordinates of this particle were recorded and the counter for the number of particles in this particular lot was increased by one. The random coordinates for the next trial particle were then generated and the process continued as before. On the other hand, if any of the projected distances were smaller than the particle diameter, then the particle was discarded before the co-ordinates of the next particle were generated. In this case, no alteration in the record of particles deposited was carried out. The deposition process was continued in this manner until the successive number of failures for the falling particle to be deposited exceeded a maximum value of 1000. At this point, it was assumed that the surface had reached its maximum coverage, i.e., the surface was "saturated".

Once saturation had been obtained, the elimination of particles touching the top and right edges of the square substrate surface was carried out before the fraction of the total area occupied by all the particles deposited on the planar surface was calculated. This process of particle elimination in the simulation model was necessary to ensure that the experimental procedures described in Section 3.7 leading to the determination of surface coverage was being followed correctly in the simulation.

In order to estimate the influence of double layer thickness on the maximum surface coverage, it was assumed that each particle has an effective
radius, $a_e$, which is larger than its actual radius, $a$, such that the difference $2(a_e-a)$ represents the minimum distance to which two particles deposited on a planar surface can approach one another because of double layer repulsion. The distance, $(a_e-a)$, cannot be accurately predicted beforehand, but it likely depends in a monotonic fashion on the double layer thickness, $1/\kappa$. For example, $2(a_e-a)$ could be the distance at which the overall interaction energy between two deposited particles is approximately $2-10$ kT; a kT being the average thermal energy of a single Brownian particle. Unfortunately, because no theory yet exists for the interaction energy under such circumstances, it was assumed, for convenience, that $a_e = (a + 1/\kappa)$ in the present analysis. This approximation can be refined when the appropriate extension to the double layer interaction theory becomes available.

Thus, if it is further assumed that the particle with its attendant double layer acts as a solid sphere having radius $a_e$, then it is easily shown that the surface coverage, $\theta$, is related to the maximum coverage, $\theta_0$, when $1/\kappa = 0$ (i.e. as obtained above) by

$$\theta = \left[ \frac{a}{a_e} \right]^2 \theta_0 = \left[ \frac{\kappa a}{1+\kappa a} \right]^2 \theta_0$$

4.2. THREE-DIMENSIONAL RANDOM PARTICLE DEPOSITION MODEL

In this model, as in the case of the two-dimensional model, particles 0.5 unit in diameter were dropped at randomly chosen $x$- and $y$- coordinate positions one at a time onto a planar surface 10 x 10 units square divided evenly into 100 identical square lots of 1 x 1 unit. The random $(x,y)$ coordinates
of the centre of the falling particle were generated using the UBC Computing Centre random number generator (RAND) while the initial z coordinate of the centre of the falling particle was arbitrarily assigned to a value of 1000 units. If it was found that the value of either one of the (x,y) coordinates generated fell outside the prescribed range (i.e., outside the substrate area), the generated (x,y) coordinates were discarded and a new set of random (x,y) coordinates generated. This process was repeated until a satisfactory set of (x,y) values was obtained. When a particle was dropped, the projected distance in the (x,y) plane between this particle and each of the previously deposited particles (regardless of their values of z coordinate) in the neighbouring lots, including the lot of the falling particle, was computed.

If this distance were bigger than the sum of the particle radii (or in this case, the particle diameter, since all particles were assumed to be of equal size), i.e., the falling particle did not overlap with the particles already in place, then it was considered permanently fixed at this position and its final value of the z coordinate would be one particle radius. The x, y and z coordinates of this particle were recorded, and the counter for the particles in this particular lot was increased by one. The random coordinates for the next trial particle were then generated and the process continued as before.

On the other hand, if any of the projected distances were found to be smaller than the particle diameter, then it was assumed that a contact between the falling sphere and the subordinate sphere(s) had occurred. If there were only one instance where the projected distance was found to be smaller than the
particle diameter, then only one sphere below had been contacted by the falling sphere. If, however, more than one of the projected distances were found to be smaller than the particle diameter, then a comparison of the z coordinates of all the subordinate spheres in question was performed so that the number of sphere(s) having the largest value of the z coordinate could be determined. These were the spheres assumed to have been contacted by the falling sphere. Depending on the number of subordinate spheres at this largest value of z, the falling sphere would either be allowed to roll over the surface(s) of the sphere(s) and continue to descend or be nested within the spheres. It was assumed that, in order for the falling sphere to be nested, simultaneous contact with at least three subordinate spheres was necessary. Thus, if either three or four spheres were encountered simultaneously, the falling sphere was assumed to have nested within the subordinate spheres and its final resting coordinates determined. The counter for the number of spheres at this lot would then be increased by one and a new set of random coordinates for the next trial sphere generated and the process continued as before.

If, however, only one or two subordinate spheres were encountered, then the falling sphere would not be nested but would roll over the surface(s) of the sphere(s). After the falling sphere had rolled over the surface(s) of the subordinate sphere(s) and its final position recorded, computation of the projected distance with all other previously deposited spheres at the same z elevation in the neighbouring lots, based on its new (x,y,z) coordinates, was again carried out. This computation was necessary to check whether or not additional sphere(s) would be encountered while rolling. If no additional sphere(s) were encountered,
then its initial \((x,y,z)\) coordinates were replaced by its final \((x,y,z)\) coordinates and the fall continued. If, indeed, sphere(s) were encountered, then the already recorded \((x,y,z)\) coordinates were discarded and a set of new \((x,y,z)\) coordinates for the final position of the falling sphere were calculated by taking the additional encountered sphere(s) into consideration. For example, when a subordinate sphere was first encountered by the falling sphere, the falling sphere was allowed to roll over the surface of the subordinate sphere until its final position was reached. Then, based on this new \((x,y,z)\) position, computation of the projected distance between the falling sphere and its neighbouring spheres was again carried out but this time only with spheres at the same \(z\) coordinate as that of the falling sphere. If it was found that another sphere was contacted at this new position, then its initial \((x,y,z)\) coordinates were restored while its newly calculated \((x,y,z)\) coordinates discarded. The falling sphere was then treated as having contacted two subordinate spheres instead of one and the direction of fall as well as the new \((x,y,z)\) coordinates of the falling sphere were recalculated based on the algorithm for a two-sphere encounter, and the falling process continued. The mathematical equations necessary for the determination of new coordinates have been formulated and their derivations are described in detail in subsequent sections of this chapter.

The deposition process was continued in this manner until the total number of spheres deposited exceeded a maximum value of 1000, at which stage the substrate surface was assumed to be "saturated". A schematic flow diagram used for computing this model is depicted in Figure 4.1.
A sphere with random (x, y) is allowed to fall

Can this sphere contact another below as it falls?

Yes

Identify the number of particle(s) it contacted

No

New (x, y) determined

One sphere?

No

Two spheres?

No

Can this sphere contact another below it while rolling on the first?

Yes

Determine its nested (x, y, z)

Record and update all relevant information

No

Has the number of spheres used exceeded the maximum allowed value?

Yes

Stop

Figure 4.1 Schematic flowchart for random sphere deposition. Rectangular boxes indicate operations. Oval-ended boxes indicate tests determining the next operation.
Once saturation had been obtained, the original "hard-sphere" surface coverage (i.e., $a_e = a$) as well as the double layer thickness dependent surface coverages (i.e., $(a_e - a) = 1/k$) were then determined according to the methods used for the two-dimensional model described earlier.

Thus, it can be seen that although there are many similarities between the two models, differences do exist in that instead of discarding the falling sphere when its projected area overlapped with the projected area of another previously deposited sphere as in the two-dimensional model, the falling sphere in the three-dimensional model was allowed to roll over the surface(s) of the sphere(s) it contacted and the process was continued until it either reached the substrate surface and was deposited or was nested among previously settled spheres. In the former case, the final value of the $z$- (elevation) coordinate of the sphere centre was always one sphere radius while, in the latter case, $z$ could be equal to (deposited) or greater than (nested) $a$. It should be noted here that in both models, the simulation did not actually involve the motion of the particle centre through successive points. Instead, the path and final resting place of the particle were determined by methods of analytic geometry.

4.2.1. One-Sphere Encounter

When the falling sphere encounters a second sphere beneath it, its configuration will resemble any of the following positions depicted in Figure 4.2.
Upon contacting the sphere below, the falling sphere will roll along the surface
curvature of the sphere it contacted in a direction parallel to the line joining the
two centres of the spheres until its elevation corresponds to that of the sphere
below. The derivation of algorithms necessary for determining its new (x,y)
coordinates is similar for cases I to IV depicted in Figure 4.2 and hence only
the derivation based on case I will be presented.
As illustrated in Figure 4.3, let the centres of the sphere below and the initial and final positions of the falling sphere be B, T and F, respectively. Then, the straight line joining the centres B, T and F can be represented by the equation

\[ y = mx + c \]

where the slope \( m = \frac{y_T - y_B}{x_T - x_B} \)

and the constant \( c = y_T - mx_T \).

At \( x = 0 \), \( y_{xo} = c \).

Let DI be the distance between \( y_{xo} \) and B, which can be determined as follows:

\[ DI = \left[ (x_B - 0)^2 + (y_B - y_{xo})^2 \right]^{0.5} \]
When the rolling of the falling sphere has stopped, i.e., when the next initial position $F$ is reached, the distance between $B$ and $F$ is equal to the diameter of the sphere ($d$). Therefore, the new position of the falling sphere is:

$$x_F = x_B \frac{(DI + d)}{DI}$$

and

$$y_F = y_{xo} + \left[ (y_B - y_{xo}) \frac{(DI + d)}{DI} \right]$$

For cases V to VIII, where one of the coordinates of the two spheres is identical, determination of the falling sphere's new coordinates is greatly simplified. For example, for case V shown in Figure 4.4 below, the new $(x, y)$ coordinates of the falling sphere are

$$x_F = x_B = x_T$$

$$y_F = y_B - d$$

Figure 4.4 Plan view showing the initial and final position of the falling sphere when a subordinate sphere is encountered (Case V)
For the special case where the (x, y) coordinates of the falling sphere were identical to those of the sphere it contacted below, i.e., the falling sphere was sitting directly on top of the subordinate sphere, a directional-indicating random number was generated and the sphere was allowed to roll in this direction.

4.2.2. Two-Sphere Encounter

When two spheres are simultaneously encountered by the falling sphere, the resultant configuration could resemble any of those shown in Figure 4.5:

![Figure 4.5](image_url)

Figure 4.5. Plan view showing various possible general configurations when two spheres below are encountered by the falling sphere (○ falling sphere; ○○ spheres below.)

Again, since the determination of the final (x, y) coordinates of the falling sphere is similar for configurations I to IV, only case I is used here to demonstrate the derivation of the necessary algorithm.
Consider the configuration illustrated in Figure 4.6. Let the centres of the spheres below be $B_1$ and $B_2$, and the initial and final positions of the falling sphere be $T$ and $F$ respectively.

![Figure 4.6 Plan view showing the initial and final positions of the falling sphere when two subordinate spheres are encountered (Case I)](image)

If $E$ is at the mid-point between $B_1$ and $B_2$, then it can be easily seen that

$$x_E = \frac{x_{B1} + x_{B2}}{2}$$
$$y_E = \frac{y_{B1} + y_{B2}}{2}$$
$$x_I = x_E$$
$$y_I = y_{B2}.$$  

Using a linear equation of the form

$$y = mx + c$$
the slope of the direction of falling particle motion, \( m = -\frac{x_{B1} - x_{B2}}{y_{B1} - y_{B2}} \),

the constant \( c = y_E - mx_E \)

and thus \( x_G = \frac{y_{B2} - c}{m} \).

Length between G and I \( (GI) = |x_G - x_I| \)

Length between E and G \( (EG) = \left[ (y_E - y_I)^2 + (x_G - x_I)^2 \right]^{0.5} \)

When rolling of the falling sphere has stopped, i.e., when the final position F has been reached, the centres of the three spheres will form an isosceles triangle. Therefore, the distances between centres F and B₁, and F and B₂, equal the sphere diameter, i.e.,

\[ FB_1 = d \]

and \[ FB_2 = d. \]

Also, the distances between the following points are:

\[ B_2 \text{ and } E \ (B_2E) = \frac{1}{2} \left[ (y_{B1} - y_{B2})^2 + (x_{B1} - x_{B2})^2 \right]^{0.5} \]

\[ F \text{ and } E \ (FE) = \left[ (FB_2)^2 - (B_2E)^2 \right]^{0.5} \]

\[ F \text{ and } G \ (FG) = FE + EG \]

\[ B_1 \text{ and } B_2 \ (B_1B_2) = \left[ (y_{B1} - y_{B2})^2 + (x_{B1} - x_{B2})^2 \right]^{0.5} \]

\[ E \text{ and } I \ (EI) = \frac{(y_{B1} - y_{B2})}{2} \]
Finally, by the principle of similar triangles,
\[
\frac{EG}{FG} = \frac{EI}{FH}
\]

Thus,
\[
FH = EI \left[ \frac{FG}{EG} \right]
\]

Again, by similar triangles,
\[
\frac{EI}{FH} = \frac{GI}{GH}
\]

and
\[
GH = GI \left[ \frac{FH}{EI} \right]
\]

Therefore, the final x and y positions of the falling sphere are:
\[
x_F = x_G - GH
\]
\[
y_F = y_{B2} + FH
\]

For positions V to VIII, where one of the (x,y) coordinates of the two spheres below is the same, determination of the final (x,y) coordinates of the falling sphere is greatly simplified. Position V, which is illustrated in more detail in Figure 4.7, is used as an illustration.

The new y position, \( y_T = \frac{y_{B1} - y_{B2}}{2} \).

Since, at the final position, the centres of the three spheres will form an isosceles triangle with \( B_1T = B_2T = d \),

therefore the new x position \( x_T = x_{B1} + \left[ (d)^2 - (y_T - y_{B2})^2 \right]^{0.5} \).
4.2.3. Three-sphere Encounter

When three spheres are simultaneously encountered at the same level, the falling sphere is assumed to be permanently nested and hence its final (x,y,z) coordinates must be calculated. The determination of the final (x,y,z) coordinates was based on the recognition of the fact that the distances from its new centre to the centres of the three subordinate spheres are identical.
Consider, for example, the configuration shown in Figure 4.8 below.

Let the centres of the three spheres encountered be A, B and C, and the centre of the final resting position of the falling sphere be D.

The x and y coordinates at the mid-point between centres A and B (mp1) are:

\[ x_{mp1} = \frac{x_A + x_B}{2} \quad \text{and} \quad y_{mp1} = \frac{y_A + y_B}{2}. \]

The slope \( m_1 \), perpendicular to slope AB and initiating from the mid-point between A and B, is

\[ m_1 = -\frac{x_A - x_B}{y_A - y_B} \]
Therefore, to describe the \( x \) and \( y \) relationship, a linear equation of the form \( y = m_1x + c_1 \) can be written, where the constant 
\[
c_1 = y_{mp1} - \left[ -\frac{x_A - x_B}{y_A - y_B} \right] x_{mp1}
\]

A similar linear expression can also be written for the line extending perpendicularly from the mid-point of \( B \) and \( C \) (mp2), as 
\[
y_2 = m_2x_2 + c_2
\]
where 
\[
c_2 = y_{mp2} - \left[ -\frac{x_B - x_C}{y_B - y_C} \right] x_{mp2}
\]
\[
x_{mp2} = (x_B + x_C)/2
\]
and 
\[
y_{mp2} = (y_B + y_C)/2
\]

When these two lines are extended, they will intersect at a point corresponding to the centre of the resting position of the falling sphere \( D \), thus enabling the determination of the \( x \) and \( y \) coordinates of centre \( D \).

