SEDIMENTATION OF A SPHERICAL PARTICLE IN AN ELECTROLYTE VISCOELASTIC SOLUTION
SEDIMENTATION OF A SPHERICAL PARTICLE IN AN ELECTROLYTE VISCOELASTIC SOLUTION

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PATRAS, JULY 2023
1. Το σύνολο της εργασίας αποτελεί πρωτότυπο έργο, παραχθέν από την συγγραφέα της, και δεν παραβιάζει δικαιώματα τρίτων καθ’ οιονδήποτε τρόπο,

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It is a common belief that graduate studies are concluded with the Diploma Thesis. So, from the second semester on, all the graduate students had the opportunity to utilize the knowledge acquired from the courses of the master's program, by choosing a research lab related to the program so as to complete their graduate studies. From the very beginning of my graduate studies, I had selected the Laboratory of Fluid Mechanics and Rheology, administrated by Professor John Tsamopoulos and associate Professor Yiannis Dimakopoulos. I made this decision because I have also completed my undergraduate diploma thesis in this lab, and I wanted to take it a step further since I’m very interested in Transport Phenomena. Both professors and all fellow researchers of the lab contributed to my advancement as a new researcher, so I want to thank each and every one of them. Most importantly, I would like to thank, Ph.D. candidate Pantelis Moschopoulos, who was always willing to guide me and advise me throughout this period and was the one who introduced me to the world of Electrokinetic Phenomena.
1. SUMMARY

When a charged particle translates through an electrolyte solution, the Electric Double Layer (EDL) around it deforms in response to the fluid motion and creates an electric force opposite to the direction of motion, decreasing the settling velocity. This is a multidisciplinary phenomenon that combines fluid mechanics and electrodynamics, differentiating it from the classical problem of an uncharged, sedimenting particle. It has many applications varying from mechanical to biomedical, such as in drug delivery in blood through charged microparticles. Related studies, so far, have focused on Newtonian fluids [1], but recent studies have proven that many biofluids, such as human blood plasma [2], have elastic properties. To this end, we perform a computational study of the steady sedimentation of a spherical, charged particle in human blood plasma due to centrifugal force. We use the Giesekus model to describe the rheological behavior of human blood plasma [2]. Assuming axial symmetry, the governing equations include the momentum and mass balances, Poisson’s equation for the electric field, and the species conservation. They are solved numerically using the finite element method [3]. The finite size of the ions is considered through the LDA approach of Carnahan-Starling [4]. We make a detailed parametric analysis, varying parameters such as the ζ potential, the size of the ions, and the centrifugal force exerted upon the particle. We observe that as the ζ potential increases, the settling velocity decreases due to a stronger electric force that slows down the particle. As a result, the stresses on the surface of the particle decrease. We also conduct a parametric analysis of the relaxation time of the material, to investigate what happens generally in viscoelastic electrolyte solutions and not only in human blood plasma. We conclude that elasticity plays a crucial role, and it should not be excluded from the study. Finally, we examine in which range of zeta potential and ratio of particle diameter to Debye length, the assumption of point-like ions gives different predictions from the Carnahan-Starling approach.