Since at the point of intersection, 
\[
x_1 = x_2 \quad \text{and} \quad y_1 = y_2
\]
therefore, by equating the two linear expressions mentioned above, 
\[
m_1x_1 + c_1 = m_2x_2 + c_2
\]
and the \( x \) and \( y \) coordinates can be determined as 
\[
x_D = \frac{c_2 - c_1}{m_1 - m_2}
\]
\[
y_D = m_1x_D + c_1
\]
The remaining $z$ coordinate can be approximately determined as follows (refer to Figure 4.9):

![Diagram of spheres](image)

Figure 4.9 Elevation view of the falling sphere nested atop two subordinate spheres

Length of $AM = \frac{1}{2} \left[ (x_B - x_A)^2 + (y_B - y_A)^2 \right]^{0.5}$

Length of $AD = d$

Therefore, $z_1 = z_A + \left[ (AD)^2 - (AM)^2 \right]^{0.5}$

$z_2$ and $z_3$ can be similarly calculated, from which the final $z_D$ coordinate can be determined as

$$z_D = \frac{(z_1 + z_2 + z_3)}{3}.$$
5. RESULTS AND DISCUSSION

5.1. INTRODUCTION

The summary of experimental results, including the conditions under which each experiment was run, as well as all the relevant experimental parameters such as the ratio of particle radius to double layer thickness, $\kappa a$, and the measured sphere and substrate zeta potentials, $\zeta_p$ and $\zeta_w$ respectively, are presented in Tables 5.1, 5.2, and 5.3. Sample calculations leading to the evaluation of these parameters are presented in Appendix A. Computer programs necessary for these and other calculations as well as for the simulation of random sphere deposition and the evaluation of the total interaction energies are listed in Appendix C.

**TABLE 5.1**

Summary of experimental data for the effect of double layer thickness on surface coverage

<table>
<thead>
<tr>
<th>Run</th>
<th>pH</th>
<th>$\lambda$</th>
<th>$[\text{KCl}]$</th>
<th>$1/\kappa$</th>
<th>$\kappa a$</th>
<th>$\zeta_p$</th>
<th>$\zeta_w$</th>
<th>Coverage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(\text{\textmu mho/cm})</td>
<td>$(10^{-6}\text{M})$</td>
<td>(\text{\textmu m})</td>
<td>(mV)</td>
<td>(mV)</td>
<td>(%)</td>
<td></td>
</tr>
<tr>
<td>A1</td>
<td>5.10</td>
<td>1.83</td>
<td>0</td>
<td>0.108</td>
<td>4.63</td>
<td>-121</td>
<td>27</td>
<td>33.37</td>
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<tr>
<td>A2</td>
<td>5.24</td>
<td>3.25</td>
<td>1</td>
<td>0.084</td>
<td>5.97</td>
<td>-140</td>
<td>41</td>
<td>35.90</td>
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<tr>
<td>A3</td>
<td>5.19</td>
<td>4.50</td>
<td>10</td>
<td>0.069</td>
<td>7.26</td>
<td>-99</td>
<td>27</td>
<td>38.14</td>
</tr>
<tr>
<td>A4</td>
<td>5.01</td>
<td>9.40</td>
<td>50</td>
<td>0.039</td>
<td>12.70</td>
<td>-83</td>
<td>25</td>
<td>39.27</td>
</tr>
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<td>A5</td>
<td>5.12</td>
<td>10.50</td>
<td>100</td>
<td>0.029</td>
<td>17.04</td>
<td>-77</td>
<td>31</td>
<td>39.27</td>
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<tr>
<td>A6</td>
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<td>82.00</td>
<td>1000</td>
<td>0.010</td>
<td>52.18</td>
<td>-76</td>
<td>12</td>
<td>39.27</td>
</tr>
</tbody>
</table>
TABLE 5.2
Summary of experimental data for the effect of pH on surface coverage

<table>
<thead>
<tr>
<th>Run</th>
<th>pH</th>
<th>( \lambda )</th>
<th>( 1/\kappa )</th>
<th>( \kappa a )</th>
<th>( \xi_p )</th>
<th>( \xi_w )</th>
<th>Coverage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(\mu\text{mho/cm})</td>
<td>(\mu\text{m})</td>
<td>(\text{mV})</td>
<td>(\text{mV})</td>
<td>(%)</td>
<td></td>
</tr>
<tr>
<td>B1</td>
<td>2.97</td>
<td>515.00</td>
<td>0.008</td>
<td>62.73</td>
<td>-</td>
<td>-</td>
<td>*</td>
</tr>
<tr>
<td>B2</td>
<td>3.71</td>
<td>123.00</td>
<td>0.014</td>
<td>35.27</td>
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<td>9.1</td>
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<tr>
<td>B3</td>
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<td>262.00</td>
<td>0.064</td>
<td>7.86</td>
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<tr>
<td>B4</td>
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<td>7.54</td>
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<td>-33</td>
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<tr>
<td>B6</td>
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<td>B8</td>
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<td>388.00</td>
<td>0.005</td>
<td>93.47</td>
<td>-45</td>
<td>-38</td>
<td>#</td>
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</table>

* Did not determine due to partial coagulation of particles.

# Particles did not adhere to the polymer coated surface due to a change in polarity of the surface potential. Hence no determination of coverage was made.

TABLE 5.3
Summary of experimental data for the effect of \( K_3PO_4 \) concentration on surface coverage

<table>
<thead>
<tr>
<th>Run</th>
<th>pH</th>
<th>( \lambda )</th>
<th>( [K_3PO_4] )</th>
<th>( 1/\kappa )_p</th>
<th>( \kappa a )_p</th>
<th>( 1/\kappa )_w</th>
<th>( \xi_p )</th>
<th>( \xi_w )</th>
<th>Coverage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(\mu\text{mho/cm})</td>
<td>(10^{-6}\text{M})</td>
<td>(\mu\text{m})</td>
<td>(\text{mV})</td>
<td>(\text{mV})</td>
<td>(%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td>5.75</td>
<td>2.40</td>
<td>0.077</td>
<td>6.45</td>
<td>0.026</td>
<td>-75</td>
<td>25</td>
<td>37.00</td>
<td></td>
</tr>
<tr>
<td>C2</td>
<td>6.00</td>
<td>3.20</td>
<td>1.067</td>
<td>7.48</td>
<td>0.022</td>
<td>-69</td>
<td>27</td>
<td>40.40</td>
<td></td>
</tr>
<tr>
<td>C3</td>
<td>6.50</td>
<td>4.05</td>
<td>5.058</td>
<td>8.57</td>
<td>0.019</td>
<td>-76</td>
<td>20</td>
<td>44.38</td>
<td></td>
</tr>
<tr>
<td>C4</td>
<td>7.03</td>
<td>4.80</td>
<td>10.055</td>
<td>9.05</td>
<td>0.018</td>
<td>-76</td>
<td>29</td>
<td>47.12</td>
<td></td>
</tr>
<tr>
<td>C5</td>
<td>8.50</td>
<td>16.00</td>
<td>50.025</td>
<td>20.12</td>
<td>0.008</td>
<td>-76</td>
<td>-50</td>
<td>#</td>
<td></td>
</tr>
<tr>
<td>C6</td>
<td>9.35</td>
<td>35.00</td>
<td>100.018</td>
<td>28.46</td>
<td>0.006</td>
<td>-72</td>
<td>-51</td>
<td>#</td>
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<tr>
<td>C7</td>
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<td>195.00</td>
<td>500.008</td>
<td>63.63</td>
<td>0.003</td>
<td>-70</td>
<td>-48</td>
<td>#</td>
<td></td>
</tr>
<tr>
<td>C8</td>
<td>10.70</td>
<td>385.00</td>
<td>1000.006</td>
<td>89.99</td>
<td>0.002</td>
<td>-68</td>
<td>-53</td>
<td>#</td>
<td></td>
</tr>
</tbody>
</table>

# Particles did not adhere to the polymer coated surface due to a change in polarity of the surface potential. Hence no determination of coverage was made.
5.2. SURFACE COVERAGE - EXPERIMENTAL

5.2.1. Effect of Double Layer Thickness

In the study of the effect of double layer thickness on surface coverage, a range of values for the double layer thickness of spheres was obtained by adding different pre-determined quantities of potassium chloride into the suspension. Experimental data pertaining to this study have been tabulated in Table 5.1 and the results of average surface coverage of silica spheres as a function of added KCl are plotted in Figure 5.1. Since the study is concerned fundamentally with the effect of double layer thickness rather than with that of the added neutral electrolyte concentration, a plot of the surface coverage versus the dimensionless product of inverse double layer thickness and sphere radius, $\kappa a$, is therefore made, as shown in Figure 5.2, to provide a more direct observation of the effect. In Figure 5.1, it can be observed that as the KCl concentration increases at approximately constant pH, the percent surface coverage of silica spheres also increases. This observation is in accordance with theory and is explainable on two counts. Firstly, as already mentioned in Section 2.3, an increase in the counter-ion (K\(^+\)) concentration causes the double layer thickness to decrease in accordance with Equation [2.10]. Secondly, increasing the KCl concentration also increases the equilibrium adsorption of counter-ions into the Stern layer surrounding each particle surface. As a result, the surface potential (which is determined by the concentration of potential determining OH\(^-\) ions in the solution) remains unchanged, but the potential at the outer Helmholtz plane and hence the $\xi$-potential is lowered. According to the theory discussed in Chapter 2,
Figure 5.1 Effect of added KCl concentration on the surface coverage of silica spheres
Figure 5.2 Surface coverage of silica spheres as a function of $\kappa a$
if the double layer thickness is reduced or the magnitude of the ζ-potential of one or both of the interacting double layers is decreased, the height and extent of the repulsive energy barrier should also decrease. These reductions cause the inter-particle distance to be decreased and, as a result, increase the percent surface coverage of silica spheres on the planar substrate. Figures 5.3 and 5.4 show how the particle zeta potential \( (\zeta_p) \) varies as a function of KCl concentration and, more specifically, as a function of \( \kappa a \), respectively.

In view of the foregoing, it would thus appear contradictory to observe in Figure 5.2 that the percent surface coverage does not continue to increase but approaches a constant value at high \( \kappa a \) values. An immediate explanation for this behaviour is that it is due to the random nature of the deposition process, i.e., as a result of the geometric exclusion effect. However, similar results obtained in runs A4 to A6 seem to suggest that the explanation given above may be inadequate, although the presence of the geometric exclusion is indisputable. It thus appears that some other factors must be present. Upon closer examination, it seems that this observed behaviour can be easily explained through consideration of the double layer thickness, in that, although \( 1/\kappa \) continues to decrease at higher electrolyte concentration, its value eventually becomes so small compared to the sphere radius that its influence on surface coverage becomes negligible. Furthermore, \( \zeta_p \) seems to approach a constant value, exerting no further influence on surface coverage. Thus, under the present experimental conditions with silica spheres as the model colloid, it would seem that a maximum surface coverage of only 39.27% is attainable when \( 1/\kappa \) is the primary controlling variable.
Figure 5.3 Particle zeta potential as a function of KCl concentration
Figure 5.4 Particle zeta potential as a function of $\kappa a$
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Since this study was aimed at investigating the effect of $1/\kappa$ on surface coverage, it would thus have been most desirable if as wide a range as possible of the double layer thickness were studied. In the deposition experiments, however, the values of $1/\kappa$ studied ranged only from 0.010 to 0.108 $\mu$m, with the lowest value corresponding to an added KCl concentration of approximately $1\times10^{-3}M$. The addition of higher KCl concentrations into the suspension was not possible because earlier observations had shown this concentration to be on the brink of the critical coagulation concentration, so that any concentration exceeding this limit would result in coagulation of the spheres. Since the study called for a stable suspension of singly-dispersed spheres, this state of coagulation was undesirable and therefore was avoided. At the higher end of the $1/\kappa$ scale, although the lowest theoretical counter-ion concentration possible is $1\times10^{-7}M$ (pure water), this value was found to be experimentally unobtainable due, firstly, to the absorption of ambient carbon dioxide gas into the deionized water, and secondly, to the presence of a multitude of ions normally associated with sea salt in the solution, probably because of the proximity of the experimental site to the sea (see Table A.1). For the range of $1/\kappa$ values studied, the extent of surface coverage of silica spheres on the planar substrate was found to be in the range 33.37–39.27%.

Figure 5.5 demonstrates visually the density of deposited spheres at two different added KCl concentrations. It should be noted here that these are not the actual micrographs of the original deposited particles, but are instead photographs taken from the video screen of the image analyser which explain the poor resolutions observed. It can be seen in the photographs that the particle
Figure 5.5 Photographs of video images of deposited spheres at added KCl concentrations of (a) 0 M and (b) $1 \times 10^{-4}$ M
deposition is indeed random. Furthermore, it can also be observed that the effect of geometric exclusion is definitely present, although its impact on overall surface coverage is difficult to quantify, since some areas on the photographs are more sparsely deposited than others. Although this observed difference in the packing density within the same photograph (i.e., at a fixed experimental condition) may also be attributed to surface heterogeneity, e.g. the presence of locally-favorable deposition site due to variations in micro-roughness and non-uniformity in the distribution of charge-sites on the the substrate surface, the consistency in the magnitude of the coverage results obtained at higher values of $\kappa a$ seems to indicate otherwise, since it is highly unlikely that such consistency would be obtained if surface heterogeneity were present.

5.2.2. Effect of $pH$

The experimental data and other relevant information pertaining to this study are listed in Table 5.2 and the results of average surface coverage of silica spheres as a function of $pH$ are plotted in Figure 5.6. In the experiments, when the suspension $pH$ was varied (using either HCl or NaOH), the magnitude of particle $\zeta$-potential changed as well. Thus, it would seem more appropriate to refer to the study as the effect of particle $\zeta$-potential rather than that of $pH$ on the surface coverage of silica spheres. A separate plot reflecting this fact is made in Figure 5.7. In both of the figures, it can be noted that the surface coverage is inversely proportional to $pH$ (or $\xi_p$) in that as $pH$ (or $\xi_p$) increases, the surface coverage decreases. Again, as in the case of changing counter-ion concentration, the explanation for these results also seems to follow directly from
Figure 5.6 Effect of pH on the surface coverage of silica spheres
Figure 5.7 Effect of particle zeta-potential on the surface coverage of silica spheres
the theory discussed in Chapter 2. Since \( \text{OH}^- \) is a potential determining ion for silica, increasing the concentration of \( \text{OH}^- \) ions in the solution increases the specific adsorption of \( \text{OH}^- \) ions on (or release of \( \text{H}^+ \)ions from) the silica surface. As a result, the surface potential and hence the  \( \zeta \)-potential of the particle increases in magnitude. For instance, changing the pH from 3.71 to 5.90 caused the magnitude of \( \zeta_p \) to increase from -44 to -82 mV. As was observed earlier in Figure 2.4, increasing the magnitude of the  \( \zeta \)-potential of one or both of two similarly charged surfaces under otherwise constant conditions increases the height of the interaction energy barrier and, presumably, the minimum distance of separation between deposited particles. It should be noted that, although the main concern here is the study of the effect of pH (or  \( \zeta_p \)) on surface coverage, during the course of altering the suspension pH, the counter-ion concentration of the suspension inevitably changed as well due to the addition of pH-changing agents into the suspension. As a result, the double layer thickness changed. Thus, the surface coverage results obtained are actually due to the combined effect of zeta potential and double layer thickness, rather than that of  \( \zeta \)-potential alone.

The observation made above thus explains the difference in the results obtained between series A and series B. In series A, it can be noted that as \( 1/\kappa \) decreases, surface coverage increases but reaches a maximum value of 39.27% and remains constant despite further decreases in \( 1/\kappa \). In series B, however, it can be seen that under comparable conditions (in terms of \( 1/\kappa \)), surface coverage continues to increase with decreasing \( \zeta_p \) and reaches a value of 49.4% without approaching a constant value. The only difference between the two
series A and B is that in the former, $\xi_p$ becomes approximately constant as $1/\kappa$ is decreased, whereas in the latter, $\xi_p$ continues to decrease, thereby reducing further the energy barrier and thereby presumably resulting in a smaller value of inter-particle distance. Thus, it seems reasonable to conclude that the absolute difference of approximately 10% in the maximum surface coverage obtained between the two series is due primarily to the effect of $\xi_p$, i.e., a reduction in $\xi_p$ from $-82$ to $-44$ mV, and that by altering the pH of the suspension, as opposed to changing the counter-ion concentration alone, a wider range of surface coverage can be attained.

The maximum surface coverage value of almost 50% obtained under the present experimental conditions would also appear to be in the vicinity of the maximum value attainable under all experimental conditions, provided the colloidal suspension is stable. This contention is supported by the fact that the value mentioned above is less than but close to the maximum theoretical value of 54.73% (47,48,51) obtained for the random deposition of non-overlapping discs on an infinite flat surface.