**KEYWORDS:** Sedimentation of a Charged Particle, Electric Double Layer, Human Blood Plasma, Viscoelasticity
Όταν ένα φορτισμένο σωματίδιο κινείται μέσα σε ένα ηλεκτρολυτικό διάλυμα, η ηλεκτροχημική διπλοστιβάδα γύρω του παραμορφώνεται ως αποτέλεσμα της κίνησης του ρευστού και δημιουργείται μια αντίθετη δύναμη, η οποία επιβραδύνει τον παραγόντα [1]. Όμως, έχει αποδειχθεί ότι πολλά βιορευστά εμφανίζουν υπολογισιακές ελαστικές ιδιότητες, όπως το πλάσμα του ανθρώπινου αίματος [2]. Για αυτόν τον λόγο, πραγματοποιούμε μία υπολογιστική μελέτη της καθίζησης ενός σφαιρικού σωματιδίου στο πλάσμα του ανθρώπινου αίματος λόγω φυγόκεντρου δυνάμεως σε μόνιμη κατάσταση. Η ταχύτητα καθίζησης μειώνεται λόγω ισχυρότερης ηλεκτρικής δύναμης που επιβραδύνει το σωματίδιο με αποτέλεσμα οι τάσεις στην επιφάνεια του σωματιδίου να μειώνονται. Πραγματοποιούμε επίσης μία παραμετρική ανάλυση ως προς τον χρόνο χαλάρωσης του υλικού, ώστε να διερευνήσουμε τον ισχυρότερο συμπεριφορά των ανθρώπινων διαλύματος και όχι μόνο στο πλάσμα του ανθρώπινου αίματος. Συμπεραίνουμε ότι η ελαστικότητα παίζει σημαντικό ρόλο στο φαινόμενο και ότι θα πρέπει να λαμβάνεται υπόψη. Τέλος, εξετάζουμε για ποιες τιμές του χρόνου και του λόγου της διαμέτρου του σφαιριδίου προς το μήκος Debye της ηλεκτρικής δυνάμεως, η υπόθεση των σημειακών ιόντων δίνει διαφορετικά αποτελέσματα από την προσέγγιση Carnahan-Starling.
# 3. TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>FOREWORD</td>
<td>4</td>
</tr>
<tr>
<td>1. SUMMARY</td>
<td>5</td>
</tr>
<tr>
<td>2. ΠΕΡΙΛΗΨΗ</td>
<td>6</td>
</tr>
<tr>
<td>3. TABLE OF CONTENTS</td>
<td>7</td>
</tr>
<tr>
<td>4. SYMBOLS</td>
<td>8</td>
</tr>
<tr>
<td>5. LIST OF TABLES</td>
<td>10</td>
</tr>
<tr>
<td>6. LIST OF FIGURES</td>
<td>11</td>
</tr>
<tr>
<td>7. INTRODUCTION</td>
<td>12</td>
</tr>
<tr>
<td>8. PROBLEM FORMULATION</td>
<td>14</td>
</tr>
<tr>
<td>8.1 FLOW FIELD</td>
<td>14</td>
</tr>
<tr>
<td>8.2 ELECTRIC FIELD</td>
<td>17</td>
</tr>
<tr>
<td>9. NUMERICAL IMPLEMENTATION</td>
<td>19</td>
</tr>
<tr>
<td>10. RESULTS AND DISCUSSION</td>
<td>21</td>
</tr>
<tr>
<td>10.1 NEWTONIAN SOLUTION – MODEL VALIDATION</td>
<td>21</td>
</tr>
<tr>
<td>10.2 PRECIPITATION IN BLOOD PLASMA</td>
<td>23</td>
</tr>
<tr>
<td>10.2.1 EFFECT OF THE g-FACTOR</td>
<td>23</td>
</tr>
<tr>
<td>10.2.2 EFFECT OF THE RELAXATION TIME</td>
<td>26</td>
</tr>
<tr>
<td>10.2.3 EFFECT OF THE ZETA POTENTIAL</td>
<td>27</td>
</tr>
<tr>
<td>10.2.4 EFFECT OF THE DEBYE LENGTH</td>
<td>30</td>
</tr>
<tr>
<td>11. CONCLUSIONS</td>
<td>34</td>
</tr>
<tr>
<td>12. REFERENCES</td>
<td>35</td>
</tr>
<tr>
<td>13. APPENDIX</td>
<td>38</td>
</tr>
</tbody>
</table>
4. SYMBOLS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\vec{f}$</td>
<td>body force [N]</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>volume of the viscoelastic material</td>
</tr>
<tr>
<td>$A_s$</td>
<td>fluid/particle interface</td>
</tr>
<tr>
<td>$S_{outer}$</td>
<td>far field boundary</td>
</tr>
<tr>
<td>$\vec{g}$</td>
<td>gravity vector [m/s²]</td>
</tr>
<tr>
<td>$D$</td>
<td>sphere diameter [m]</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>coefficient of gravitational or centrifugal field</td>
</tr>
<tr>
<td>$\rho_s$</td>
<td>particle density [kg/m³]</td>
</tr>
<tr>
<td>$\vec{U}_s$</td>
<td>particle velocity [m/s]</td>
</tr>
<tr>
<td>$\vec{U}_f$</td>
<td>fluid velocity [m/s]</td>
</tr>
<tr>
<td>$\rho_f$</td>
<td>fluid density [kg/m³]</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>relaxation time [s]</td>
</tr>
<tr>
<td>$\zeta_{surface}$</td>
<td>surface electric potential, zeta potential [V]</td>
</tr>
<tr>
<td>$\tilde{\zeta}$</td>
<td>dimensionless surface electric potential, zeta potential</td>
</tr>
<tr>
<td>$\tilde{r}$</td>
<td>radial coordinate of the coordinate system</td>
</tr>
<tr>
<td>$z$</td>
<td>axial coordinate of the coordinate system</td>
</tr>
<tr>
<td>$\theta$</td>
<td>azimuthal angle</td>
</tr>
<tr>
<td>$\tilde{e}_z$</td>
<td>unit vector of the cylindrical coordinate system</td>
</tr>
<tr>
<td>$\Delta \tilde{\rho}$</td>
<td>density difference between the particle and the fluid [kg/m³]</td>
</tr>
<tr>
<td>$\vec{U}<em>{Stokes} = \tilde{u}</em>{\text{ref}}$</td>
<td>Stokes velocity [m/s]</td>
</tr>
<tr>
<td>$\tilde{p}$</td>
<td>pressure</td>
</tr>
<tr>
<td>$\dot{\gamma}$</td>
<td>Rate of strain tensor</td>
</tr>
<tr>
<td>$\tilde{e}$</td>
<td>elementary charge [C]</td>
</tr>
<tr>
<td>$\tilde{k}_B$</td>
<td>Boltzmann constant [J/K]</td>
</tr>
<tr>
<td>$\tilde{T}$</td>
<td>temperature [K]</td>
</tr>
<tr>
<td>$z_i$</td>
<td>valence of the ionic species</td>
</tr>
<tr>
<td>$\bar{n}_i$</td>
<td>ionic concentration of the ambient solution [m⁻³]</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>total stress tensor</td>
</tr>
<tr>
<td>$\tilde{E}$</td>
<td>electric field strength [V/m]</td>
</tr>
<tr>
<td>$\tilde{\rho}_E$</td>
<td>free charge density [C/m³]</td>
</tr>
<tr>
<td>$\tilde{L}_D$</td>
<td>Debye length [m⁻¹]</td>
</tr>
<tr>
<td>$\tilde{G}_i$</td>
<td>Elastic modulus [Pa]</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>dimensionless Giesekus mobility factor</td>
</tr>
<tr>
<td>$\tilde{j}_i^{**}$</td>
<td>ionic flux [1/m²s]</td>
</tr>
<tr>
<td>$\tilde{T}$</td>
<td>tensor elastic part [N/m²]</td>
</tr>
<tr>
<td>$\tilde{D}_i$</td>
<td>the particle diffusion coefficient in [m²/s]</td>
</tr>
<tr>
<td>$\mu_{\pm}^{ex}(r)$</td>
<td>excess chemical potential [J]</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>local volume fraction of ions</td>
</tr>
<tr>
<td>$\Phi_B$</td>
<td>steric factor</td>
</tr>
<tr>
<td>$\tilde{F}_e$</td>
<td>electric force [N]</td>
</tr>
<tr>
<td>$\tilde{F}_{st}$</td>
<td>Stokes force [N]</td>
</tr>
<tr>
<td>$H a$</td>
<td>Hartman number</td>
</tr>
<tr>
<td>$Re$</td>
<td>Reynolds number</td>
</tr>
<tr>
<td>$Wi$</td>
<td>Weissenberg number</td>
</tr>
<tr>
<td>$Re_{el}$</td>
<td>Reynolds number in electrophoresis</td>
</tr>
<tr>
<td>$Sc_i$</td>
<td>Schmidt number</td>
</tr>
<tr>
<td>$I$</td>
<td>Unity tensor</td>
</tr>
</tbody>
</table>
\( x \)  
Arbitrary 2\(^{nd}\) order tensor

\( C \)  
Conformation tensor

\( R \)  
antisymmetric matrix

\( V_B \)  
dimensionless volume of the particle

\( \varepsilon_0 \)  
dielectric permittivity in vacuum [Fm\(^{-3}\)]

\( \varepsilon_r \)  
relative permittivity

\( u \)  
Velocity vector

\( T \)  
Extra stress tensor

\( \beta \)  
Ratio of Newtonian solvent to total viscosity

\( \tilde{\eta}_{P,0} \)  
Polymeric zero-shear rate viscosity

\( \tilde{\eta}_s \)  
Newtonian solvent viscosity

\( \tilde{\eta}_t \)  
Total zero shear rate viscosity

\( T^M \)  
Maxwell stress tensor \( Pe \pm \) Peclet number

\( K \)  
Ratio of the Diameter to the Debye length

\( \bar{I}_D \)  
Debye length [m]

\( \psi \)  
electric potential

\( \rho_E \)  
free charge density

\( Q \)  
a symmetric positive definite matrix

\( \bar{g} \)  
Continuous velocity gradient tensor

\( q \)  
Galerkin finite elements weighting function for the pressure

\( w \)  
Galerkin finite elements weighting function for the velocity vector

\( k \)  
Galerkin finite elements weighting function for the electric potential

\( l \)  
Galerkin finite elements weighting function for the number concentration of cations

\( m \)  
Galerkin finite elements weighting function for the number concentration of anions

\( M \)  
Galerkin finite elements weighting function for the natural logarithm of the conformation tensor

\( E \)  
Galerkin finite elements weighting function for the continuous velocity gradient

\( \tau_{p,spg} \)  
parameter of the the Pressure-Stabilized-Petrov-Galerkin stabilizing technique

\( u_e \)  
characteristic element velocity

\( n_{en} \)  
the number of the nodes in the element

\( \eta_{\alpha} \)  
modified dimensionless continuous adaptive viscosity

\( h_e \)  
characteristic element length

\( \tau_{sup,g} \)  
parameter of the Streamline-Upwind-Petrov-Galerkin or SUPG technique

\( \sim \)  
dimensional variables and parameters
5. LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.1</td>
<td>Physical properties of the symmetric electrolyte KCl at 25 °C [1]</td>
<td>21</td>
</tr>
<tr>
<td>10.2</td>
<td>Zeta potential in dimensionless and in dimensional form.</td>
<td>21</td>
</tr>
<tr>
<td>10.3</td>
<td>Typical values of $\mathcal{C}$ and corresponding values of the dimensionless numbers in the Newtonian solution.</td>
<td>21</td>
</tr>
<tr>
<td>10.4</td>
<td>Rheological properties of blood plasma [2].</td>
<td>23</td>
</tr>
<tr>
<td>10.5</td>
<td>Values of $\mathcal{C}$ and the corresponding values of the dimensionless numbers for blood plasma.</td>
<td>23</td>
</tr>
<tr>
<td>10.6</td>
<td>Variation of $K$ and the corresponding values of ionic concentration and Hartmann number.</td>
<td>30</td>
</tr>
</tbody>
</table>
6. LIST OF FIGURES

Figure 8.1: Schematic of the spherical particle sedimenting through a viscoelastic fluid under the effect of body force, \( f \), which in this study is a centrifugal force. Here \( \Omega \) represents the area that the viscoelastic material occupies. \( A_2 \) and \( S_{\text{outer}} \) denote the axis of symmetry and the far-field boundary, respectively. ................................................................. 14

Figure 10.1: Effect of the Reynolds number on the particle velocity for \( K = 2 \) and different values of zeta potential. The range of \( \zeta \) and the other dimensionless numbers is summarized in Table 10.3. ................................................................................................. 22

Figure 10.2: Effect of the g-factor, \( \zeta \), on (a) the Particle Velocity and (b) the Electric Force for different values of \( \zeta \) and \( \Phi B = 0 \). ........................................................................................................ 23

Figure 10.3: Contours of \( Tzz \) for (a) \( \zeta = 11652 \) and (b) \( \zeta = 466080 \), when \( \zeta = 3 \) and \( \Phi B = 0 \). The extent of the EDL is indicated by the white dashed lines. ......................................................... 25

Figure 10.4: Distortion of the dimensionless counter ion concentration profiles for different Weissenberg numbers: (a) \( \zeta = 50845 \) (b) \( \zeta = 183254 \), and (c) \( \zeta = 466080 \) when \( \zeta = 3 \) and \( \Phi B = 0 \)..... 26

Figure 10.5: Effect of the Weissenberg number on the particle velocity for \( \zeta = 10593 \), when \( \zeta = 3, 4, \Phi B = 0 \). ........................................................................................................ 27

Figure 10.6: Effect of the Zeta Potential on the Particle Velocity for (a) \( \zeta = 10593 \) and (b) \( \zeta = 105927 \)................................................................. 27

Figure 10.7: Effect of the Zeta Potential on the Electric Force for \( \zeta = 105927 \). ................................. 28

Figure 10.8: Steric Effect on Ionic Concentration for \( \zeta = 105927 \), when \( \zeta = 3 \), (a) cations, (b) anions. The left-hand side of each panel corresponds to \( \Phi B = 0.2 \), and the right-hand side corresponds to \( \Phi B = 0 \)................................................................. 29

Figure 10.9: Contours of \( Trr \) for \( \zeta = 10593 \) and for two different values of zeta potentials (a) \( \zeta = 2 \) and (b) \( \zeta = 4 \). ........................................................................................................ 29

Figure 10.10: Contours of \( Trz \) for \( \zeta = 10593 \) and for two different values of zeta potential (a) \( \zeta = 2 \) and (b) \( \zeta = 4 \). ........................................................................................................ 29

Figure 10.11: Effect of the Ratio of the Diameter to the Debye Length at \( \zeta = 4 \) for (a) \( \zeta = 10593 \), (b) \( \zeta = 105927 \). ........................................................................................................ 31

Figure 10.12: Effect of the Ratio of the particle Diameter to the Debye Length on (a) the Form Drag (left) and on (b) the Viscoelastic Drag (right) for \( \zeta = 10593 \), with \( \zeta = 4 \). ........................................................................................................ 31

Figure 10.13: Contours of the pressure field for (a) \( K = 0.09 \), (b) \( K = 2 \), (c) \( K = 4 \). The values of the other dimensionless numbers correspond to \( \zeta = 10593 \), with \( \zeta = 4 \). ........................................................................................................ 32

Figure 10.14: Contours of \( Trz \) for (a) \( K = 0.5 \), (b) \( K = 1 \). The values of the other dimensionless numbers correspond to \( \zeta = 10593 \) and \( \zeta = 4 \). ........................................................................................................ 32

Figure 10.15: Contours of \( Trz \) for (a) \( \Phi B = 0 \) (b) \( \Phi B = 0.2 \). The values of the other dimensionless numbers correspond to \( K = 1 \), for \( \zeta = 10593 \) with \( \zeta = 4 \). ........................................................................................................ 33
7. INTRODUCTION

Heterogeneous mixtures, consisting of small particles dispersed in a continuous medium, are encountered in a plethora of applications ranging from the chemical and beauty industry to environmental studies and medicine [5–10], contributing to their importance and increased research interest. Colloidal dispersions differ from homogeneous solutions. In homogeneous systems, the solute loses its identity, but in colloidal suspensions, the particles retain their identity [5], being one order of magnitude larger than the solvent molecules [5]. Typically, they have dimensions between $10^{-9}$ m and $10^{-6}$ m. Their small size, or equivalently their high surface area, prompt outstanding electrical, optical, and magnetic properties [6,7]. Furthermore, their size is similar to biomacromolecules, which renders them the perfect candidates for biomedical applications [8], because they can interact better with cells and biomolecules. Typically, they are charged and spherical.

When a charged particle is suspended in an electrolyte solution, it attracts ions of the opposite charge. The cloud of attracted counterions surrounds it and creates the well-known electrochemical double layer (EDL), which extends up to a specific distance characterized by the Debye Length [9]. As the particle translates through the medium under the influence of gravity or centrifugation, it disrupts the equilibrium shape of the EDL, creating a dipole moment. The sum of all the dipoles generates an electrical field called sedimentation potential [10]. The present work concerns this electrokinetic phenomenon. Its most important consequence is the decrease in the sedimentation velocity of the particle because it generates a force that acts in the direction opposite to gravity [1]. The sedimentation potential is found in several applications, varying from mechanical, mainly centrifuge devices, to medical, in drug delivery.

One of the most important heterogeneous mixtures is blood. Red blood cells, white blood cells, and platelets are dispersed in an aqueous solution called human blood plasma, which is an aqueous solution of organic molecules, proteins, and salts [11]. When the blood flow stops, the cells start sedimenting. For example, red blood cells possess a negative charge; thus, we can correlate their sedimentation to that of a spherical particle bearing the same amount of charge. The human blood plasma, used as a prototype material in this study, is a biofluid with many applications of biological interest [11], one of them being the movement of microparticles, like drug carriers, through it. Until recently, it has been considered a Newtonian fluid, but Varchanis et al. [2] and Brust et al. [12] deduced that human blood plasma exhibits a viscoelastic and mildly shear thinning behavior. They proposed also [2] that fibrinogen is the protein that causes the viscoelastic behavior of human blood plasma stemming from its highly extensible nature [2]. Viscoelastic materials remember their state prior to deformation: stresses generated in viscoelastic materials do not relax immediately but decay over time [13]. The time for the decay is commonly termed the relaxation time of the fluid, and it is denoted as $\lambda$. Also, when a material demonstrates a shear-thinning behavior, its viscosity decreases with the shear rate.

The motion of a particle through a stationary fluid is a classical fluid mechanics problem that has been investigated thoroughly over the past centuries. The problem was investigated initially with Newtonian fluids, but requirements in industrial polymer processing led scientists to examine its viscoelastic counterpart [14–17]. King et al. [14] studied the unsteady motion of a sphere in viscoelastic liquids and compared their results with the Newtonian case. Jones et al. [15] focused on how the terminal velocity is affected by viscoelasticity for two different fluids. Also, the sedimentation of the sphere through a viscoelastic fluid was explored experimentally and theoretically via numerical simulations by Arigo et al. [16] in steady state and by Rajagopalan et al. [17] in transient motion over a wide range of Deborah numbers and for a range of particle/tube radii ratios. They [16,17] were the first to compare directly experiments and simulations both in steady state and time-dependent cases. Later, Haward et al. [18] designed a new experimental approach for the flow of polymer solutions around particles in steady state, which allowed them to measure the forces exerted on the particle as a function of the flow rate.
They showed that a birefringent strand emerged at the trailing stagnation point of the sphere due to material elasticity, which resulted in an increased drag force.