Because of the nature of the experiments, it was necessary that the spheres adhere permanently to the substrate surface upon contact. Thus, in order to fulfil the required experimental conditions, a cationic copolymer of 2-vinyl pyridine/styrene (2VP/S) was prepared and coated over the glass deposition surface. Nevertheless, the copolymer of 2VP/S may not have been the best choice of coating material as it became negatively charged under alkaline conditions. As a consequence of the double layer repulsion between the similarly-charged particle
and substrate, particle that had already reached the polymer coated surface were found not to adhere to the surface but to be in a continuous state of Brownian motion just above it, such that they were readily resuspended when the deposition cell was inverted. Thus, in these cases, no determination of the surface coverage could be carried out. Details of these observations are given in Table 5.2 for runs B5 to B8 inclusively. It can also be noted from the same table that no result is given for case B1, where the suspension pH was 2.97 (in the vicinity of the iso-electric point of silica). This is because during the experiment, it was observed that although the spheres adhered permanently upon contacting the polymer coated surface, they were found to be in a state of partial coagulation. Under these conditions, the extraction of results would not be meaningful and was hence excluded. Further, values of $\xi_p$ and $\xi_w$ were not measured for this case because the electrophoretic mobility at the stationary levels was too slow to be measurable, suggesting further that the pH was near the iso-electric point of silica.

5.2.3. Effect of Counter-ion Valence Number

As mentioned earlier in Chapter 2, under the conditions where more than two double layers are present, as would be the case in the present study when two equally negatively charged spheres are deposited on a positively charged planar substrate, it is anticipated that the potential distribution between the spheres will be distorted by the presence of this additional surface. Since the charge on the particles and the substrate is opposite, it is very likely that the resulting double layer interaction energy between the two equally charged spheres
will be smaller than that predicted by Equation [2.20] or any other similar equations given in Chapter 2.

In view of the above, it was thus of interest to observe what the final surface coverage would be when the double layer thickness of the planar substrate was sufficiently suppressed to exert negligible influence on the double layer interaction energy between the deposited spheres. The easiest way by which this reduction in the substrate double layer thickness could be brought about would be to add to the suspension greater quantities of KCl than were added in series A. However, since both the potassium and chlorine ions are univalent, the addition of KCl inevitably results in an equal reduction in the double layer thickness of the spheres, rendering the experiment meaningless. Thus, to avoid this phenomenon, an electrolyte with a greater anion (which is the counter-ion for the positively charged substrate) valence number than that of the cation had to be used so that the double layer thickness of the substrate would be affected differently than that of the spheres. The rationale behind this stems from Equation [2.10], where the double layer thickness is seen to be inversely proportional to the counter-ion valence number $z$. Potassium tri-phosphate ($K_3PO_4$), whose anion ($PO_4^{3-}$) valence number is thrice that of its cation, was chosen for the present study. The experimental results for this series of runs are tabulated in Table 5.3 and the values of average surface coverages obtained as a function of $\kappa\eta$ are plotted in Figure 5.8. Along with this plot, the surface coverages obtained as a function of $\kappa\eta$ when KCl was used as the electrolyte are also plotted to provide a direct comparison of the results.
Figure 5.8 reveals that, instead of approaching a constant value as in the case where the electrolyte was KCl, the values of surface coverages obtained using $K_3PO_4$ as the electrolyte continue to increase as $\kappa a$ increases (although the experimental range is small) with no sign of approaching a constant value. Furthermore, the values of surface coverages obtained in the present series, which are greater than those obtained when KCl was used as the electrolyte at similar $\kappa a$ values, contradict what would have been predicted. That is, since the charges on the particles and the substrate are opposite, the resulting double layer interaction energy between the two spheres should be reduced in the presence of this additional surface and the thicker the substrate double layer, the greater this reduction will be. Thus, under the present circumstance where the substrate double layer thickness has been greatly reduced (although a reduction in the substrate double layer thickness was qualitatively deduced, an accurate quantitative calculation of $1/\kappa$ for the substrate was not possible since the values of the dissociation constants for the incomplete reduction of $PO_4^{3-}$ to $HPO_4^{2-}$ and of $HPO_4^{2-}$ to $H_2PO_4^-$ were not obtainable in the literature), it was anticipated that its effect on the double layer interaction energy between deposited spheres would accordingly be reduced and hence a smaller value of surface coverage would be attained. However, since the opposite trend was actually obtained, it is apparent that the observed results cannot be attributed to a reduction in the substrate double layer thickness. Or, more conservatively, it can at least be concluded that its effect on the surface coverage of silica spheres, if any, is negligible. In fact, a similar observation was earlier reported by Hamai et al. (6) in their study of the static deposition of cationic polystyrene latex particles onto anionic synthetic fibers, in which the use of NaCl as
Figure 5.8 Comparison of surface coverages obtained as a function of $\kappa a$ between series A and C.
compared with Na₂SO₄ as the neutral electrolyte showed no difference in the results obtained.

Since the surface coverage results of series C cannot be attributed to a reduction in the substrate double layer thickness, some other factors must be responsible for the observed behaviour. A closer examination of the experimental data in Table 5.3 reveals that these contributing factors may very well be none other than the particle double layer thickness and the particle zeta potential. The role of particle double layer thickness on surface coverage was discussed earlier and hence no repetition will be made here. The role of $\xi_p$, however, may not be so obvious in the present study since Table 5.3 shows that for all the runs in series C, the measured values of $\xi_p$ are approximately constant, which would seem to indicate $\xi_p$ to be a non-contributing factor. Thus, in order to explain the observed behaviour and the role of $\xi_p$ in the present study, it is necessary to begin by pointing out that the approximately constant values of $\xi_p$ observed may well be fortuitous. Further, it can be observed in Table 5.3, that as the concentration of K₃PO₄ increases, the suspension pH increases too. As discussed earlier, this increase in pH results in a corresponding increase in the magnitude of the surface potential. However, due to a greater amount of added K₃PO₄ to the suspension (c.f. runs C2 and C4) and hence a further reduction in the double layer thickness, the range of potential distribution in the double layer in run C4 will be larger than that in run C2, resulting in a cross-over of the potential distribution curves. If, fortuitously, this cross-over point were located near the shear plane, this would explain the approximately constant values of $\xi_p$ observed. Figure 5.9 serves to illustrate this hypothesis. Thus, since smaller
values of $\xi_p$ result in series C compared to series A for a given $\kappa a$, the repulsive interaction energy will be lower for series C and the number of spheres that can be deposited per unit area of the substrate surface will be larger.

5.3. SURFACE COVERAGE - SIMULATION

In the simulation of random particle deposition using the simple two-dimensional rejection model, the average simulated value obtained for the fraction of the total area occupied by all the deposited particles on the planar surface, i.e., the surface coverage, based on five independent simulations, was 0.495±0.006. This value was obtained using the assumption that the deposition process was complete when the successive number of failures for a particle to be deposited exceeded 1000, and it represents the case where the particle double layer thickness is infinitely small. Clearly, it can be seen that the assumed number of particles is inadequate since, by allowing an extremely large number ($10^8$) of particles to be deposited, a maximum surface coverage of 54.73% has been reported (47,51). Thus, in view of the foregoing, this latter value of 54.73% was used as the maximum final surface coverage obtained. Based on this value, calculations were then performed using the method described in Chapter 4 so that a series of new surface coverages as a function of $\kappa a$ could be predicted. These results are plotted in Figure 5.10, along with the experimental results of series A listed in Table 5.1. It should be noted here that no comparison was made for the experimental results obtained when both the double layer thickness and the suspension pH were changing (i.e., as in series B and C). This -is
Figure 5.9 Qualitative sketches of the potential distributions in the particle double layer for runs C2 and C4
because under these situations, a comparison between simulated and experimental surface coverages based on $\kappa a$ is both inappropriate and inadequate, since the effect of changes in the magnitude of $\xi_p$ is not accounted for in the present simulation model.

It can be seen in Figure 5.10 that although the trend in the experimentally obtained results are qualitatively well described by the simulated results, poor quantitative agreement is obtained between the two, with the latter consistently overpredicting the measured coverages. A closer examination of the model reveals that the overpredicted results can likely be attributed to the unrealistic use of the double layer thickness, $1/\kappa$, as the basis for the calculation of the simulated surface coverages. Since, as mentioned earlier in Section 2.1.4, the double layer thickness represents the distance from the particle surface at which the potential drops to approximately $1/e$ ($\approx 37\%$) of its surface value, the repulsive interaction between two neighbouring deposited particles will still be considerable at this degree of double layer overlap. Hence, the assumption that $a_e = (a + 1/\kappa)$ likely underpredicts the effective radius leading to simulated surface coverages which, in all cases, exceed the values measured experimentally. Therefore, in order to obtain a meaningful quantitative comparison between theory and experiment, a more appropriate basis for the calculation of simulated surface coverages has to be chosen. One such basis is the distance of separation between two deposited particles at which the overall interaction energy is equal to $2kT$ ($8.232 \times 10^{-21} J$ at $25^\circ C$), i.e. equivalent to their combined average thermal energy. The reason why this parameter is considered an appropriate basis for comparison is that, if each particle has an average Brownian energy of $1kT$, two
Figure 5.10 Plots of surface coverage of silica spheres as a function of $\kappa a$
such particles will presumably, on average, be unable to move into regions where the repulsive energy exceeds twice this value. An additional benefit of this approach is that the interaction energy calculation automatically takes into account the effects of changing $1/k$ and $\xi_p$. The previous basis yielded the unrealistic prediction that the surface coverage was independent of $\xi_p$.

In order to employ this new basis, it becomes necessary to obtain for, each run in the series, the separation distance (H) between deposited particles at which the combined electric double layer and van der Waals interaction energy equals 2kT. In general, the value of this separation distance cannot be determined directly since it is implicitly dependent upon a number of other parameters as shown in Equations [2.20] and [2.40]. Thus, instead of a straightforward substitution of the values of relevant parameters into the two equations to obtain the required separation distance, a simple bisection root-finding technique was used. A graph depicting the overall interaction energy obtained as a function of the separation distance between the particles for all the appropriate runs in series A is shown in Figure 5.11.

Once the values for the separation distance are obtained, the ratios of the circular area occupied by the particle (diameter = 2a) to that occupied by the particle and its double layer (diameter = 2a+H) are then calculated. The calculation of these ratios enables the determination of corresponding new values of surface coverages in the two-dimensional simulation model. For example, in run A1, the separation distance between the spheres when $\phi_T = 2kT$ is determined to be 0.8935 µm from Figure 5.11. Based on this value, the ratio
Figure 5.11 The total interaction energy as a function of the separation distance between the particles for series A.
mentioned above, which is \[ \frac{\pi(0.5)^2}{\pi(0.5+0.8935/2)^2} \], equals 0.279. Hence, the value of the surface coverage obtained in the two-dimensional model under the condition where \( H=0.8935 \, \mu m \) is 15.26% (0.279 \times 54.73%). Similar calculations were carried out for other runs in the same series A. The results are plotted in Figure 5.12, together with the experimentally obtained results for comparison.

As can be seen in the figure, the trend in the experimental results are again qualitatively well described by the simulation. However, with the use of the separation distance when the total interaction energy equals \( 2kT \) as the basis for comparison in the present case, the simulation now underpredicts the experimental results as opposed to the overpredictions obtained when the double layer thickness was used as the basis. It is suspected that this underprediction of the experimental results when a more reasonable basis for choosing an effective radius is used is largely due to the limitations of the two-dimensional model which, by discarding spheres which overlap previously-deposited ones, greatly over simplifies the nature of the particle deposition process. If the overlapping particles were allowed to roll over the surfaces of those below before continuing their downward progress, as was planned in the three-dimensional simulation model, it is expected that higher packing densities and hence higher surface coverages will result.

Another possible cause of the low predicted surface coverages shown on Figure 5.12 is that the separation distance corresponding to \( \phi_T = 2kT \) may be too large. The overall interaction energies were calculated on the basis of Equations [2.20] and [2.40], which apply only to the interaction of two particles.
Figure 5.12 Surface coverages as a function of $\kappa a$ for series A
in an infinite medium. Unfortunately, as has been pointed out before, there is no theory available at the present time which describes either the van der Waals or double layer interaction energies for two spheres located on an infinite flat surface. Although the limited number of experimental results obtained in series C suggest that the underlying surface has little effect on the surface coverage, it is strongly suspected that, at least at large double layer thicknesses, the positively-charged substrate will distort the potential distribution between the two negatively-charged particles in such a way that the repulsive double layer interaction may be significantly reduced. In other words, the separation distance corresponding to $\phi_T = 2kT$ is likely smaller than that predicted on the basis of two spheres in an infinite medium. To approximately compensate for this effect, surface coverages based on the separation distances corresponding to interaction energies (for two spheres in an infinite medium) equal to 5, 10 and 20 kT were also calculated and shown for comparison in Figure 5.12. As can be seen, as the interaction energy is increased (i.e., separation distance is reduced), the predicted coverages are in better quantitative agreement with the measured values. However, even at the largest interaction energy chosen, the two-dimensional simulation model generally continues to underpredict the measured results. This is further evidence of the inadequacy of the two-dimensional model and the need for an improved three-dimensional simulation.

Similar computations of separation distances corresponding to $\phi_T = 2$, 5, 10 and 20 kT were performed for series B and C (refer to Figures 5.13 and 5.14, respectively). These distances were then used to estimate equivalent radii and hence surface coverages based on the two-dimensional model saturation limit.
These predicted results, plotted with their experimental counterparts for comparison, are shown as a function of pH for series B (Figure 5.15) and as a function of $\kappa a$ for series C (Figure 5.16). Again, even though the simulation was able to predict the correct qualitative trends, it always gave underestimates of the experimentally measured surface coverages.

As expected, the quantitative agreement between theory and experiment improved if separation distances corresponding to interaction energies larger than $2kT$ were employed.

Based on the above findings, it can be concluded that, although the trends in the measured surface coverages are qualitatively described by the simulation, poor quantitative agreement is obtained because of the oversimplifying nature of the two-dimensional model.

Figure 5.17 shows a computer-generated depiction of the final orientation of deposited particles obtained using the two-dimensional model along with a photograph (taken from the image analyser monitor) of an experimental deposition substrate. The size of the plotted spheres has been reduced by $a/a_e$ to simulate the coverage determined experimentally. It can be seen in the figure that both photographs show a high degree of randomness in the particles deposited.

In the case of the three-dimensional simulation model, although the program is partially functioning, successful completion of the simulation leading to a tangible value for the surface coverage when $1/\kappa$ approaches zero did not
Figure 5.13 The total interaction energy as a function of the separation distance between the particles for series B
Figure 5.14 The total interaction energy as a function of the separation distance between the particles for series C.
Figure 5.15 Surface coverages as a function of pH for series B
Figure 5.16 Surface coverages as a function of $\kappa a$ for series C
Figure 5.17 Comparison of simulated and experimentally obtained photographs at approximately similar values of coverage.
materialize due, firstly, to the very complex nature of the simulation process and, secondly, to the exclusion of some conditions deemed essential in the program. Unfortunately, due to a lack of time, further debugging of, and the inclusion of more generalized conditions in, the program were not carried out.
6. CONCLUSIONS AND RECOMMENDATIONS

The effects of the random nature of the deposition process, the electrical double layer thickness and the surface potential on the surface coverage of gravitationally deposited colloidal spheres have been experimentally studied by allowing spherical, uniform-size, colloidal silica spheres, suspended in an aqueous medium, to settle onto cationic polymer-coated glass cover slips under stagnant conditions.

Unfortunately, the techniques that were available for the production of colloidal silica spheres were unable to reliably produce uniform particles in the size range (> 1\(\mu\)m) where they could be easily observed in an optical microscope. Thus, before the primary investigation could get underway, a study aimed at developing a satisfactory technique for producing colloidal silica spheres which met this important requirement had to be carried out. It was found, after an extensive investigation, that by simply varying the reaction temperature and/or the chain length of alcoholic solvent, spherical, uniform-size, colloidal spheres in the size range of 0.2 - 2.0 \(\mu\)m could be produced.

Under the conditions of the present experiments, the experimental results revealed that the surface coverage is dependent upon both the particle zeta potential (\(\xi_p\)) and the double layer thickness (1/\(\kappa\)); as 1/\(\kappa\) or \(\xi_p\) increases, the surface coverage decreases. This observation is found to be in accordance with expectation, since an increase in either 1/\(\kappa\) or \(\xi_p\) causes an increase in the total repulsive interaction energy between a pair of particles and hence -a
reduction in the surface coverage obtained. Furthermore, it was found that the range of surface coverages obtained when both \(1/\kappa\) and \(\xi_p\) were changing was greater than that when \(1/\kappa\) alone was used as the primary controlling variable. A separate series of experiments examining the effect of substrate double layer thickness on surface coverage was also performed by dissolving different predetermined quantities of \(K_2PO_4\) into the suspension. Because of the different valences of the resulting cations and anions, the double layer thicknesses of the substrate and the particle are affected differently. The surface coverages obtained in these experiments showed that any influence exerted by this factor did not manifest itself in the results. Besides these findings, the presence of geometric exclusion due to the random nature of the deposition process was also noted, although its effect was difficult to quantify due to the unavailability of a value for the maximum surface coverage without interaction effects.