Although theoretical studies heretofore tackled the problem of the sedimentation potential, they were restricted to Newtonian electrolytes. Initially, Booth [19] attempted to describe the sedimentation of a charged spherical particle in a Newtonian fluid. His method had drawbacks because it was applicable only to small zeta potentials, and the net electric current was not zero under all conditions, which is implied by the definition of the sedimentation potential [19]. Following the work of Booth, Saville applied the zero current constraint [20] making his method independent of the ion mobilities, a limitation that Booth’s method had. However, his results were also limited to small zeta potentials because they were obtained by performing a perturbation expansion for small zeta potentials. Later, Ohshima et al. [21] introduced a new perturbation scheme [21], but the results were valid only for slight distortions of the double layer. Other researchers employed the Lattice Boltzmann method. A uniform grid was used, but the application of boundary conditions on curved surfaces displayed difficulties [22,23]. Keller et al. [1] solved numerically the complete problem of the sedimentation of a charged spherical particle. They extended the available results and overcame the limitations of the previous works. They used a body-fitted grid coupled with the finite element method and assumed axial symmetry. For small Reynolds numbers, their results coincided with the ones of Ohshima et al. [21]. For large Reynolds numbers, they showed that the distortion of the double layer was not minor, invalidating the perturbation analysis derived in previous works. Finally, earlier works treated ions as volumeless points leading to the classical Poisson-Boltzmann formulation, which overestimated critical quantities, like the charge density around the particle [24].

In this work, we combine viscoelasticity and the finite size of the ions in a mathematical formulation for the sedimentation of a spherical particle through human blood plasma under the action of a centrifugal field. We conduct numerical simulations altering the dimensionless numbers that govern the problem. We examine the electric effect on the viscoelastic stresses and the sedimentation velocity and elucidate the impact of considering the finite size of ions. Some questions regarding the problem we address here are: What variations do the increase of the centrifugal force induce in the sedimentation velocity and the electrostatic effects? How do the electrostatic interactions alter the viscoelastic response of the material? How does the zeta potential affect the sedimentation velocity and the stresses? Does the variation of the ratio of the diameter to the Debye length impact the flow dynamics, and if so, by how much? Does the assumption of the finite size of ions give better results than the point-like assumption, and if so, in which cases?

This study is organized as follows: In Section 8, the physical formulation, the boundary conditions, and the employed constitutive model are presented. In Section 9, we briefly outline the numerical implementation. Following, Section 10 gives a validation of our implementation based on already published results on the Newtonian case, and the results concerning the viscoelastic case are presented. Finally, conclusions are drawn in Section 11.
8. PROBLEM FORMULATION

8.1 FLOW FIELD

![Figure 8.1: Schematic of the spherical particle sedimenting through a viscoelastic fluid under the effect of body force, \( \tilde{f} \), which in this study is a centrifugal force. Here \( \Omega \) represents the area that the viscoelastic material occupies. \( A_s \) and \( S_{\text{outer}} \) denote the axis of symmetry and the far-field boundary, respectively.](image)

We examine the steady-state sedimentation of a charged, spherical particle of diameter \( \tilde{D} \) and density \( \tilde{\rho}_s \) under the influence of a centrifugal force, \( \tilde{f} \), through human blood plasma with velocity \( \tilde{U}_s \), as shown in Figure 8.1. The external force is given as \( \tilde{f} = C g \), where \( C \) (\( C \geq 0 \)) is a multiplicative factor, or \( g \)-factor, which controls the strength of the centrifugal force, and \( g \) is the gravity vector. Large values of \( C \) (equal to \( 10^6 \)) correspond to modern centrifugal devices [1,25]. Throughout the remainder of the paper, a tilde (\( \tilde{\cdot} \)) denotes a dimensional parameter, while the absence of one denotes the dimensionless counterpart of this parameter. The human blood plasma behaves as an incompressible, electrolytic, viscoelastic solution with constant density, \( \tilde{\rho}_f \), relaxation time, \( \tilde{\lambda} \), and total, zero shear rate viscosity, \( \tilde{\eta}_t \). The particle bears a constant surface potential, \( \tilde{\zeta} \), the so-called zeta potential. In this study we consider that the particle is positively charged. As a result, it attracts ions of the opposite charge (anions), and a diffusive cloud of counter ions, known as the electrochemical double layer (EDL), develops around it. Note that the particle is impenetrable to ions. When it settles inside the solution, the flow field distorts the electrochemical double layer and drifts more counterions towards the trailing pole. This deformation is known as the relaxation effect [5] and is shown schematically in Figure 8.1. Considering the constraint that the total electrical current must be zero, an electric field is created due to the excess counterions downstream. The electric potential is known also as the Dorn effect, named after E. Dorn [26], who discovered the effect of the electric field on the sedimenting particle. It is known also as sedimentation potential.

We adopt a cylindrical coordinate system \( \{\tilde{r}, \tilde{z}, \theta\} \), where \( \tilde{r} \) and \( \tilde{z} \) denote the radial and axial coordinates, respectively and \( \theta \) denotes the azimuthal angle. We assume axial symmetry, so the
solution is independent of the azimuthal coordinate. The \( \hat{z} \)-coordinate is aligned vertically along the gravity vector, \( \hat{g} \), which points to the negative direction, i.e., \( \hat{g} = -\hat{g}e_2 \). The center of the coordinate system is placed at the center of the spherical particle and travels with it. Hence with respect to it, the particle remains stationary, and the surrounding fluid moves upwards with a velocity \( \bar{U}_f = -\bar{U}_s \).

We adopt the non-dimensionalization proposed by Keller et al. [1], where the diameter of the sphere, \( \bar{D} \), is the characteristic length and the Stokes velocity, \( \bar{U}_{\text{Stokes}} = \frac{1}{18} \frac{\bar{D}^2 \varepsilon_0 A \bar{\rho}}{\eta_\varepsilon} \), is chosen as the characteristic one, which corresponds to the velocity of a single, spherical, and uncharged particle of diameter \( \bar{D} \) settling in an unbounded, Newtonian fluid assuming Stokes flow. \( \Delta \bar{\rho} = \bar{\rho}_s - \bar{\rho}_f \) denotes the density difference between the particle and the fluid. Pressure can be normalized using different stress scales; we choose the dominant one as usual. Here, we expect negligible inertial effects; therefore, the characteristic stress is defined as \( \frac{\eta_\varepsilon \bar{U}_{\text{Stokes}}}{\bar{D}} \). Moreover, we make the electric potential dimensionless adopting again the idea by Keller et al.[1], and introducing as characteristic potential the thermal potential, \( \frac{\kappa_B \bar{\rho}^e}{\bar{g}} \). Based on the above considerations, three dimensionless numbers arise:

\[
Re = \frac{\bar{\rho} \bar{U}_{\text{Stokes}} \bar{D}}{\eta_\varepsilon}, \quad Ha = \frac{(\sum_{i=1}^2 \bar{\rho}_i^B) \kappa_B \bar{\rho} \bar{T} \bar{D}}{\eta_\varepsilon \bar{U}_{\text{Stokes}}}, \quad Wi = \frac{\lambda \bar{U}_{\text{Stokes}}}{\bar{D}} \tag{8.1}
\]

The first one is the Reynolds number, which measures the importance of inertial forces relative to viscous forces. The second number is the Hartmann number, which measures the importance of electric forces compared to viscous forces, where \( \kappa_B \) is the Boltzmann constant, \( \bar{T} \) is the absolute temperature, \( \bar{\rho}_i^B \) is the ion concentration of the ambient solution and \( z_i \) is the valence of ionic species. The last number is the Weissenberg number, which is the material relaxation time times the shear rate characterizing the flow.