In addition to the systematic experimental study of colloidal deposition, attempts were made to develop two computer simulation models to generate predicted deposition results which could be compared with those measured experimentally. The first scheme involved a simple two-dimensional rejection model where only non-overlapping particles were deposited, while the second scheme consisted of a three-dimensional model where the rolling of sedimenting particles over the surfaces of previously-deposited particles as well as the stacking of particles were allowed. Comparison of experimental results with those obtained using the two-dimensional model revealed that for all cases, the simulated results consistently underpredict those of the experimental results due to the oversimplifying nature of the deposition process simulation. The trends in the
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experimental results, however, were approximated by the simulations. Owing to various reasons, such as the very complex nature of the simulation process involved and time constraints, successful completion of the three-dimensional model, which is more realistic than the two-dimensional model, did not materialize. It is speculated that the surface coverages provided by the former model will likely be greater than those obtained using the two-dimensional model and hence the three-dimensional model will yield results which are in better quantitative agreement with those measured experimentally. Thus, it is suggested that, in a future study, further debugging and refinement of the three-dimensional model be undertaken so that a tangible value for the simulated maximum coverage may be obtained.

Before a meaningful comparison of the simulated and experimental results can be carried out, the raw simulated data obtained must be manipulated to correctly reflect the experimental conditions studied. However, this manipulation requires a knowledge of the interaction energy between two spheres situated on a differently charged substrate, which is unavailable at the present time. Thus, it is also suggested that the derivation of this interaction theory be undertaken.

In series A of the present study, where the effect of $1/\kappa$ on surface coverage was investigated, the range of $1/\kappa$ used was unfortunately rather narrow due to several reasons discussed earlier. While not too much can be done at the lower end of the range (since further reductions in the double layer thickness through the addition of more electrolyte into the suspension would result in particle coagulation), expansion in the upper range of $1/\kappa$ is presumably
attainable if the experiments were to be carried out in a controlled environment (e.g., in an inert chamber where only nitrogen is present) so that no unwanted ions would be absorbed into the suspension. Thus, it is suggested that in a future study, experiments be carried out in the above-mentioned manner so that a far greater (lower) range of measured surface coverages can be obtained. This extended range would provide a more comprehensive test for any future simulation models and, hopefully, would allow a clarification of the separate roles played by $1/\kappa$ and $\xi_p$ on the coverage-dependent deposition process.

Besides the above, it is also suggested that deposition study should be extended to include situations where the suspension is flowing. The difference in surface coverages obtained under static and flowing, but otherwise identical, experimental conditions must be attributable to new effects introduced by the motion of the suspension. In this way, it would be possible to investigate the significance of hydrodynamic exclusion on the surface coverage of depositing particles.
# NOMENCLATURE

Only those symbols used in the main text of the thesis are defined here. Those in the Appendices are defined in the particular section in which they occur. The units given are those which are most frequently used.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>half-width of flat electrophoresis cell</td>
<td>cm</td>
</tr>
<tr>
<td>a</td>
<td>the radius of spherical particle</td>
<td>cm</td>
</tr>
<tr>
<td>A</td>
<td>Hamaker constant</td>
<td>J</td>
</tr>
<tr>
<td></td>
<td>cross-sectional area of flat electrophoresis cell at the plane of viewing</td>
<td>cm</td>
</tr>
<tr>
<td>A,B,C,D</td>
<td>constants used in Equation [2.36]</td>
<td>–</td>
</tr>
<tr>
<td>A_{ijk}</td>
<td>Hamaker constant for the interaction of material i with material k in a medium j</td>
<td>J</td>
</tr>
<tr>
<td>b</td>
<td>half thickness of flat electrophoresis cell</td>
<td>cm</td>
</tr>
<tr>
<td>C</td>
<td>concentration of electrolytes in the solution</td>
<td>moles/litre</td>
</tr>
<tr>
<td>e_0</td>
<td>electronic charge (4.80324 \times 10^{-10})</td>
<td>esu</td>
</tr>
<tr>
<td>f</td>
<td>(= f(p)), fitted correction factor used in Equation [2.34]</td>
<td>–</td>
</tr>
<tr>
<td>H</td>
<td>distance of separation between two solid surfaces</td>
<td>–</td>
</tr>
<tr>
<td>I_{sp}</td>
<td>parameter used in Equation [2.36]</td>
<td>–</td>
</tr>
<tr>
<td>I_{ss}</td>
<td>parameter used in Equation [2.37]</td>
<td>–</td>
</tr>
<tr>
<td>k</td>
<td>Boltzmann constant (1.380662 \times 10^{-23})</td>
<td>J/K</td>
</tr>
<tr>
<td>l</td>
<td>interelectrode distance for electrophoresis cell</td>
<td>cm</td>
</tr>
<tr>
<td>n_0</td>
<td>bulk ionic concentration</td>
<td>ions/cm³</td>
</tr>
<tr>
<td>n_+</td>
<td>numbers of positive ions per unit volume</td>
<td>ions/cm³</td>
</tr>
</tbody>
</table>
\( n_- \) numbers of negative ions per unit volume \( \text{ions/cm}^3 \)

\( N_A \) Avogadro's constant \((6.02276 \times 10^{23})\) \( \text{molecules/mole} \)

\( p \) \( = 2\pi H/\lambda \), parameter used in Equation [2.34] —

\( r \) distance from the centre of a sphere \( \text{cm} \)

\( R \) interelectrode resistance of electrophoresis cell \( \text{ohm} \)

\( T \) absolute temperature \( \text{K} \)

\( U_E \) true electrophoretic mobility of particles \( \text{cm}^2/\text{volt-sec} \)

\( U_0 \) apparent electrophoretic mobility of particles at the mid-plane \( \text{cm}^2/\text{volt-sec} \)

\( V \) voltage drop across electrophoresis cell \( \text{V} \)

\( x \) distance in the double layer from a charged surface \( \text{cm} \)

\( X \) applied potential gradient \( \text{V/cm} \)

\( y \) distance normal to median plane of flat electrophoresis cell \( \text{cm} \)

\( z \) valency of counter-ions —

\( a, \beta, \gamma \) parameters used in Equation [2.37] —

\( \delta \) distance from the solid surface to Stern plane \( \text{cm} \)

\( \epsilon \) dielectric constant of the dispersion medium —

\( \xi \) electrokinetic (zeta) potential \( \text{mV} \)

\( \theta \) particlal surface coverage —

\( k \) inverse electric double layer thickness \( \text{cm} \)

\( 1/k \) electric double layer thickness \( \text{cm} \)

\( \lambda \) — wavelength of atom dipole fluctuations \( \text{Å} \)

— electrical conductivity of electrolyte solution \( \mu\text{mho/cm} \)

\( \lambda_0^{\pm} \) limiting conductances of the ions in solution \( \text{cm}^2/\text{ohm-equiv} \)
\( \rho \) volume charge density \( \text{coul/cm}^3 \)

\( \rho, \rho' \) parameters used in Equation [2.36] \( \text{cm} \)

\( \sigma \) surface charge density \( \text{coul/cm}^2 \)

\( \phi \) interaction energy between two solids \( J \)

\( \psi \) electric potential at a distance x from the charged surface \( \text{mV} \)

\( \psi_o \) electric potential at the charged surface \( \text{mV} \)

\( \psi_{\delta} \) Stern potential \( \text{mV} \)

\( \mu \) viscosity of the solution \( \text{poise} \)

**SUBSCRIPTS**

- **a-a** atom pair van der Waals interaction
- **edl** electrical double layer interaction
- **p** particle
- **sp** interaction between a particle and a planar surface
- **ss** interaction between two particles
- **T** total
- **vdw** van der Waals interaction
- **w** wall

**SUPERSCRIPTS**

- **ret** retarded
- **\( \sigma \)** constant charge density
- **\( \psi \)** constant potential
REFERENCES


39. Vold, M.J., J. Colloid Interface Sci., 14, 168 (1959)
42. Vold, M.J., J. Colloid Interface Sci., 18, 684 (1963)
43. Sutherland, D.N., J. Colloid Interface Sci., 22, 300 (1966)
44. Sutherland, D.N., J. Colloid Interface Sci., 25, 373 (1967)
45. Meakin, P., J. Colloid Interface Sci., 96, 415 (1983)


67. Hückel, E., Phyzik. Z., 25, 204 (1924)


78. Hamaker, H.C., Physica, 4, 1058 (1937)
90. Stöber, W., Fink, A. and Bohn, E., J. Colloid Interface Sci., 26, 62 (1968)
94. Iler, R.K., Surface Colloid Sci., 6, 1 (1973)

96. LaMer, V.K. and Dinegar, R., J. Am. Chem. Soc., 72, 4847 (1950)


98. Revell, R.S.M. and Agar, A.W., Brit. J. Appl. Phys., 6, 23 (1955)


100. Komagata, S., Researches Electrotech. Lab. Tokyo, Comm. no. 348 (1933)


APPENDICES

A. SAMPLE CALCULATIONS

A.1. Double Layer Thickness

The inverse double layer thickness was calculated using Equation [2.10]. At 25°C,

\[ e_0 = 4.8030 \times 10^{-10} \text{ e.s.u.} \]
\[ N_A = 6.0226 \times 10^{23} \]
\[ \epsilon = 78.54 \]
\[ k = 1.3805 \times 10^{-16} \text{ erg/K} \]
\[ T = 298.15 \text{ K} \]

and for predominantly univalent counter-ions, Equation [2.10] reduces to

\[ \kappa = 0.3286 \times 10^8 \times C^{0.5} \text{ cm}^{-1} \]  \[\text{[A.1]}\]

where C is the counter-ion concentration in moles/litre. A knowledge of C was therefore vital to the calculation of \( \kappa \). For high solution conductivities, where the electrolyte concentration has been adjusted by the addition of KCl, NaOH or HCl, the concentration of ionic species present was assumed to be made up predominantly of those ions added and the concentration can be determined by measuring the conductivity of the suspension and using the concentration-conductivity calibration curve given in Appendix B.1.3. For low solution conductivities, however, due to the fact that the nature of the ionic content of suspensions was very complex, exact determination of C is impossible.
Hence only approximate ion concentrations can be calculated from the suspension pH and conductivity data on the basis of the assumption that the contributions of the individual species to the overall conductivity through their mobilities was additive. In that case (101)

$$\lambda = \sum_{i} \frac{N_A C_i |z_i e_0| U_i}{1000}$$  \[A.2\]

where $\lambda$ is the conductivity of the solution ($\mu$mho/cm), $N_A$ the Avogadro number, $C_i$ the concentration of ionic species (moles/litre), $z_i$ the valence of ionic species $i$, $e_0$ the charge of an electron (Coulomb) and $U_i$ the mobility of the ionic species $i$ ($cm^2/volt$-sec).

Consider, for example in run A2, where the measured pH and conductivity of the suspension were 5.24 and 3.25 $\mu$mho/cm respectively. In this case, the suspension was freshly prepared and the pH of the suspension was not adjusted. A chemical analysis (see Table A.1) performed on the suspension before the addition of $1 \times 10^{-6} M$ KCl revealed that, besides the presence of $H^+$ and $OH^-$ ions from the complete dissociation of water, and $HSiO_3^-$ and $HCO_3^-$ from the dissolution of silica and absorption of $CO_2$, a multitude of other ionic species were also present, although a great majority of them constituted insignificant proportions. It was found that $Na^+$ was by far the most abundant, followed by $Ca^{2+}$ and $K^+$. Thus, these quantities were reflected in the determination of average mobilities of cations and anions. For the run in question, since

$$pH = 5.24,$$

$$[H^+] = 10^{-5.24} = 5.754 \times 10^{-6} \text{ moles/litre}$$
<table>
<thead>
<tr>
<th>Element</th>
<th>Quantity (&lt; mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron</td>
<td>0.01</td>
</tr>
<tr>
<td>Beryllium</td>
<td>0.001</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.002</td>
</tr>
<tr>
<td>Cobalt</td>
<td>0.005</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.002</td>
</tr>
<tr>
<td>Copper</td>
<td>0.01</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.05</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>0.01</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.005</td>
</tr>
<tr>
<td>Lead</td>
<td>0.02</td>
</tr>
<tr>
<td>Antimony</td>
<td>0.05</td>
</tr>
<tr>
<td>Selenium</td>
<td>0.05</td>
</tr>
<tr>
<td>Thorium</td>
<td>0.05</td>
</tr>
<tr>
<td>Vanadium</td>
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</tr>
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<td>Zinc</td>
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<td>Barium</td>
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</tr>
<tr>
<td>Calcium</td>
<td>0.26</td>
</tr>
<tr>
<td>Iron</td>
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</tr>
<tr>
<td>Potassium</td>
<td>0.2</td>
</tr>
<tr>
<td>Lithium</td>
<td>0.05</td>
</tr>
<tr>
<td>Magnesium</td>
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</tr>
<tr>
<td>Manganese</td>
<td>0.001</td>
</tr>
<tr>
<td>Sodium</td>
<td>0.78</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>0.1</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.1</td>
</tr>
<tr>
<td>Strontium</td>
<td>0.001</td>
</tr>
<tr>
<td>Titanium</td>
<td>0.001</td>
</tr>
<tr>
<td>Zirconium</td>
<td>0.005</td>
</tr>
</tbody>
</table>

TABLE A.1
Results of chemical analysis showing the types and quantities of ions present in the freshly prepared silica suspension.
Therefore, \([\text{OH}^-] = 10^{-14}/[H^+] = 0.001738 \times 10^{-6}\) moles/litre, since the dissociation constant of water is about \(10^{-14}\).

Also, in order to maintain electroneutrality,

\[
[H^+]+[K^+]+[\text{other cations}] = [\text{HS_iO_j}]+[\text{HCO_3}^-]+[\text{OH}^-]+[\text{Cl}^-]+[\text{other anions}]
\]  

[A.3]

It can be noted from the literature that the ionic mobility values for most types of ions are similar. Thus, to simplify calculations, most cations and anions were respectively lumped together, giving

\[
[H^+]+[K^+]+[\text{other cations}] = [\text{OH}^-]+[\text{Cl}^-]+[\text{other anions}]
\]  

[A.4]

From Equations [A.2] and [A.4], the two unknown concentrations, [other cations] and [other anions], could then be computed.