Using these scalings, the dimensionless momentum and mass conservation equations for an incompressible fluid become:

\[
\nabla \cdot \bar{u} = 0 \tag{8.2}
\]

\[
Re \nabla \cdot \bar{u} = \nabla \cdot \bar{\sigma} - Ha \rho_E \nabla \Psi \tag{8.3}
\]

where \( \bar{u} \) is the velocity vector, \( \bar{\sigma} \) is the Cauchy stress tensor and \( \nabla \) is the usual gradient operator, \( \Psi \) is the electric potential and \( \rho_E \) (\( = z^+ n^+ + z^- n^- \)) is the free charge density. The extra term in the right-hand-side of the momentum equation is the extra contribution to the total stress tensor emerging from the electrostatic interactions between the charged particle and the electrolytic medium.

The stress tensor \( \bar{\sigma} \) is split into an isotropic, a viscous, and an elastic part, as:

\[
\bar{\sigma} = -P \mathbb{I} + \beta \dot{\gamma} + \bar{T} \tag{8.4}
\]

where \( P \) is the pressure, \( \mathbb{I} \) is the identity tensor, \( \beta = \bar{\eta}_s / (\bar{\eta}_s + \bar{\eta}_{p,0}) \) is the ratio of the Newtonian solvent to the total viscosity of the solution at zero-shear rate and \( \dot{\gamma} = \nabla \bar{u} + (\nabla \bar{u})^T \) is the rate of strain tensor. The viscous part relates to the solvent contribution, which is assumed to be an incompressible Newtonian fluid with constant density and constant viscosity, \( \bar{\eta}_s \). The total zero
Shear rate viscosity is decomposed as: $\tilde{\eta}_1 = \tilde{\eta}_s + \tilde{\eta}_{p,0}$, where $\tilde{\eta}_{p,0}$ is the polymeric zero-shear rate viscosity and it is given as $\tilde{\eta}_{p,0} = \sum_{i=1}^{N} \tilde{\gamma}_i \tilde{\lambda}_i$, where $N$ refers to the number of different viscoelastic modes, $\tilde{\gamma}_i$ and $\tilde{\lambda}_i$ are the elastic moduli and the relaxation times, respectively, corresponding to each mode $i$. Varchanis et al. [2] determined that three viscoelastic modes are adequate to capture accurately the viscoelastic response of human blood plasma. However, we choose to use the simplified approach of a single mode, because it gives reasonably accurate results without the additional computational cost that the three-mode approach introduces.

To close mathematically the viscoelastic flow problem, we need a constitutive equation that relates the viscoelastic stress tensor to the rate-of-strain tensor. In this study, we use the Giesekus constitutive equation, according to Varchanis et al. [2]. Its dimensionless form in terms of the polymer conformation tensor is given by [27]:

$$Wi \tilde{C} = -\tilde{C} + \tilde{I} - a \left( \tilde{C} - \tilde{I} \right)^2$$  \hspace{1cm} (8.5)

where $a$ is the dimensionless Giesekus mobility factor. The relation between the extra stress tensor and the conformation tensor is:

$$T = \frac{1-\beta}{Wi} \left( \tilde{C} - \tilde{I} \right)$$  \hspace{1cm} (8.6)

The upper convective derivative, which is found in Eq. (8.5) and acts on any $2^\text{nd}$-order tensor $\tilde{X}$, is defined as:

$$\tilde{v} \tilde{X} = u \cdot \nabla \tilde{X} - (\nabla u)^T \cdot \tilde{X} - \tilde{X} \cdot (\nabla u)$$  \hspace{1cm} (8.7)

The time derivative is omitted in Eq. (8.7) because we assume steady state. In Eq. (8.7), superscript $T$ denotes the transpose.

Here, we briefly review the square-root representation [28] that we follow in the present study to deal with the High Weissenberg Number Problem (HWNP). The main idea is that the conformation tensor can be decomposed in the form:

$$\tilde{C} = Q^T Q,$$  \hspace{1cm} (8.8)

where $Q$ is a symmetric, positive definite matrix. This decomposition is permitted because the conformation tensor is symmetric and positive definite. The square-root conformation tensor methodology is presented also in detail in the work of Balci et al. [28] and Palhares et al. [29]. The employed reformulation is robust for flows with high Weissenberg numbers and allows us to obtain numerically stable solutions. Moreover, it does not require the computations of eigenvectors and eigenvalues, as does the log-conformation reformulation [30,31]. Thus, it has a smaller computational overhead.

The Giesekus constitutive equation is expressed in terms of $Q$ instead of $\tilde{C}$ as:

$$u \cdot \nabla Q = R Q + Q(\nabla u)^T + \frac{q^{-1}(I - c - a(c - I)^2)}{2Wi},$$  \hspace{1cm} (8.9)

where $R$ is an antisymmetric matrix. Since $R$ is an antisymmetric matrix, and we are solving for an axisymmetric case: $R_{12} = -R_{21}$ and $R_{11} = R_{22} = 0$. 

16
In the present work, we do not impose the sedimentation velocity but calculate it as part of the solution. We introduce the constraint that the net force acting on the particle is zero, which reads in dimensionless form as [1]:

\[ 0 = 18V_B \hat{g} + \int_{\partial S} \hat{\sigma} \cdot n \, dS + \frac{Re_{el}}{Re} \int_{\partial S} \hat{T}^M \cdot n \, dS \]  

(8.10)

where \( V_B (\equiv \frac{\pi}{6}) \) is the volume of the particle and \( \frac{\sigma}{\hat{\sigma}} \) and \( \frac{T^M}{\hat{T}^M} \) are the dimensionless hydrodynamic stress tensor and the Maxwell stress tensor, respectively. The Maxwell stress tensor is defined in terms of the electrostatic potential as:

\[ \hat{T}^M = \nabla \psi \times \nabla \psi - \frac{1}{2} \nabla \psi \cdot \nabla \psi \]  

(8.11)

The electrophoresis Reynolds number, \( Re_{el} \), is defined as:

\[ Re_{el} = \frac{(\bar{E}_B T)^2 \varepsilon_0 e r_f}{\varepsilon_0^2 \eta t} \]  

(8.12)

where, \( \varepsilon_0 \) is the dielectric permittivity in vacuum, \( \varepsilon_r \) is the relative permittivity and \( e \) denotes the elementary charge. In terms of boundary conditions, no slip and no-penetration conditions are applied [1,5] along the surface of the particle, which read as \( \mathbf{u} = 0 \). The boundary condition for the far field velocity is \( \mathbf{u} = U_f \hat{e}_z = -U_s \hat{e}_z \) because the fluid moves upward with respect to the particle and parallel to the \( z \)-axis. The typical symmetry conditions are applied in the axis of symmetry, \( A_s \).

8.2 ELECTRIC FIELD

When a charged particle is immersed in an electrolyte solution, it attracts ions of opposite charge, creating a cloud of counterions known as the electrochemical double layer (EDL). According to the Stern model, the EDL is divided into two layers. The first layer, the Stern or immobile layer, is considered immobile and the electrostatic potential decays linearly inside it because it follows the simple capacitor model [5]. The second layer is the diffusive double layer, which starts beyond the Stern layer and is considered the mobile part [5]. This study focuses on the diffusive part, so the Stern layer does not concern us further. As the particle translates under the influence of centrifugation, its movement disrupts the equilibrium shape of the EDL, which results in the sedimentation potential and an electric force opposite to the motion.

We adopt again the non-dimensionalization proposed by Keller et al.[1], where the thermal potential, \( \frac{\bar{E}_B T}{\eta} \), is chosen as the characteristic potential, as we have already discussed. Also, \( \sum_{n=1}^{2} z^2 n^B \) is chosen as the characteristic concentration. Based on the above, two dimensionless numbers arise: \( Pe_{\pm}, K \) given by:

\[ Pe_{\pm} = \frac{\theta_{Stokes} \bar{D}}{\bar{D}_i \pm}, K = \bar{D}/\bar{D}_D \]  

(8.13)

The first one is the Peclet number and describes the ratio of convection to species diffusion, where \( \bar{D}_{i \pm} \) is the ion diffusion coefficient in \( m^2/s \). Also, the Peclet number can be represented as the product \( Re \ Sc_i \), where \( Sc_i \) stands for the Schmidt number and is equal to, \( Sc_i = \frac{\eta_t}{\rho_f \bar{D}_i \pm} \), describing the ratio of momentum diffusivity to mass diffusivity. The second dimensionless
number is the ratio of the particle diameter to the Debye length, which is the characteristic length of the EDL, and is given as
\[ l_0 = \frac{\varepsilon_0 \varepsilon_r k_B T}{2 z_i e^2 a_i^2} \]

For the electrostatic problem, we solve the Poisson equation and the equation of the conservation species, which in dimensionless form are:

\[ -\Delta \Psi - K^2 \rho_e = 0, \quad (8.14) \]

\[ Pe u \cdot \nabla n_+ - \nabla \cdot (\nabla n_+ + z_+ n_+ \nabla \Psi + n_+ \nabla \mu_{CS}^\pm) = 0, \quad (8.15) \]

The Poisson equation relates the electrostatic potential and the free charge density. The first term in Eq. (8.15) represents the flux due to convection. The first term in the parenthesis in Eq. (8.15) accounts for the ion diffusion due to concentration gradients and the second term accounts for migration under the influence of the electric force. To overcome the limitation of the assumption of point-like ions, we introduce steric effects through a local density, mean-field approximation [4,32], so an extra term is added in the parenthesis in Eq. (8.15). The advantage of the mean-field approximation is that it is easy to use. Local-density approximations (LDA) are mean-field approaches that assume that ions interact with electrostatic or steric interactions rather than ion-ion interactions. Giera et al. [4] conduct MD simulations that treat ions as charged spheres and compare their results with the Bikerman and Carnahan-Starling LDA. The Carnahan-Starling LDA (CS-LDA) approximation predicts accurately the excess chemical potential and captures the mean and integrated quantities associated with the EDL, which other models fail to do [4]. So, in the present study, we choose the CS-LDA to account for the finite size of the ions, given by the term of excess chemical potential, \( n_+ \nabla \mu_{CS}^\pm \).

We introduce the CS-LDA model via the following equation that describes the excess chemical potential:

\[ \mu_{CS}^\pm = \frac{\Phi (8 - 9 \phi + 3 \phi^2)}{(1 - \phi)^3} - \frac{\Phi_B (8 - 9 \phi_B + 3 \phi_B^2)}{(1 - \phi_B)^3}, \quad (8.16) \]

where \( \Phi \) is the local volume fraction of ions and is equal to \( \Phi = \frac{\phi_B}{2} (n^+ + n^-) \). It is important to note that far from the spherical particle, \( \Phi \) approaches a constant bulk value, which is given by: \( \Phi_B = \frac{\pi}{3} (\sum_{n=1}^{2} z_i^n n_i^n) A^3 \), where \( A \) is the diameter of the considered equisized ions. From the above equation, it is obvious that CS-LDA is not analytically tractable and is solved numerically.

In order to solve these equations, we impose the appropriate boundary conditions. At the interface between the Stern layer and the diffusive part, the electrostatic potential becomes equal to the zeta potential, \( \zeta = \frac{ze_i}{k_B T} \). As discussed before, we are only concerned about the diffusive part, which leads to the boundary condition, \( \Psi = \zeta \), at the particle surface. Also, the impermeability boundary condition reads: \( \mathbf{n} \cdot \mathbf{j}_i = 0 \), where \( \mathbf{n} \) is the outward unit normal vector to the surface of the particle and \( \mathbf{j}_i \) is the ionic flux vector of ion \( i \), given by:

\[ \mathbf{j}_i = Pe n_ \mathbf{u} - (\nabla n_ + z_+ n_+ \nabla \Psi + n_+ \nabla \mu_{CS}^\pm). \quad (8.17) \]

Also, at large distances from the particle, each ion concentration is equal to \( n_+ = \frac{1}{2} \) due to the fact that we have two different ionic, but symmetric, species, and the sum of their charges in the far field should be equal to one, and the electrostatic potential should be \( \Psi = 0 [1,5] \).
9. NUMERICAL IMPLEMENTATION

The Galerkin finite element method is employed to solve the system of partial differential equations formed by Eq. (8.2), Eq. (8.3), Eq. (8.10), Eq. (8.14) and Eq. (8.15). The stabilized finite element techniques for viscoelastic flow are combined with the square root conformation representation of the constitutive equation. The domain is discretized into triangular elements. We choose not to present an illustration of the mesh because it is very dense, due to the large number of elements, and as a result, the structure would not be obvious.

We approximate all unknowns with linear Lagrangian basis functions. This means that velocities, pressure, the square root of the conformation tensor, continuous velocity gradient components, electric potential and the number concentration of the ions are approximated with 3-node Lagrangian basis functions, as:

\[ u = \sum_{i=1}^{3} u^i w^i \]  
\[ p = \sum_{i=1}^{3} p^i q^i \]  
\[ q = \sum_{i=1}^{3} q^i M^i \]  
\[ G = \sum_{i=1}^{3} G^i E^i \]  
\[ \psi = \sum_{i=1}^{3} \psi^i k^i \]  
\[ n^+ = \sum_{i=1}^{3} n^{+i} l^i \]  
\[ n^- = \sum_{i=1}^{3} n^{-i} m^i \]

where \( q, w, M, E, k, l, m \) are the weighting functions for the pressure, velocity, square root of the conformation tensor and continuous velocity gradient, electric potential, number concentration of cations and anions, respectively. We incorporate the DEVSS-TG numerical scheme and introduce the variable \( G \), which represents the traceless velocity gradient and is computed by:

\[ G = \nabla u - \frac{\nabla u}{\text{tr}(\nabla u)} \]

The last term in Eq. (9.8) is used to ensure that \( G \) remains traceless even in finite precision and offers improved numerical stability in viscoelastic flow simulations.