Thus if [other cations] = \(y \times 10^{-6}\) moles/litre,

then \([\text{other anions}] = (y+5.754+1-1-0.001738) \times 10^{-6}\)

\[= (y+5.7522) \times 10^{-6}\text{ moles/litre}\]

and substituting these expressions into Equation [A.2],

\[
\lambda = \frac{6.023 \times 10^2 \times 1.602 \times 10^{-19}}{10^3} \left[ 5.754U_{H^+} + 0.001738U_{OH^-} + 1.0U_{K^+} + 1.0U_{Cl^-} + yU_{cation} + (y + 5.7522)U_{anion} \right] \times 10^{-6}
\]

[A.5]
where the individual mobilities are (101)

\[
\begin{align*}
U_{H^+} &= 36.30 \times 10^{-4} \text{ cm}^2/\text{volt-sec} \\
U_{OH^-} &= 20.50 \times 10^{-4} \\
U_{K^+} &= 7.61 \times 10^{-4} \\
U_{Cl^-} &= 7.91 \times 10^{-4} \\
U_{cation} &= 5.614 \times 10^{-4} \text{ (average)} \\
U_{anion} &= 6.255 \times 10^{-4} \text{ (average)}
\end{align*}
\]

Thus for a conductivity value of \(3.25 \times 10^{-6}\) mho/cm, [other cations] can be solved from Equations [A.5] as

\[
y \times 10^{-6} = \text{[other cations]} = 6.432 \times 10^{-6} \text{ moles/litre}
\]

The total counter-ion concentration \(C\) is then obtained as

\[
C = \text{[other cations]} + [H^+] + [K^+]
= (6.432 + 5.754 + 1.0) \times 10^{-6}
= 13.186 \times 10^{-6} \text{ moles/litre}
\]

and from Equation [A.1],

\[
\kappa = 0.3286 \times 10^8 \times (13.186 \times 10^{-6})^{0.5}
= 1.193 \times 10^5 \text{ cm}^{-1}
\]

For a particle radius, \(a\), of \(0.50 \times 10^{-4}\) cm,

\[
\kappa a = 1.193 \times 0.50 \times 10^5 \times 10^{-4}
= 5.97
\]
A.2. Particle Zeta Potential

As mentioned in Section 3.8.1, the conversion of the measured particle electrophoretic mobility to zeta potential was based on the numerical tables of Wiersema et al. (70) that accounted for retardation, relaxation and surface conductance effects. Their results were reported in terms of dimensionless variables and were tabulated in the form of

\[ E = E(y_0, q_0, \eta_\pm) \]  \[ \text{[A.6]} \]

where \( E \), the dimensionless electrophoretic mobility, is given by

\[ E = \frac{6\pi\varepsilon_0}{\varepsilon kT} \cdot U_E \]

\[ = 0.7503 \times 10^4 \cdot U_E \quad \text{at } 25^\circ \text{C} \]  \[ \text{[A.7]} \]

\( q_0 \), the dimensionless double layer thickness, by

\[ q_0 = \kappa a \]  \[ \text{[A.8]} \]

\( y_0 \), the dimensionless zeta potential, by

\[ y_0 = \frac{\varepsilon_0 \xi_p}{kT} \]

\[ = \frac{\xi_p}{25.69} \quad \text{at } 25^\circ \text{C} \]  \[ \text{[A.9]} \]

and \( \eta_\pm \), the dimensionless mobilities of the positive and negative ions in solution, by

\[ \eta_\pm = \frac{NA \varepsilon kT}{6\pi \mu} \cdot \frac{Z_\pm}{\lambda_\pm^0} \]
with $\mu$ = the viscosity of the solution (poise)

$e_o$ = the unit of electrostatic charge (stat-coulombs)

$\xi_p$ = the particle zeta potential (mV)

$\epsilon$ = the dielectric constant of the solution

$k$ = the Boltzmann constant (ergs/K)

$T$ = the absolute temperature (K)

$U_E$ = the electrophoretic mobility (cm$^2$/Volt-sec)

$\kappa$ = the reciprocal double layer thickness (cm$^{-1}$)

$a$ = the particle radius (cm)

$N_A$ = Avogadro's constant

$Z_{\pm}$ = the valence of cations and anions

$\lambda_{\pm}^o$ = the limiting conductances of cations and anions in solution

(cm$^2$/ohm-equiv).

Because of the form of the Wiersema tables, a solution for $y_o$ cannot be obtained explicitly for known values of $E$, $q_o$, and $m_{\pm}$. Instead, for a given value of $q_o$, $E$ and $y_o$ are obtained by graphical interpolation of Table I in the reference. Furthermore, since this table gives only the results obtained for $m_{\pm} = 0.184$, the interpolated values of $E$ must be corrected to correspond to the actual $m_+$ and $m_-$ values. This can be accomplished using the equation

$$E' = E + (m_+ - 0.184) \frac{\partial E}{\partial m_+} + (m_- - 0.184) \frac{\partial E}{\partial m_-}$$

[A.11]
where $E'$ is the corrected mobility and $\partial E/\partial m_+$ and $\partial E/\partial m_-$ must be interpolated from Table III of the reference. The value of $y_0$ corresponding to the experimental value of $E'$, $E_{ex}$, is then extracted from a final plot of $E'$ versus $y_0$.

Consider the case of Run A2, where the concentration of various ionic species in the solution as well as the double layer thickness have been estimated in Section A.1.

The average electrophoretic time = 3.85 sec
1-grid spacing = 119.0 x 10^{-4} cm (Appendix B.1.2)
The interelectrode distance = 7.085 cm
Applied voltage = 51.0 volts
Therefore, electrophoretic mobility $U_E = \frac{(0.0119cm)(7.085cm)}{(51V)(3.85sec)}$

$$= 4.2939 \times 10^{-4} \text{ cm}^2/\text{Volt-sec}$$

Substituting this value into Equation [A.7],

$$E_{ex} = 0.7503 \times 10^4 \times U_E \quad \text{at 25°C}$$

$$= 0.7503 \times 10^4 \times 4.2939 \times 10^{-4}$$

$$= 3.22$$

From Section A.1, $q_0 = \kappa a = 5.97$

The dimensionless mobilities $m_+$ and $m_-$ can be calculated from the numerical averages of the individual limiting ionic mobilities, $\lambda_+^0$ and $\lambda_-^0$ of the ions present.
At 25°C, the $\lambda^0_\pm$ values for the various ionic species are (101):
\[
\begin{align*}
H^+ &= 349.82 \text{ cm}^2/\text{ohm-equiv} \\
OH^- &= 198.00 \text{ cm}^2/\text{ohm-equiv} \\
K^+ &= 73.52 \text{ cm}^2/\text{ohm-equiv} \\
Cl^- &= 76.34 \text{ cm}^2/\text{ohm-equiv}
\end{align*}
\]

Other cations = 54.216 (average) cm²/ohm-equiv
Other anions = 60.376 (average) cm²/ohm-equiv

and their corresponding $m_\pm$ values from equation [A.10] are:
\[
\begin{align*}
H^+ &= 0.0368 \\
OH^- &= 0.0649 \\
K^+ &= 0.1749 \\
Cl^- &= 0.1685
\end{align*}
\]

Other cations = 0.2372 (average)
Other anions = 0.2130 (average)

Subsequently, from the concentrations obtained in Section A.1, the number average values of $m_\pm$ are:
\[
\begin{align*}
m_+ &= \left[ \frac{5.754 \times 10^{-6}}{13.186 \times 10^{-6}} \right] 0.0368 + \left[ \frac{1.0 \times 10^{-6}}{13.186 \times 10^{-6}} \right] 0.1749 \\
&\quad + \left[ \frac{6.43 \times 10^{-6}}{13.186 \times 10^{-6}} \right] 0.2372 \\
&= 0.145
\end{align*}
\]
From Table I of Wiersema et al. (70), values of E are obtained by graphical interpolation at \( q_0 = 5.97 \), \( m_\pm = 0.184 \) for various values of \( y_0 \). Then, from Table III of the same reference, values of \( \partial E/\partial m_+ \) and \( \partial E/\partial m_- \) are obtained at \( q_0 = 5.97 \) for the same values of \( y_0 \) by graphical extrapolation. Values of E are then corrected to \( E' \) using equation \([A.11]\) together with the \( m_\pm \) and \( \partial E/\partial m_\pm \) values determined above. These data are tabulated in Table A.2.

<table>
<thead>
<tr>
<th>( y_0 )</th>
<th>E</th>
<th>( \partial E/\partial m_+ )</th>
<th>( \partial E/\partial m_- )</th>
<th>( E' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.1506</td>
<td>-0.0855</td>
<td>-0.0166</td>
<td>1.1627</td>
</tr>
<tr>
<td>2</td>
<td>2.1216</td>
<td>-0.6524</td>
<td>-0.5156</td>
<td>2.1338</td>
</tr>
<tr>
<td>3</td>
<td>2.8034</td>
<td>-0.2566</td>
<td>-0.7733</td>
<td>2.7936</td>
</tr>
<tr>
<td>4</td>
<td>3.1444</td>
<td>-0.3161</td>
<td>-1.3804</td>
<td>3.1214</td>
</tr>
<tr>
<td>5</td>
<td>3.2272</td>
<td>-0.3755</td>
<td>-1.9875</td>
<td>3.1910</td>
</tr>
</tbody>
</table>
The $E'$ versus $y_0$ curve is then plotted. Since $E_{ex} = 3.22$, the corresponding value of $y_0$ obtained from this plot is $y_0 = 5.443$. Thus, from Equation [A.9], the zeta potential of the particles used in run A2 is calculated as

$$\xi_p = 25.69 \times 5.443 = 139.8 \text{ mV}$$

which is in fact negative, as indicated by the direction of the particles in relation to the applied voltage during the mobility measurements.

A.3. Wall Zeta Potential

The wall zeta potential can be calculated using Equation [3.3], the electrophoresis cell dimensions, and other information used in the calculation of particle zeta potential. For Run A2, electrophoretic time measured at mid-plane = 2.63 sec

Therefore, apparent mobility $U_o = \frac{(0.0119 \text{ cm})(7.085 \text{ cm})}{(51 \text{ V})(2.63 \text{ sec})} = 6.286 \times 10^{-4} \text{ cm}^2/\text{volt-sec}$

Electrophoretic mobility $U_E$ found in Section A.2 = $4.2939 \times 10^{-4} \text{ cm}^2/\text{volt-sec}$

From Section B.1.1,

Cell half-width, $a = 0.4922 \text{ cm}$

Cell half-thickness, $b = 0.05605 \text{ cm}$

At 25°C,

$\mu = 0.008937 \text{ poise}$

$\epsilon = 78.54$
Thus, substituting the above values into Equation [3.3], yields the wall zeta potential

$$\xi_w = +41.4 \text{ mV}.$$  

A.4. Errors in Electrophoresis and Electro-osmosis Measurements

Although there are many potential sources of error in electrophoresis and electro-osmosis, such as errors due to locating the measuring levels, errors due to converting time to electrophoretic mobility, etc., it is thought that the primary source of error in the present measurements may be attributed to the errors in measuring the electrophoretic time resulting from the effects of Brownian motion and the finite depth-of-field of the observing system. Many of the potential errors can be largely eliminated through proper design of the measuring apparatus, whereas the errors due to Brownian motion and depth-of-field are difficult to eliminate. Thus, the problem here is to determine the error limits on the resulting particle and wall $\xi$-potentials which arise when a number of time measurements are taken at each of the prescribed levels.

In order to determine the error limits, it will be necessary to assume that the measured electrophoretic times are approximately normally distributed, so that the 95% confidence limits based on the student t-distribution will be adopted to predict the closeness of the sample mean to the population mean.

Thus, if the measured electrophoretic mobility obtained at the stationary
level is $U_E$, the 95% confidence interval for $U_E$ is (102)

$$U_E \pm (t_{N_E-1, 0.025}) \times \frac{\sigma_{UE}}{N_E^{0.5}}$$ \quad [A.12]

where $(t_{N_E-1, 0.025})$ is the $t$-distribution with $N_E-1$ degrees of freedom for a 95% probability that $U_E$ represents the true electrophoretic mobility within the limits shown, $N_E$ is the sample size and $\sigma_{UE}$ the sample standard deviation.

Since the electrophoretic mobility is a function of the measured electrophoretic time, the mobility variance will also be a function of the variance of the electrophoretic times. According to Mickley et al. (103), if $y = f(x_1, x_2, ..., x_n)$, then the standard deviation of $y$ will be:

$$\sigma_y = \left[ \sum_{i=1}^{n} \left( \frac{dy}{dx_i} \right)^2 \cdot \sigma^2_{x_i} \right]^{0.5}$$ \quad [A.13]

In the present case, the measured electrophoretic mobility obtained at the stationary level is given by

$$U_E = \frac{l}{X \tilde{t}_E}$$ \quad [A.14]

where $l$ = graticule spacing

$X$ = applied potential gradient

$\tilde{t}_E$ = mean electrophoretic time measured at the stationary level

Therefore, from Equation [A.13], assuming $n=1$, $y=U_E$, $x = \tilde{t}_E$, $\sigma_{x} = \sigma_{\tilde{t}_E}$, and $\sigma_y = \sigma_{UE}$, the standard deviation of $U_E$, $\sigma_{UE}$, can be written as

$$\sigma_{UE} = \frac{l}{X \tilde{t}_E^2} \cdot \sigma_{\tilde{t}_E}$$ \quad [A.15]
where $\sigma_{\bar{t}_E}$ is the standard deviation of $\bar{t}_E$ given by the expression:

$$\sigma_{\bar{t}_E}^2 = \frac{\sum_{i=1}^{N_E} (t_i - \bar{t}_E)^2}{N_E - 1}$$

Thus, from the above equations, together with a table of t-distribution (102), the range of mobilities are estimated and consequently the errors in the particle zeta potentials are calculated. Consider, for example, Run A2 where $N_E = 25$

$\bar{t}_E = 4.62$ sec

$\sigma_{\bar{t}_E} = 0.1247$ sec

$l = 0.0119$ cm

$X = 7.1983$ V/cm

Therefore from Equation [A.15],

$$\sigma_{U_E} = \frac{(0.0119 \text{ cm})(0.1247 \text{ sec})}{(7.1983 \text{ V/cm})(4.62 \text{ sec})^2} = 9.658 \times 10^{-6} \text{ cm}^2/\text{volt-sec.}$$

From t-distribution tables (102), $(t_{24}, 0.025) = 2.064$

Thus, from Equation [A.12] the 95% confidence limits are

$$U_E \pm 2.064 \times \frac{9.658 \times 10^{-6}}{(25)^{0.5}} = U_E \pm 3.9873 \times 10^{-6}$$

and using Equation [A.7], the 95% confidence limits on $E$ are

$$E \pm 3.987 \times 10^{-6} \times 0.7503 \times 10^4 = E \pm 0.0299$$

From Appendix A, Section A.2, $E$ was found to be 3.22. Thus, the range of $E$ becomes

$$3.1901 \leq E \leq 3.2499$$
The corresponding \( y_0 \) values obtained from the plot of \( E' \) versus \( y_0 \) in Table A.2 for \( E' \) values of 3.1901 and 3.2499 are 4.9878 and 5.8476 respectively. It follows from Equation [A.9] that the lower and upper 95% confidence limits on the particle \( \xi \)-potential for Run A2 are -128.14 and -150.22 mV respectively. In other words, \( \xi_p = -139.8 \ (+11.66, -10.42) \) mV. The confidence limits are no longer symmetrically positioned about the mean value because the \( E' \) versus \( y_0 \) curves are not linear.

The error limits on the wall \( \xi \)-potential, \( \xi_w \), can be similarly evaluated with slight variations. As mentioned in Section 3.8.2, \( \xi_w \) as determined by a combined electrophoresis-electro-osmosis experiment is given by

\[
\xi_w = \frac{8\pi \mu}{\varepsilon X} \left[ \frac{1 - (192b)/(\pi^5a)}{1 + (384b)/(\pi^5a)} \right] \left[ U_E - U_O \right] \\
= 2.087 \times 10^5 \ (U_E - U_O) \quad \text{at} \ 25^\circ C
\]

[A.17]

where \( \xi_w \) is the wall potential (mV), \( \mu \) the fluid viscosity (poise), \( \varepsilon \) the fluid dielectric constant, \( X \) the applied potential gradient (V/cm), \( b/a \) the thickness to width ratio (=0.1139), \( U_E \) the electrophoretic mobility measured at the stationary level (cm²/sec-volt), and \( U_O \) the electrophoretic mobility measured at the mid-plane (cm²/sec-volt).

Thus, if it is assumed that the \( U_E \) and \( U_O \) values were approximately normally distributed, then the 95% confidence limits on \( \xi_w \) can be obtained as
\[ \xi_w = 2.087 \times 10^5 (t_M, 0.025) \left[ \frac{\sigma_{UE}^2}{N_E} + \frac{\sigma_{UO}^2}{N_O} \right] \]  

where

\[ \frac{1}{M} = \left[ \frac{P^2}{N_E - 1} \right] + \left[ \frac{(1-P^2)}{N_O - 1} \right] \]

\[ P = \frac{(\sigma_{UE}^2/N_E)}{(\sigma_{UE}^2/N_E) + (\sigma_{UO}^2/N_E)} \]

\[ \sigma_{UO} = \frac{l}{Xt_0^2} \cdot \sigma_{\tau_0} \]

and \( \sigma_{UE} \) as defined in Equation [A.15].

Consider, for example, the same run (Run A2) where

\[ N_E = 25 \]
\[ N_O = 21 \]
\[ \bar{t}_o = 3.16 \text{ sec} \]
\[ \sigma_{\bar{t}_o} = 0.1045 \text{ sec} \]
\[ l = 0.0119 \text{ cm} \]
\[ X = 7.1983 \text{ V/cm} \]
\[ \sigma_{UE} = 9.658 \times 10^{-6} \text{ cm}^2/\text{Volt-sec} \]

Using Equation [A.21],

\[ \sigma_{UO} = \frac{(0.0119 \text{ cm})(0.1045 \text{ sec})}{(7.1983 \text{ V/cm})(3.16 \text{ sec})^2} = 1.73 \times 10^{-5} \text{ cm}^2/\text{Volt-sec} \]
Using Equation [A.20],
\[
\]
\[= 0.2075\]

Using Equation [A.19],
\[
\frac{1}{M} = \frac{(0.2075)^2}{24} + \frac{(0.7925)^2}{20}
\]
or
\[M = 30.12\]

When \(M = 30.12\), \((t_M 0.025) = 1.96 (102)\). Thus, the 95% confidence limits on \(\xi_w\) may be found, using Equation [A.18], as
\[
\Delta \xi_w = \pm 2.087 \times 10^5 \times 1.96 \times \left[\frac{(9.658 \times 10^{-6})^2/25}{(1.73 \times 10^{-5})^2/21}\right]^{0.5}
\]
\[= \pm 1.73 \text{ mV.}\]

Therefore, the lower and upper 95% confidence limits on the wall \(\xi\)-potential for Run A2 are 39.67 and 43.13 mV respectively.

B. CALIBRATIONS

B.1. Calibrations Made for Electrophoresis Apparatus
B.1.1. Inter-electrode Distance and Cell Dimensions

A knowledge of the inter-electrode distance in the micro-electrophoretic cell was required to evaluate the applied potential gradient during electrophoretic mobility measurements. In view of the complex geometry of the whole cell, this distance cannot be measured directly. It can, however, be obtained from indirect measurement based on a knowledge of the solution conductivity, the resistance across the electrodes, and the cross-sectional area of the viewing region. Thus, if \( R \) and \( \lambda \) are the electrical resistance and the conductivity respectively of a solution placed in the cell, then the effective inter-electrode distance \( l \) is given by

\[
l = R\lambda A
\]

where \( A \) is the cross-sectional area of the viewing region. This area can be obtained from the product of the thickness and width of the cell, which were determined as follows.

The thickness of the cell was measured using the micrometer focussing adjustment of the electrophoresis microscope. The cell was first clamped in the water bath of the electrophoresis apparatus in the same manner as in mobility measurements. The microscope was then adjusted to focus on both the far and near inner walls of the cell and the micrometer readings taken so that the thickness of the cell could be determined by difference. All measurements were made at the centre of the cell in the viewing plane, and several measurements were made before an average value of 0.1121 cm was obtained.

The width of the rectangular section of the cell was also measured by
means of a travelling microscope. In this case, the cell was removed from the
bath and placed in an upright position on a horizontal level. The cell was then
filled with potassium permanganate (KMnO₄), the distinct colour of which
facilitated an accurate viewing of the boundaries of the cell. Several
measurements were taken and the average value was determined to be 0.9844

The resistance R in the above expression for the inter-electrode distance
was determined by measuring the resistance across a solution of known
conductivity placed in the cell with the electrodes in position. A standard solution
of 0.1M KCl was prepared by carefully weighing 7.4555g of KCl and dissolving
it in one litre of distilled and deionised water. A small quantity of the prepared
solution was then used to rinse and fill up the electrophoresis cell. The electrodes
were placed in position and the cell clamped in the electrophoresis water bath.
The water bath and its contents were then allowed to reach thermal equilibrium
at 25°C, after which the resistance across the cell was measured by means of
a Beckman Model 16B2 A.C. conductivity bridge operating at 1000Hz.

The conductivity $\lambda$ of the same solution at the same temperature was
measured using a Seibold LTA conductivity meter.

In this case, the interelectrode distance was determined to be 7.085 cm.
B.1.2. Eyepiece Graticule and Timing Device

The graticule spacing in the eyepiece of the electrophoresis microscope over which the particles were timed during mobility measurements was calibrated using a "stage micrometer", which is a glass slide engraved for 1 mm with 0.01 mm divisions. The "stage micrometer" was held in a vertical position in the water bath maintained at 25°C with clamps. Several measurements were taken and averaged to obtain a graticule spacing of 119.0 ± 0.9 μm.

The electrical timer which was incorporated in the apparatus was also calibrated against a Heuer stop watch. The two timing devices were allowed to run together for short times (1-2 minutes) on several occasions. It was observed that the ratio of the two records, stopwatch to timer, was always constant and equal to 5/6. Therefore all measured times for electrophoretic velocities were corrected by multiplying by a factor of 5/6.

B.1.3. Conductivity of Potassium Chloride and Potassium Phosphate as a Function of Concentration

In the experiments, for high electrolyte concentrations and when the solution pH was not adjusted, the solution conductivity was assumed to be mainly due to the presence of added electrolyte (KCl or K₃PO₄). A calibration curve for the solution conductivity versus various known amounts of added electrolyte in the solution was therefore prepared to facilitate the determination of solution concentration in the calculation of double layer thickness. The results
obtained are presented in Figures B.1 and B.2 for KCl and K$_3$PO$_4$, respectively. In the case of potassium phosphate, as the amount of added K$_3$PO$_4$ increases, the pH of the solution increases. Thus, a separate plot of the solution pH as a function of K$_3$PO$_4$ concentration was also made (Figure B.3).
Figure B.1 Solution Conductivity as a function of added KCl concentration
Figure B.2 Solution Conductivity as a function of added $K_3PO_4$ concentration
Figure B.3 Solution pH as a function of added $\text{K}_3\text{PO}_4$ concentration
C. COMPUTER PROGRAMMES
C Two-dimensional Random Particle Deposition Model

C IMPLICIT REAL*8(A-H,O-Z)
DIMENSION X(100,100),Y(100,100),Z(100,100),
1 TX(100),TY(100),TZ(100),TXY(100),TYZ(100),TZX(100),
2 NX(100),NZ(100),NZ(100),DGL(100),
3 AREAL(20),THICK(20)

C INTEGER FLAGX1,FLAGX2,FLAGX3,FLAGY1,FLAGY2,FLAGY3,
* FLAGZ1,FLAGZ2
C ICOUNT=0
EPS=0.01
ZMIN=0.25
DIA=0.50
RAD=DIA/2.0
RAD1=3.0*RAD/4.0
IND=0
NP=0
ID=0
N=0
C DO 10 I=1,100
N(I)=0
TX(I)=0.0
TY(I)=0.0
TZ(I)=0.0
TXY(I)=0.0
TYZ(I)=0.0
TZX(I)=0.0
IF(I.GT.20)GO TO 10
NZ(I)=0
NZ(I)=0
DO 5 J=1,100
X(I,J)=0.0
Y(I,J)=0.0
Z(I,J)=0.0
CONTINUE
CONTINUE
C Random number generator
C Initialize
C 10000 XX=PRAND0.0) I=IRAND(O)
YY=PRAND(O)

C Generate
C
C XX=PRAND(1.0)
I=IRAND(20)
XX=XX-I
YY=FPRAND(1.0)
J=IRAND(20)
YY=YY-J
WRITE(6,4321)XX,YY

C IF((XX ) .GE.( 10.0+RAD) .OR. (YY).GE.( 10.0+RAD)
* .OR. XX.LE.RAD .OR. YY.LE.RAD)GO TO 10000
C 4444 ICOUNT=ICOUNT+1
IF(ID.EQ.1001)GO TO 88888
C Compute the distance between centres (OBC) in the (X,Y) plane
C (I) Lower level
C IF(J.EQ.0)GO TO 123
C LL=LL+1
LLP2=LL+2
C (b) Check if the particle is at the left and right edges
C IF(I.EQ.1)GO TO 112
GO TO 114
112 LL=L+1
GO TO 114
113 LLP2=LLP2+1
C 114 DD 20 LP1=LL,LLP2
C (c) If no particle at a certain slot, do not compute
C IF(NLP1).EQ.0 GO TO 20
NNTT=NLP1
GO TO NLP1,1,1
NLP1=NL+1,1
DD 5=DD+5,MM
DBC=DDBC((IX*X(LP1,LPP2)))**2+(YY-Y(LP1,LPP2))**2)
1 IF(DBC.LT.DIA*100 TO 10001
30 CONTINUE
20 CONTINUE
C  (II)  Main level
C
C 123 ML=ML+1
MLP2=ML+2
C  (a) Check if the particle is at the left and right edges
C
C
C C (a) Check if the particle is at the left and right edges
C
C IF(I.EQ.0)GO TO 124
IF(I.EQ.9)GO TO 125
GO TO 156
C 124 ML=ML+1
GO TO 156
C 125 MLP2=MLP2+1
C 126 DD 40 LP1=ML,MLP2
C  (b) If no particle at a certain slot, do not compute
C
C
C IF(N(LP1).EQ.0)GO TO 40
NNTT=N(LP1)
C
C
C (a) Check if the particle is at the left or right edges
C
C IF(I.EQ.0)GO TO 236
IF(I.EQ.9)GO TO 237
GO TO 238
236 NL=NL+1
GO TO 238
237 MLP2=MLP2-1
238 DO 60 LP2=1,NNTT
DBC=DSQRT((XX-X(LP1,LP2))**2+(YY-Y(LP1,LP2))**2)
IF(DBC.LT.DIA)GO TO 10001
CONTINUE
60 CONTINUE
C
C (III)  Upper level
C
C
C (a) Check if the particle is at the highest Y level
C
C IF(J.EQ.9)GO TO 90000
NL=JLP1+1
NLP2=NL*2
C
C (b) Check if the particle is at the left or right edges
C
C IF(I.EQ.0)GO TO 236
IF(I.EQ.9)GO TO 237
GO TO 238
236 NL=NL+1
GO TO 238
237 MLP2=MLP2-1
238 DO 60 LP2=1,NNTT
DBC=DSQRT((XX-X(LP1,LP2))**2+(YY-Y(LP1,LP2))**2)
IF(DBC.LT.DIA)GO TO 10001
CONTINUE
60 CONTINUE
C 90000 XTTEMP=XX
YTTEMP=YY
IF(XTTEMP.LT.0.0)XTTEMP=0.0
IF(YTTEMP.LT.0.0)YTTEMP=0.0
IF(XTTEMP.GE.10.0)XTTEMP=9.5
IF(YTTEMP.GE.10.0)YTTEMP=9.5
IF(XTTEMP.JE.YTTEMP)
IBOX=(J*10)+I*1
C
C N(IBOX)=N(BOX)+1
NUM=N(IBOX)
C
C X(IBOX,NUM)=XX
Y(IBOX,NUM)=YY
C
C GO TO 10000
C
C 10001 IF(I(I,ID).EQ.0)GO TO 10002
10004 ID=ID+1
GO TO 10000
C 10003 IF((ID=1).EQ.0)COUNT GO TO 10003
10004 ID=ID+1
GO TO 10000
C 88888 SUM=0.
DO 8765 LOOP=1,100
SUM=SUM+Y(LOOP)
8765 CONTINUE
C
C AREA(I)=SUM+9.1415926*DIA*DIA/4.0
THICK(I)=1000.0
D D 8766 LOOP=1,20
DIA=DIA-0.02*DIA*(LOOP-1)
AREA(LOOP1)=SUM+9.1415926*DIA*DIA/4.0
THICK(LOOP1)=THICK(LOOP1)+DIA/2
8766 CONTINUE
C
C WRITE(6,5436)
5436 FORMAT(9X,'A4',13X,'% AREA='//)
DO 8767 LOOP=1,20
WRITE(6,98765)THICK(LLP2),AREA(LLP2)
8767 CONTINUE
98765 FORMAT(3X,F10.2,7X,F10.2)
C
C CALL PLOT(0.
CALL PLOT(0.,10.,2)
CALL PLOT(10.,10.,2)
CALL PLOT(10.,0.,2)
CALL PLOT(0.,0.,2)

C
NORAW=RAW/0.02
DO 200 LP20=1,100
   NBOX=N(LP20)
   IF(NBOX.EQ.0) GO TO 200
   DO 210 LP21=1,NBOX
      DO 220 LP22=1,NORAW
         PX=LP20,LP21
         PY=LP20,LP21
         R=RAD-(LP22-1)*0.02
         CALL PLOT(PX,PY,R)
         CALL PCIRC(PX,PY,R)
   220 CONTINUE
   210 CONTINUE
  200 CONTINUE
CALL PLQTND
C
STOP
99999 STOP
END
Three-Dimensional Random Particle Deposition Model

I MPLICIT REAL *8(A-H,O-2)
DIMENSION X(100,150),Y(100,150),Z(100,150),
1 TX(150),TY(150),TZ(150),TTX(150),TTY(150),TTZ(150),
2 xxx(150),yyy(150),zzz(150),
3 XPX(150),YPY(150),
4 INTEGER FLAGX1,FLAGX2,FLAGX3,FLAGY1,FLAGY2,FLAGY3,
* FLAGZ1,FLAGZ2,
5 ICOUNT,0
EPS=0.010
EPS1=0.005
ZMIN=0.250
DIA=0.50
RAD=DIA/2.0
MORAY=RAD/0.015
IND3=0
NP=0