All spaces are formed by using continuous, over the element domains, first-order polynomials in space. The proposed stabilized Galerkin formulation is:

\[ \int_{\Omega} w \cdot \left[ Re(u \cdot \nabla u) + H a \rho_k \nabla \psi \right] d\Omega + \int_{\partial \Omega} \nabla w : \left[ \sigma + (1 - \beta) \left( \nabla u + (\nabla u)^T - G - \frac{G^T}{C} \right) \right] d\Omega + \int_{\partial \Omega} k(-\nabla \cdot \nabla \psi - \nabla \cdot \nabla \psi) d\Omega + \int_{\partial \Omega} l[Pe_+ u \cdot \nabla n_+ - \nabla \cdot (\nabla n_+ + z_+ n_+ \nabla \psi + n_+ \mu_{CS}^+)]d\Omega + \int_{\partial \Omega} m[Pe_- u \cdot \nabla n_- - \nabla \cdot (\nabla n_- + z_- n_- \nabla \psi + n_- \mu_{CS}^-)]d\Omega \]
\[- \int_{\Gamma} \mathbf{w} \cdot \mathbf{n} \, d\Gamma + \int_{\Omega} q \mathbf{V} \cdot \mathbf{u} \, d\Omega + \int_{\Omega} E : \left( \mathbf{G} - \mathbf{V} \mathbf{u} + \frac{\mathbf{V} \cdot \mathbf{u}}{\mathbf{tr} \left( \mathbf{I} \right)} \frac{\mathbf{I}}{2} \right) \, d\Omega + \int_{\Omega} M : \left[ \mathbf{u} \cdot \mathbf{V} \mathbf{Q} = R \mathbf{Q} + Q(\nabla \mathbf{u})^T + \frac{Q^{-1}[\mathbf{e} - a(\mathbf{e} - \mathbf{b})]}{2wi} \right] \, d\Omega + \sum_{\ell=1}^{\text{ne}} \int_{\Omega_{\ell}} \tau_{\text{supg}} \left[ \mathbf{u} \cdot \mathbf{V} \mathbf{M} : \left( \mathbf{u} \cdot \mathbf{V} \mathbf{Q} = R \mathbf{Q} + Q(\nabla \mathbf{u})^T + \frac{Q^{-1}[\mathbf{e} - a(\mathbf{e} - \mathbf{b})]}{2wi} \right) + \mathbf{u} \cdot \nabla \left( Pe \cdot \mathbf{u} \cdot \nabla \mathbf{u} \right) \right] \, d\Omega + \sum_{\ell=1}^{\text{ne}} \int_{\Omega_{\ell}} \tau_{\text{pspg}} \left[ \mathbf{V} q \cdot \left( Re(\mathbf{u} \cdot \nabla \mathbf{u}) + H a \rho e \mathbf{V} \Psi - \mathbf{V} \sigma \right) \right] \, d\Omega = 0 \] (9.9)

Both velocities and pressure unknowns are approximated with same order polynomials, which leads to severe oscillations in pressure or even no solution at all in case of a creeping flow. This set of basic functions does not satisfy the LBB condition, which concisely states that only specific pairs of polynomial interpolant orders between velocity and pressure are applicable. According to it, same order polynomials are not an acceptable combination [33]. To resolve this, the Pressure-Stabilized-Petrov-Galerkin (abbreviated as PSPG) stabilizing technique is introduced. The generalized \( \tau_{\text{pspg}} \) parameter for non-Newtonian flows according to the work of Varchanis et al.[3], is given by:

\[
\tau_{\text{pspg}} = \left[ \left( Re \frac{u_e}{h_e} \right)^2 + \left( \frac{\beta}{h_e^2} \right)^2 + \left( \frac{\eta_a}{h_e^2} \right)^2 \right]^{-\frac{1}{2}} \quad (9.10)
\]

where \( u_e \) is the characteristic element velocity defined as:

\[
u_e = \frac{n_{en} \parallel \mathbf{u} \parallel}{n_{en}} \quad (9.11)
\]

where \( n_{en} \) denotes the number of the nodes in the element and \( \parallel \mathbf{u} \parallel \) the magnitude of the fluid velocity at each node, \( i \). Also, the characteristic "element length" \( h_e \) is defined to be equal to the square root of the area of the element. The term \( \eta_a \) corresponds to the modified continuous adaptive viscosity and is defined as:

\[
\eta_a = \frac{(1-\beta)+0.5(\beta^{1-\beta})}{\sqrt{1+0.5(\beta+\mathbf{g})^T(\beta+\mathbf{g})}} \quad (9.12)
\]

Additionally, the hyperbolic nature of the constitutive model dictates the use of Streamline-Upwind-Petrov-Galerkin or SUPG technique, to maintain numerical stability. The \( \tau_{\text{supg}} \) term stabilizes the velocity-stress coupling and is given by:

\[
\tau_{\text{supg}} = \frac{h_e}{u_e} \quad (9.13)
\]

Finally, the square-root-conformation representation further stabilizes the scheme, even in the presence of regions of high stresses, e.g., in stagnation points or geometrical singularities. For further information on the stabilizing techniques or the suitable values for their parameters the interested reader is referred to [3,34–36].
10. RESULTS AND DISCUSSION

10.1 NEWTONIAN SOLUTION - MODEL VALIDATION

First, we validate our proposed formulation with the simulation results of Keller et al. [1]. They consider a single charged spherical particle with diameter \( D = 6 \cdot 10^{-7} \text{m} = 0.6 \mu \text{m} \), made of titanium dioxide with density \( \rho_B = 4000 \text{kg} \cdot \text{m}^{-3} \). The electrolyte solution is a symmetric \((\pm z)\) KCl aquatic solution with properties given in Table 10.1 (at room temperature of 298.15 \(K\)). Note that only when we compare our results with the ones of Keller et al. [1], we neglect the inertial effects in the momentum balance just like they do. The examined cases in their work exhibit small Reynolds numbers; thus, this approximation is reasonable. Also, they do not consider the finite size of the ions, following the point-like ions assumption, which corresponds to \( \Phi_B = 0 \).

Table 10.1: Physical properties of the symmetric electrolyte KCl at 25 \(^\circ\)C [1].

<table>
<thead>
<tr>
<th>( \bar{\rho}_f ) (( \text{kg} \cdot \text{m}^{-3} ))</th>
<th>( \bar{\eta}_f ) (( \text{Pa} \cdot \text{s} ))</th>
<th>( \varepsilon_0 ) (( \text{F} \cdot \text{m}^{-3} ))</th>
<th>( \varepsilon_r )</th>
<th>( D_{K^+} ) (( \text{m}^2 \cdot \text{s}^{-1} ))</th>
<th>( D_{\text{Cl}^-} ) (( \text{m}^2 \cdot \text{s}^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>0.000891</td>
<td>8.85 ( \times ) 10(^{-12} )</td>
<td>78.5</td>
<td>1.96 ( \times ) 10(^{-9} )</td>
<td>2.04 ( \times ) 10(^{-9} )</td>
</tr>
</tbody>
</table>

Keller et al. [1] investigate the dependence of the sedimentation velocity on the zeta potential \( \zeta \), the \( g \)-factor \( (\mathcal{C}) \), and the Debye length \( (\bar{L}_D) \). Generally, the zeta potential for nanoparticles and microparticles that are mainly used in biomedical applications varies between \(-20 \text{mV}\) to \(-60 \text{mV}\) [37,38]. Table 10.2 summarizes the dimensionless and corresponding dimensional values of the zeta potential, as chosen by Keller et al. [1]. In our study following Keller et al. [1], the particle is positively charged thus it bears a positive zeta potential. The sign of the zeta potential does not affect the dynamics of the sedimentation of the particle; only its magnitude does. For zeta potential equal to 0, the formulation is reduced to Stokes flow. The value of \( K \) is held constant and equal to 2, which corresponds to an ionic concentration equal to \( 1.03 \times 10^{-6} \text{M} \).