DO 10 I=1,100
N(I)=0
TX(I)=0.0
TY(I)=0.0
TZ(I)=0.0
TTX(I)=0.0
TTY(I)=0.0
TTZ(I)=0.0
CONTINUE
IF(I.GT.20)GO TO 10
N2(I)=0
NZ2(I)=0
CONTINUE
C Random number generator
C Initialize
10000 XX=PRAND(I), I=IRAND(I)
YY=PRAND(J), J=IRAND(J)
C Generate
XX=FPRAND(I)
I=IRAND(25)
XX=XX-I
YY=FPRAND(J)
J=IRAND(25)
YY=YY-J
IF((XX+RAD).GT.10.0 .OR. (YY+RAD).GT.10.0
.. OR. XX.LT.RAD .OR. YY.LT.RAD)GO TO 10000
22*100.0
C
ICHQ1=0
ICHQ2=0
ICOUNT=ICOUNT+1
IF(ICOUNT.EQ.1500)GO TO 88888
C
C (a) Check if the particle is at the lowest level
IF(J.EQ.0)GO TO 123
LL=JM1*10+I
LLP2+LL+2
C
C (b) Check if the particle is at the left or right edges
IF(I.EQ.9)GO TO 113
GO TO 114
112 LL=LL+1
GO TO 114
113 LLP2=LLP2+1
C
C (c) If no particle at a certain slot, do not compute
IF(LP(LP1).EQ.0)GO TO 20
NNN=LP(LP1)
/ 183
ICL=0
GO TO 30 LP2+1.NNTT
IF(ICHEQ1.EQ.1 .OR. ICHEQ2.EQ.1)GO TO 2176
GO TO 2177
2176 IFF2ZG.EQ.(LP1,LP2))GO TO 2178
GO TO 30
2177 IFF(Z2.0.05).LE.Z(LP1,LP2))GO TO 30
2178 ICL+1
ICLN+1
XXX(ICL)=X(LP1,LP2)
YYY(ICL)=Y(LP1,LP2)
ZZZ(ICL)=Z(LP1,LP2)
IF(ICL.EQ.1)GO TO 2178
GO TO 44
44 CONTINUE
2178 DBC=DSQRT((XX-X(LP1,LP2))**2+(YY-Y(LP1,LP2))**2)
IF((DBC+EPS1).LT.DIA)GO TO 111
GO TO 30
111 NP=NP+1
TX(NP)=X(LP1,LP2)
TY(NP)=Y(LP1,LP2)
TZ(NP)=Z(LP1,LP2)
30 CONTINUE
20 CONTINUE
C (I) Main level
C 123 ML+J+1=1
MLP2=ML+2
C (a) Check if the particle is at the left and right edges
C
IF(I.EQ.0)GO TO 124
IF(I.EQ.9)GO TO 125
GO TO 126
124 ML=ML+1
GO TO 126
125 NLP2=MLP2-1
126 00 40 LP1=ML.MLP2
C (b) If no particle at a certain slot, do not compute
C
IF(N(LP1).EQ.0)GO TO 40
NNTT=N(LP1)
ICM=0
DO 50 LP2=1,NNTT
IF(ICHEQ1.EQ.1 .OR. ICHEQ2.EQ.1)GO TO 2276
GO TO 2277
2276 IF(ZZ.EQ.Z(LP1,LP2))GO TO 2278
GO TO 50
2277 IF((ZZ-0.05).LE.Z(LP1,LP2))GO TO 50
2278 ICMM+1
ICMN=ICM-1
XXX(ICM)=X(LP1,LP2)
YYY(ICM)=Y(LP1,LP2)
ZZZ(ICM)=Z(LP1,LP2)
IF(ICM.EQ.1)GO TO 2278
GO TO 55
55 CONTINUE
2278 DBC=DSQRT((XX-X(LP1,LP2))**2+(YY-Y(LP1,LP2))**2)
IF((DBC+EPS1).LT.DIA)GO TO 222
GO TO 50
222 NP=NP+1
TX(NP)=X(LP1,LP2)
TY(NP)=Y(LP1,LP2)
TZ(NP)=Z(LP1,LP2)
50 CONTINUE
40 CONTINUE
C (II) Upper level
C (a) Check if the particle is at the highest Y level
C
IF(J.EQ.9)GO TO 234
ML+J+1=1
MLP2=ML+2
C (b) Check if the particle is at the left or right edges
C
IF(I.EQ.0)GO TO 236
IF(I.EQ.9)GO TO 237
GO TO 238
236 ML=ML+1
GO TO 238
237 MLP2=MLP2+1
238 00 40 LP1(LP1,LP2)
C (c) If no particle at a certain slot, do not compute
C
IF(N(LP1).EQ.0)GO TO 60
NNTT=N(LP1)
ICM=0
DO 50 LP2=1,NNTT
IF(ICHEQ1.EQ.1 .OR. ICHEQ2.EQ.1)GO TO 2376
GO TO 2377
2376 IF(ZZ.EQ.Z(LP1,LP2))GO TO 2378
GO TO 50
2377 IF((ZZ-0.05).LE.Z(LP1,LP2))GO TO 50
2378 ICMN+1
ICM=ICMN+1
XXX(ICMN)=X(LP1,LP2)
YYY(ICMN)=Y(LP1,LP2)
TY(NP)=Y(LP1,LP2)
TZ(NP)=Z(LP1,LP2)
XXZ(1) = X2(LP1,LP2)
IF(X1(1).EQ.0) GO TO 23787
DO 66 LP66 = 1,ICN
  IF(DABS(LP66-XX(XX(LP1,LP2)))**3+(YY-(LP1,LP2)))**2)/LE EPS .AND.
    DABS(LP66-XX(XX(LP1,LP2)))**3+(YY-(LP1,LP2)))**2)/LE EPS .AND.
    DABS(LP66-XX(XX(LP1,LP2)))**3+(YY-(LP1,LP2)))**2)/LE EPS .AND.
    DABS(LP66-XX(XX(LP1,LP2)))**3+(YY-(LP1,LP2)))**2)/LE EPS .AND.
  CONTINUE
33787 DO = DSOBT((XX-XUP1,LP2)/2* (YY-(LP1,LP2))/2)
  IF((DSOBT.EQ.1).LT.0IA) GO TO 333
  GO TO 70
66 CONTINUE
23787 OBC-DSOBT((XX-XUP1,LP2)/2* (YY-(LP1,LP2))/2)
IF((OBC.EQ.1).LT.0IA) GO TO 333
70 CONTINUE
60 CONTINUE
C (a) Check if there is 0 or 1 particle below the falling sphere
C --------------------------
C
C 334 IF(NP.EQ.0) GO TO 1911
    GO TO 1918
1911 IF(ICHE01.EQ.1 OR ICHE02.EQ.1) GO TO 1912
    GO TO 90000
1912 IF(NP.EQ.0 .AND. ICHE01.EQ.1) GO TO 1916
    GO TO 1912
1914 IF(NP.EQ.0 .AND. ICHE02.EQ.1) GO TO 1917
    GO TO 1912
1916 ICHE01 = 0
    GO TO 5555
1917 ICHE02 = 0
    GO TO 5555
1918 ICHE01 = 0
    TX(1) = TX(1)
    TY(1) = TY(1)
    TZ(1) = TZ(1)
    TX(3) = XBOT1
    TY(3) = YBOT1
    TZ(3) = ZBOT1
    GO TO 1444
1920 ICHE02 = 0
    TX(1) = TX(1)
    TY(1) = TY(1)
    TZ(1) = TZ(1)
    TX(3) = XBOT1
    TY(3) = YBOT1
    TZ(3) = ZBOT1
    GO TO 892
1922 ICHE01 = 0
    TX(1) = TX(1)
    TY(1) = TY(1)
    TZ(1) = TZ(1)
    TX(3) = XBOT1
    TY(3) = YBOT1
    TZ(3) = ZBOT1
    GO TO 892
1923 ICHE02 = 0
    TX(1) = TX(1)
    TY(1) = TY(1)
    TZ(1) = TZ(1)
    TX(3) = XBOT1
    TY(3) = YBOT1
    TZ(3) = ZBOT1
    GO TO 888
1924 ICHE01 = 0
    TX(1) = TX(1)
    TY(1) = TY(1)
    TZ(1) = TZ(1)
    TX(3) = XBOT1
    TY(3) = YBOT1
    TZ(3) = ZBOT1
    GO TO 888
1925 CALL ONES(DIA,XX,XBOT,YY,YBOT,ZZ,ZBOT,XTOP2,YTOP2)
C
C 334 XBOT+TX(1)
    YBOT+TY(1)
    ZBOT+TZ(1)
C 335 CALL ONES(DIA,XX,XBOT,YY,YBOT,ZZ,ZBOT,XTOP2,YTOP2)
C
C XX = XTOP2
    YY = YTOP2
    ZZ = ZBOT
    ICHE01 = 1
    GO TO 5555
C (a) Find Z1MAX
C
C 346  NPZ1=0  
C  -  NPZ2=0  
C  1ND=0  
C
C Z1MAX=Z1(1)  
DO 80 LP3=2,NP  
IF(Z1(LP3).GT.Z1MAX)Z1MAX=Z1(LP3)  
80 CONTINUE  
C
C (c) Find number of particles at Z1MAX (NPZ1)  
C
C DO 90 LP4=1,NP  
IF(Z1(LP4).EQ.Z1MAX)GO TO 444  
GO TO 90  
444 NPZ1=NPZ1+1  
NZK(NPZ1)=LP4  
90 CONTINUE  
C (d) Check if there is only 1 particle at level Z1  
C
IF(NPZ1.EQ.1)GO TO 445  
GO TO 446  
445 NTZ1=NZ1(NPZ1)  
XBOT=X(TX(NTZ1))  
YBOT=TY(TY(NTZ1))  
ZBOT=TZ(TZ(NTZ1))  
GO TO 335  
C
C Determine the next highest Z level (Z2)  
C
C (a) If all the particles are at Z1 level, then skip checking at Z2  
C
446 IF(NPZ1.EQ.NP)GO TO 778  
C (d) Find Z2MAX  
C DO 100 LP5=1,NP  
IF(Z1(LP5).LT.Z1MAX)GO TO 555  
GO TO 100  
555 Z2MAX=Z1(LP5)  
GO TO 666  
100 CONTINUE  
C 666 00 110  LP6=1,NP  
IF(Z1(LP6).GT.Z2MAX).AND.(Z1(LP6).LT.Z1MAX)Z2MAX=Z1(LP6)  
110 CONTINUE  
C (c) Find number of particles at Z2MAX  
C
C DO 120 LP7=1,NP  
IF(Z1(LP7).EQ.Z2MAX)GO TO 777  
GO TO 120  
777 NPZ2=NPZ2+1  
NZ2(NPZ2)=LP7  
120 CONTINUE  
C
C Determine the distance between the two Z levels  
C ZDIFF=Z1MAX-Z2MAX  
C
C Assign the particles at Z1 level to a temporary array (TT/X/Y/Z)  
C
C 778 DO 130 LP13=1,NPZ1  
NTNZ1(LP13)=NZ1(LP13)  
TTX(LP13)=TX(LP13)  
TTY(LP13)=TY(LP13)  
TZ(LP13)=TZ(LP13)  
130 CONTINUE  
C
C Check if the number of particles at Z1 is greater than 2  
C
IF(NPZ1.EQ.3)GO TO 892  
IF(NPZ1.EQ.4)GO TO 888  
C
C For 2 spheres below, determine which sphere has a bigger Y  
The bigger Y will be assigned the position of 1  
C
C 1444 FLAG2A=0  
FLAG2B=0  
IF(TTY(1).GT.TTY(2))FLAG2A=1  
IF(LT(TTY(1),1))GO TO 999  
IF(LT(TTY(1),1))GO TO 1010  
C 989 XBOT1=TTX(2)  
XBOT2=TTX(1)  
YBOT1=TTY(2)  
YBOT2=TTY(1)  
ZBOT1=TTZ(2)  
ZBOT2=TTZ(1)  
GO TO 1111  
C 999 XBOT1=TTX(1)  
XBOT2=TTX(2)  
YBOT1=TTY(1)  
YBOT2=TTY(2)  
ZBOT1=TTZ(1)  
ZBOT2=TTZ(2)  
GO TO 1111  
C 1010 IF(LT(TTY(1),2))FLAG2A=1  
IF(LT(TTY(1),1))GO TO 999  
GO TO 989  
C
For the 2 spheres below, determine if the falling particle is actually touching both of them.

```
C 1111
DBC = SQRT((XX-XBOT1)**2+(YY-YBOT1)**2)  
DBC2 = SQRT((XX-XBOT2)**2+(YY-YBOT2)**2)  
IF(DBC.EQ.DBC2)GO TO 1222
AVG = (DBC+DBC2)/2.0
C CALL TWO5(AVG,XX,XX,XY,YY,YY,ZBOT1,ZBOT2,  
XTOP2,YTOP2)
C 1222 CALL TWO5(DIA,XX,XX,XY,YY,YY,ZBOT1,ZBOT2,  
XTOP2,YTOP2)
C CALL TWO5(AVG,XX,XX,XY,YY,YY,ZBOT1,ZBOT2,  
XTOP2,YTOP2)
```

Assign XTOP2 and YTOP2 as XX and YY and repeat.

```
C CHECK if the falling particle will be permanently rested.
C
FLAGX1 = 0
FLAGX2 = 0
FLAGX3 = 0
FLAGY1 = 0
FLAGY2 = 0
FLAGY3 = 0
C
DO 160 LP16 = 1,NPZ1
IF(XX.GT.TTX(LP16))FLAGX1 = 1
IF(XX.LT.TTX(LP16))FLAGX2 = 1
IF(YY.GT.TTY(LP16))FLAGY1 = 1
IF(YY.LT.TTY(LP16))FLAGY2 = 1
160 CONTINUE
C
IF(FLAGX1.EQ.1 .AND. FLAGX2.EQ.1 .AND. FLAGX3.EQ.1)GO TO 90000
IN03 = 1
GO TO 5555
C
896 DGL(1) = SQRT((TTX(1)-TTX(2))**2+(TTY(1)-TTY(2))**2)
DGL(2) = SQRT((TTX(1)-TTX(3))**2+(TTY(1)-TTY(3))**2)
DGL(3) = SQRT((TTX(2)-TTX(3))**2+(TTY(2)-TTY(3))**2)
C
IF(DGL(1).GT.DGL(2).AND. DGL(1).GT.DGL(3))GO TO 1444
IF(DGL(2).GT.DGL(1).AND. DGL(2).GT.DGL(3))GO TO 1334
TTX(1) = TTX(2)
TTY(1) = TTY(2)
TTZ(1) = TTZ(2)
TTX(2) = TTX(3)
TTY(2) = TTY(3)
TTZ(2) = TTZ(3)
GO TO 1444
C
1334 TTX(2) = TTX(3)
TTY(2) = TTY(3)
TTZ(2) = TTZ(3)
GO TO 1444
C
```

Determine the biggest Y position for the case of more than 3 particles at the highest Z level (z1).

```
YBIG = TTY(1)
C
DO 140 LP14 = 2,NPZ1
IF(TTY(LP14).GT.YBIG)YBIG = TTY(LP14)
140 CONTINUE
C
DO 150 LP15 = 1,NPZ1
IF(TTY(LP15).EO.YBIG)NP0S = LP15
150 CONTINUE
C
IF(NP0S.EQ.1)GO TO 889
XBOT2 = TTX(1)
YBOT2 = TTY(1)
ZBOT2 = TTZ(1)
C
IF(NP0S.EQ.2)GO TO 890
XBOT3 = TTX(2)
YBOT3 = TTY(2)
ZBOT3 = TTZ(2)
C
IF(NP0S.EQ.3)GO TO 891
XBOT4 = TTX(3)
YBOT4 = TTY(3)
ZBOT4 = TTZ(3)
C
GO TO 894
C
889 XBOT1 = TTX(1)
YBOT1 = TTY(1)
ZBOT1 = TTZ(1)
```
**C**: XBOT2-TTX(2)
YBOT2-TTY(2)
ZBOT2-TTZ(2)

**C**: XBOT3-TTX(3)
YBOT3-TTY(3)
ZBOT3-TTZ(3)

**C**: XBOT4-TTX(4)
YBOT4-TTY(4)
ZBOT4-TTZ(4)

**GO TO 894**

**C**: 890 CALL FOURS(DIA,XX,XBOT1,XBOT2,XBOT3,XBOT4,YY,YBOT1,YBOT2,
YBOT3,YBOT4,XBOT2,YBOT2,HEIGHT)

**C**: 895 XX-XTOP2
YY-YP2
ZZ-HEIGHT

---

**C**: Recording the permanent X,Y,Z values for the settled particle

**C**: **********

**C**: **STOP**

**END**
SUBROUTINE ONEStDIA, XTOP1, XBOT, YTOP1, YBOT, ZBOT, XTOP2, YTOP2
C
IMPLICIT REAL A-H.0-Z
100 DELX=XTOP1-XBOT
DELY=YTOP1-YBOT
C
IF(DELX.EQ.0 .AND. DELY.EQ.0)GO TO 40
GO TO 45
C
40 I=IRAND(6)
I=IRAND(4)
C
IF(I.EQ.1)XTOP1=XTOP1+0.1
IF(I.EQ.2)YTOP1=YTOP1+0.1
IF(I.EQ.3)XTOP1=XTOP1-0.1
IF(I.EQ.4)YTOP1=YTOP1-0.1
GO TO 100
C
45 IF(DELX.EQ.0)GO TO 50
IF(DELY.EQ.0)GO TO 60
C
SLOPE=DELY/DELX
C
IF(SLOPE.GT.0)GO TO 10
C
XYQ=C/SLOPE
DI=DSQRT((YTOP1-YBOT)**2+(XTOP1-XBOT)**2)
D=DSQRT(YBOT**2+(XBOT-XYQ)**2)
C
IF(DELX.LT.0)GO TO 20
C
XTOP2=XYQ+(D-DIA)*(XBOT-XYQ)/D
YTOP2=(D-DIA)*YTOP1/D
GO TO 999
C
20 XTOP2=XYQ+(D-DIA)*(XTOP1-XYQ)/(D-DIA)/D
YTOP2=(D-DIA)*YTOP1/(D-DIA)
GO TO 999
C
10 YXQ=C
DI=DSQRT(XBOT**2+(YBOT-YXQ)**2)
IF(DELX.LT.0)GO TO 30
C
XTOP2=XYQ+(D-DIA)/D
YTOP2=(YBOT-YXQ)/(D-DIA)/D
GO TO 999
C
30 XTOP2=YBOT+(D-DIA)/D
YTOP2=(YBOT-YXQ)*(D-DIA)/D)
GO TO 999
C
50 IF(YTOP1.GT.YBOT)GO TO 70
XTOP2=XTOP1
YTOP2=YBOT-DIA
GO TO 999
C
70 XTOP2=XTOP1
YTOP2=YBOT+DIA
GO TO 999
C
60 IF(XTOP1.GT.XBOT)GO TO 80
YTOP2=YTOP1
XTOP2=XTOP1-DIA
GO TO 999
C
80 YTOP2=YTOP1
XTOP2=XTOP1+DIA
C
999 RETURN END
C
SUBROUTINE TWOS(DIA, XTOP1, XBOT1, XBOT2, YTOP1, YBOT1, YBOT2,
ZBOT1, ZBOT2, XTOP2, YTOP2)
C
IMPLICIT REAL A-H.0-Z
C
C Common equations for all cases
C
EPS=0.005
C
IF(OABS(XBOT1-XBOT2).LE.EPS OR OABS(YBOT1-YBOT2).LE.EPS)GO TO 40
C
SLOPE=(XBOT1-XBOT2)/(YBOT1-YBOT2)
XQ=(XBOT1+XBOT2)/2.0
YQ=(YBOT1+YBOT2)/2.0
C=C+SLOPE*XQ
C
IF(YTOP1.GT.YBOT1)GO TO 10
C
Equations for Cases 1 and 2
C
X1=XQ
Y1=YBOT1
XYIQ=(XBOT1-XQ)/SLOPE
X1=OABS(XYIQ-XQ)
X1=DSQRT((YQ-Y1)**2+(XYIQ-XQ)**2)
40L=DIA
A0L=DIA
B0L=DIA
C0L=DSQRT((YBOT1-YBOT2)**2+((XBOT1-XBOT2)**2)/2.0)
G1=4*(I.0.0)
G1=4*(I.0.0)
D=NSQRT(1.0)
W=x+y
E0=L+0.0
A0L=+A0L
W=x+y
E0=L+0.0
A0L=+A0L
X1=X1+(40L-40L)*E0
C
YTOP2=YBOT2+AA1
C
IF(XTOP1.GT.XBOT1)GO TO 20
XTOP2=XYIQ+AA1
GO TO 999
C
20 XTOP2=XYIQ+AA1
C
GO TO 999
C Equations for Cases 3 and 4

C 10 YXB2=C*SLQPF*XBOT2

B1B2=SQRT((XBOT1-XBOT2)**2+(YBOT1-YBOT2)**2)

EB2=B1B2/2.0

FB1=DABS(XBOT1-XBOT2)

EI=FB1/2.0

C XI-XBOT2 YI=Y2-B1B2

B2=0.0

C 0IF(E12>=EB2)**2

IF((IF(LT.0.0))I=0.0)

ET2=SQRT(E12)

EYXB2=2*SQRT((YBOT2-YI)**2+(E1)**2)

C New Y for Case 3 and 4

C YTOP2=YXB2-((YXB2-YI)*12YXB2/EYXB2)

C IF(XTOP1.LT.XBOT2)GO TO 30

C New X for Case 3

C YTOP2=((XI-XI)*12YXB2/EYXB2)+XBOT2 GO TO 999

C New X for Case 4

30 YTOP2=XBOT2-((XI-XI)*12YXB2/EYXB2)

GO TO 999

C 40 IF(DABS(XBOT1-XBOT2).LE.EPS)GO TO 50

C New X for Case 4

C YTOP2=XBOT1+XL GO TO 999

C 50 YTOP2=YTOP1+YL GO TO 999

C 60 YTOP2=YBOT1-12+XL GO TO 999

C 70 YTOP2=YBOT1-12+XL GO TO 999

C 80 YTOP2=YBOT1-12+XL GO TO 999

C 90 IF(1013.EQ.1)GO TO 100

C New X for Case 4

C 100 RETURN

END

C SUBROUTINE THREESGIA,XTOP1,XBOT1,XBOT2,YBOT1,YBOT2,YBOT3,ZBOT1,ZBOT2,ZBOT3,YTOP1,YTOP2,HEIGHT

C IMPLICIT REAL*8(A-H,O-Z)

DIMENSION AD(3),HT(3),XBOT(3),YBOT(3)

EPS=0.005

C ID12=0

ID13=0

ID23=0

C IF(DABS(YBOT1-YBOT2).LE.EPS)GO TO 10

C GO TO 20

10 ID12=1

GO TO 30

C 20 S12=-(XBOT1-XBOT2)/(YBOT1-YBOT2)

XMP12=(XBOT1+XBOT2)/2.0

YMP12=0.5*(YBOT1+YBOT2)

C12=YMP12-(S12*XMP12)

C IF(1012.EQ.1)GO TO 110

C GO TO 120

C 30 IF(DABS(YBOT2-YBOT3).LE.EPS)GO TO 40

C GO TO 50

40 ID23=1

GO TO 60

C 50 S23=-(YBOT2-YBOT3)/(YBOT2-YBOT3)

XMP23=(YBOT2+YBOT3)/2.0

YMP23=0.5*(YBOT2+YBOT3)

C23=YMP23-(S23*XMP23)

C IF(DABS(YBOT1-YBOT3).LE.EPS)GO TO 70

C GO TO 80

60 ID3=1

GO TO 90

C 70 IF(1013.EQ.1)GO TO 100

C GO TO 110

C GO TO 120
C
100 IF(S12.EQ.S23 .AND. ID13.NE.ID3)GO TO 110
XTOP2=(XTOP2+ID13)/2
YTOP2=(YTOP2+ID13)/2
GO TO 888
C
110 IF(S13.EQ.S23 .AND. ID12.NE.ID0)GO TO 120
XTOP2=(XTOP2+ID12)/2
YTOP2=(YTOP2+ID12)/2
GO TO 888
C
888 XBOTI=
XBOT1+XBOT2+XBOT3+XBOT4
YBOT1+YBOT2+YBOT3+YBOT4
C
SUM=0.0
DO 2345 L=1,4
ADL=(XTOP2-XBOT(L))**2+(YTOP2-YBOT(L))**2
DIFF=2*ADL
IF(DIFF.LT.0)DIFF=0
HT(L)=SORT(DIFF)
SUM=SUM+HT(L)
2345 CONTINUE
C
HEIGHT=SUM/3.0
C
RETURN
END
C
C
SUBROUTINE FOURSDIA(XTOP1,XBOT1,XBOT2,XBOT3,XBOT4,
YTOP1,YBOT1,YBOT2,YBOT3,YBOT4,HEIGHT)
C
IMPLICIT REAL *8(A-H,O-Z)
DIMENSION XB0T(4), YB0T(4), HT(4), DBC(3,4), AO(4)
C
EPS=0.005
I04A=0
I04B=0
C
XBOT(1)=XBOT1
XBOT(2)=XBOT2
XBOT(3)=XBOT3
XBOT(4)=XBOT4
YB0T(1)=YBOT1
YB0T(2)=YBOT2
YB0T(3)=YBOT3
YB0T(4)=YBOT4
C
C Compute the distance between centres(DBC) for the 4 bottom
C spheres and also determine the largest DBC
C
DBIG=0.0
NL=1
DO 10 L=1,3
NL=NL+1
DO 20 L2=NL,4
DBC(L,L2)=SORT((XBOT(L)-XBOT(L2))**2+
(YBOT(L)-YBOT(L2))**2)
1 IF(DBC(L,L2).GT.DBIG)GO TO 1000
GO TO 20
1000 DBIG=DBC(L,L2)
ID1=L
I02=L2
20 CONTINUE
10 CONTINUE
C
C Determine the next largest DBC
C
DBIG2=0.0
NN=1
DO 30 L3=1,3
NN=NN+1
DO 40 L4=NN,4
IF(DBC(L3,L4).GT.DBIG2 .AND. DBC(L3,L4).LT.DBIG)GO TO 2000
GO TO 40
30 CONTINUE
20 CONTINUE
40 CONTINUE
C
IF(OABS(YBOT(ID1)-YBOT(ID2)).LE.EPS)GO TO 50
GO TO 70
60 ID4A=1
GO TO 80
C
70 S1=(XBOT(ID1)-XBOT(ID2))/(YBOT(ID1)-YBOT(ID2))
80 XBOT1=XBOT(ID1)
XBOT2=XBOT(ID2)
YBOT1=YBOT(ID1)
YBOT2=YBOT(ID2)
XMP1=(XBOT1+XBOT2)/2.0
YMP1=(YBOT1+YBOT2)/2.0
C
IF(ID4A.EQ.1)GO TO 80
C1=1
C
90 IF(OABS(YBOT(ID3)-YBOT(ID4)).LE.EPS)GO TO 100
GO TO 110
100 ID4B=1
GO TO 120
C
110 S2=(XBOT(ID3)-XBOT(ID4))/(YBOT(ID3)-YBOT(ID4))
120 XBOT3=XBOT(ID3)
XBOT4=XBOT(ID4)
YBOT3=YBOT(ID3)
YBOT4=YBOT(ID4)
XMP2=(XBOT3+XBOT4)/2.0
YMP2 + YB0T (YB0T13 + YB0T14) / 2.0

C IF (ID4A EQ 1) GO TO 130
C C2 + YMP2 - (S2 - XMP2)
C 130 IF (ID4A EQ 1) GO TO 140
C IF (ID4A EQ 1) GO TO 150
C XT0P2*(C2-C1)/(S1-S2)
C YTOP2*(S1*XTOP2+C1)
C GO TO 888
C C 140 YTOP2*(S2*XMP1)+C2
C XT0P2*XMP1
C GO TO 888
C 150 YTOP2*(S1*XM P2)+C1
C XT0P2*XMP2
C C Determine the Z position of the settled particle
C C *********************************************************
C C 888 SUM=0.0
C DO 50 L5=1,4
C AD(L5) = XT0P2*XR0T(L5)**2 + YTOP2*YB0T(L5)**2
C DIFF = D1A**2 - AD(L5)
C IF (DIFF LT 0) DIFF = 0
C HT(L5) = DSORT(DIFF)
C SUM = SUM + HT(L5)
50 CONTINUE
C C HEIGHT = SUM/4.0
C C RETURN
C END
Calculation of total potential energy for the interaction between two spheres in an aqueous medium.

Equations from thesis used in the calculation:

(i) \[ (2.18) \] for electrical double layer interaction
(ii) \[ (2.40) \] for van der Waals interaction

Units used:
- Length: cm
- Energy: ergs
- Temp: K
- Potential: statvolt

Parameters to be changed: PSI1, PSI2, KAPPA

```
IMPLICIT REAL*8 (A-H,O-Z)
REAL*8 KAPPA,TOTAL(80),EDL(80),VDW(80),HH(80),KT
COMMON/BLKA/PSI1,PSI2,KAPPA
EXTERNAL FUNC1,FUNC2

EDLT2=1.38064244D-16
TEMP=298.15
KT=EDLT2*TEMP
STA*=3.33566830D-6

PSI1=75.83,83*STATV
PSI2=75.83,83*STATV
KAPPA=61818.1818

HI=1.00-5
HII=1.00-5
DO 10 LP 1=1.80 HH(LP1)=H*1.D4 £DL(LP1)=FUNCl(LP1) VDW(LP1)=FUNC2(LP1)

TOTAL(LP1)=(EDL(LP1)+VDW(LP1))/KT HH(LP1)=HI

WRITE(6,2000)KAPPA,PSI1,PSI2
2000 FORMAT(/2X,'KAPPA = ',E13.6,' STATV'/2X,'PSI1 = ',E13.6,' STATV'/2X,'PSI2 = ',E13.6,' STATV')

CONTINUE

DO 20 LP2=1.80 WRITE(6,1000)HH(LP2),E0L(LP2),V0W(LP2),TOTAL(LP2)
1000 FORMAT(/2X,E13.6,2X,E13.6,2X,E13.6,2X,E13.6)
20 CONTINUE

STOP END
```

```
DOUBLE PRECISION FUNCTION FUNCl(H)

IMPLICIT REAL*8 (A-H,0-Z)
COMMON/BLKA/PSI1,PSI2,KAPPA
REAL*8 KAPPA

EPS=78.54
A=5.0-5
B=5.0-5

TE1=(EPS*A**2+(EPS1+EPS2))/(4*(A+B))
TE2=(2*EPS1*EPS2)/(EPS1+EPS2)
TE3=LOG(1+EXP(-KAPPA*H))
TE4=LOG(1-EXP(-2*KAPPA*H))

FUNCl=TE1*(TE2*TE3-TE4)

RETURN END
```

```
DOUBLE PRECISION FUNCTION FUNC2(H)

IMPLICIT REAL*8 (A-H,0-Z)
REAL*8 LAMBDA,IS1,IS2,IS3,IS4,IS5,IS6,HAMAKE

HAMAKE=0.63920-13
BOLTZ=1.38050-16

A=5.0-5
B=5.0-5

LAMBDA=1.0-5
RH0=0.477464829*LAMBDA
AA=1.01
BB=0.876569032*LAMBDA
CC=0.3893261*LAMBDA
DD=0.0167803*LAMBDA

RH0D=RH0
ALPHA=(AA/(2*RH0**2))-(BB/(RH0*2))-(CC/(3*RH0**3))-(DD/(4*RHO**4))
BETA=(-2*AA/(3*RH0**3))+(BB/(RH0**2))-(CC/(2*RH0**4))+(DD/(5*RHO**5))

GAMMA=(AA/(4*RHO**4))-(BB/(3*RHO**3))-(CC/(5*RHO**5))+(DD/(6*RHO**6))

Q=1+(2+B)*H=1+(2+B)*H

IF(RH0.GT.(H+2.0))GO TO 1000

Calculate IS1

```

1+DLG((IS+2K)*((H+2B)))/(IS+2K)
1+DLG((IS+2K)*((H+2B)))/(IS+2K)
1+DLG((IS+2K)*((H+2B)))/(IS+2K)
```

```
``
ELECTRIC DOUBLE LAYER AND KAPPA-\(A\) CALCULATION

REAL \(K_A, \text{MINUS, MPLUS, WMINUS, K, KAPPA}\)

REAL \(W_M, \text{MDW, W_M, MPLUS, WMINUS}\)

\[
\begin{align*}
U_H &= 36.3 \times 10^{-4} \\
U_{OH} &= 20.3 \times 10^{-4} \\
U_{NH_4} &= 7.6 \times 10^{-4} \\
U_{HCO_3^-} &= 6.3 \times 10^{-4} \\
U_{Cl^-} &= 7.91 \times 10^{-4} \\
U_{Na^+} &= 7.61 \times 10^{-4} \\
U_{\text{PLUS}} &= 5.614 \times 10^{-4} \\
U_{\text{MINUS}} &= 6.255 \times 10^{-4}
\end{align*}
\]

\[
\begin{align*}
M_H &= 0.3676 \\
M_{OH^-} &= 0.06495 \\
M_K &= 0.1749 \\
M_{Cl^-} &= 0.1685 \\
M_{PLUS} &= 0.2372 \\
M_{MINUS} &= 0.213
\end{align*}
\]

\[
A = 0.50
\]

\[
\begin{align*}
E_L &= 1.6023 \times 10^{-19}
\end{align*}
\]

111 WRITE(6, 100)

100 FORMAT('INPUT PH VALUE : FORMAT XX.XX'/)

READ(5, 1000) PH

1000 FORMAT(G5.2)

IF(PH.EQ.0.0) GO TO 999

WRITE(6, 101)

101 FORMAT('INPUT CONDUCTIVITY VALUE : FORMAT 0.00000000X'/)

READ(5, 2000) COND

2000 FORMAT(G13.8)

WRITE(6, 105)

105 FORMAT('INPUT KCL CONCENTRATION : FORMAT 0.XXXXXXX'/)

READ(5, 2005) K

2005 FORMAT(G13.8)

\[
\begin{align*}
\text{CL} &= K \times 10^{-\text{PH}} \\
\text{OH}^- &= \frac{10^{(14.0 - \text{PH})}}{\text{H}^+} \\
\text{PLUS} &= \frac{\text{COND} \times \text{H}^+ \times \text{OH}^-}{(\text{H}^+ + \text{OH}^- + \text{Cl}^- + \text{K} + \text{CL}^-)} \\
\text{MINUS} &= \frac{\text{COND} \times \text{OH}^-}{(\text{OH}^- + \text{Cl}^-)}
\end{align*}
\]

KAPPA = 0.3286 \times (\text{COND} \times 0.5)

EDL = 10000.0 / KAPPA

\[
K = \text{KAPPA} \times 10000.0
\]

\[
\begin{align*}
\text{XMP} &= \frac{(\text{H}^+ \times \text{OH}^-) + (\text{K} \times \text{CL}^-) + (\text{PLUS} \times \text{OH}^- + \text{OH}^- \times \text{Cl}^- + \text{K} \times \text{CL}^- + \text{Cl}^- \times \text{MINUS} + \text{MINUS} \times \text{MINUS})}{\text{COND}}
\end{align*}
\]

WRITE(6, 102) CONC, K, PLUS, OH, CL, MINUS, EDL, KA, XMP, XMI

102 FORMAT('INPUT \text{CONC}, K, PLUS, OH, CL, MINUS, EDL, KA, XMP, XMI'/)

\[
\begin{align*}
1 &= \text{K}^+ \times 10^{-6} \\
2 &= \text{Ca}^{2+} \times 10^{-6} \\
3 &= \text{Na}^+ \times 10^{-6} \\
4 &= \text{Cl}^- \times 10^{-6} \\
5 &= \text{OH}^- \times 10^{-6} \\
6 &= \text{K}^+ \times 10^{-6} \\
7 &= \text{M}^+ \times 10^{-6} \\
8 &= \text{M}^- \times 10^{-6}
\end{align*}
\]

GO TO 111

999 STOP END