Table 10.2: Zeta potential in dimensionless and dimensional form.

<table>
<thead>
<tr>
<th>( \zeta )</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>4.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \bar{\zeta} ) (( \text{mV} ))</td>
<td>0</td>
<td>25.68</td>
<td>51.37</td>
<td>77.05</td>
<td>102.73</td>
<td>115.58</td>
</tr>
</tbody>
</table>

Regarding \( \mathcal{C} \), the Reynolds number and the Peclet number are proportional to it, but the Hartmann number is inversely proportional to it. Note that the Reynolds number affects only the advection of ions, through \( Pe \), but not the momentum balance because we neglect inertia effects, as stated before. Keller et al. [1] vary \( \mathcal{C} \) from \( 2248 \) to \( 100033 \), as given in Table 10.3, along with the corresponding values for these three dimensionless numbers.

Table 10.3: Typical values of \( \mathcal{C} \) and corresponding values of the dimensionless numbers in the Newtonian solution.

<table>
<thead>
<tr>
<th>( \mathcal{C} )</th>
<th>( Re )</th>
<th>( Ha ) ((K = 2))</th>
<th>( Pe )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2248</td>
<td>0.001</td>
<td>2.309</td>
<td>0.455</td>
</tr>
<tr>
<td>4496</td>
<td>0.002</td>
<td>1.154</td>
<td>0.91</td>
</tr>
<tr>
<td>100033</td>
<td>0.0445</td>
<td>0.052</td>
<td>20.237</td>
</tr>
</tbody>
</table>

Figure 10.1 compares our results and those of Keller et al. [1]; solid lines depict the results of the present formulation, whereas symbols correspond to the results of Keller et al. [1]. Very good agreement is observed. The velocities are smaller than one because we scale all velocities with
the Stokes velocity of an uncharged particle, which is always larger than the corresponding velocity of a charged one. If the particle is charged, then the developed electric force hinders its motion. For larger ζ, (larger Re), the sedimentation velocity approaches the Stokes one, because \( Ha \) obtains smaller values (Table 10.3) and reduces the electric force in the momentum balance. Simultaneously, the Peclet number increases, and the convection of ions is stronger than diffusion, which results also in smaller electric forces. As a result, the motion is not significantly affected by electrostatic effects, and the sedimentation velocity increases. Concerning the zeta potential, its effect is straightforward. When it increases, the electrokinetic phenomena are stronger for the same value of ζ, and the sedimentation velocity decreases.

Figure 10.1: Effect of the Reynolds number on the particle velocity for \( K = 2 \) and different values of zeta potential. The range of ζ and the other dimensionless numbers is summarized in Table 10.3.
10.2 Precipitation in Blood Plasma

10.2.1 Effect of the g-Factor

Next, we present the particle precipitation in viscoelastic solutions, like blood plasma. Initially, we examine the effect of $\mathcal{C}$. Then, to assess the viscoelastic effects alone, we change only $Wi$ for a given $\mathcal{C}$. Subsequently, we vary the value of the zeta potential ($\zeta$) and of the ratio of the diameter to the Debye length ($K$) to evaluate their effect on the terminal velocity and the stresses. Another novel aspect of our study is the introduction of the steric factor $\Phi_B$, arising from the Carnahan-Starling model [4] that accounts for the finite size of ions. We investigate its influence on both the particle velocity and the stresses.

Here as well, we adopt the physical properties for KCl in solution given in Table 10.1, (Keller et al. [1]). The optimal parameters for the single-mode Giesekus model representing blood plasma were determined by Varchanis et al. [2]. They are given in Table 10.4.

Table 10.4 Rheological properties of blood plasma [2].

<table>
<thead>
<tr>
<th>$\mathcal{C}$ (kg m$^{-3}$)</th>
<th>$\tilde{\eta}_l$ (Pa $\cdot$ s)</th>
<th>$\tilde{\eta}_{p,0}$ (Pa $\cdot$ s)</th>
<th>$\tilde{\eta}_s$ (Pa $\cdot$ s)</th>
<th>$\tilde{\lambda}$ (s)</th>
<th>$\alpha$</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1025</td>
<td>0.00195</td>
<td>6.5 $\cdot$ 10$^{-5}$</td>
<td>0.001885</td>
<td>0.00014</td>
<td>0.000075</td>
<td>0.97</td>
</tr>
</tbody>
</table>

We investigate the effect of the g-factor ($\mathcal{C}$) ranging from 10593 to 466080, for different zeta potential values on the sedimentation velocity of a particle translating through human blood plasma. Table 10.5 summarizes the values of the dimensionless numbers for different values of $\mathcal{C}$. Note that, because of the different solution properties, the resulting values of the dimensionless numbers are not the same with those in Table 10.3. The value of $K$ is equal to 2, and the steric factor, $\Phi_B$, is zero.

Table 10.5: Values of $\mathcal{C}$ and the corresponding values of the dimensionless numbers for blood plasma.

<table>
<thead>
<tr>
<th>$\mathcal{C}$</th>
<th>$Re$</th>
<th>$Wi$</th>
<th>$Ha$</th>
<th>$Pe$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10593</td>
<td>0.001</td>
<td>0.528</td>
<td>0.494</td>
<td>0.971</td>
</tr>
<tr>
<td>11652</td>
<td>0.0011</td>
<td>0.58</td>
<td>0.449</td>
<td>1.068</td>
</tr>
<tr>
<td>50845</td>
<td>0.0048</td>
<td>2.56</td>
<td>0.103</td>
<td>4.661</td>
</tr>
<tr>
<td>105927</td>
<td>0.01</td>
<td>5.28</td>
<td>0.049</td>
<td>9.71</td>
</tr>
<tr>
<td>183254</td>
<td>0.0173</td>
<td>9.16</td>
<td>0.029</td>
<td>16.798</td>
</tr>
<tr>
<td>466080</td>
<td>0.044</td>
<td>23.232</td>
<td>0.011</td>
<td>42.724</td>
</tr>
</tbody>
</table>

Figure 10.2: Effect of the g-factor, $\mathcal{C}$, on (a) the Particle Velocity and (b) the Electric Force for different values of $\zeta$ and $\Phi_B = 0$. 

23
SEDIMENTATION OF A SPHERICAL PARTICLE IN AN ELECTROLYTE VISCOELASTIC SOLUTION

Figure 10.2 (a) presents the sedimentation velocity as a function of $C$. Through the same mechanism as in the Newtonian solution, electrostatic forces decrease the sedimentation velocity from its Stokes value. Hence, when the zeta potential increases, the electric force increases for a given value of $C$, leading to a smaller sedimentation velocity, as shown in Figure 10.2(a). Additionally, now elastic forces act synergistically decreasing it further. This is explained as follows: In front of the particle, the material is subjected to biaxial stretching. The polymeric chains oppose this compression, resulting in increased drag. However, this is not the only mechanism for the elasticity-induced drag increase. For large enough $C$, a thin strand of highly extended polymers arises downstream (see discussion related to Figure 10.3), which increases the drag force resulting in even smaller velocities [39]. We attribute this contribution to two reasons. Firstly, if we consider the stretched polymers behind the particle as an elastic strand connected to the stagnation point, then the shear forces that arise between the birefringent strand and the rest of the solution amplify the drag force. Secondly, the material inside the birefringent strand is constantly trying to return to a randomly coiled conformation. So, an entropically-developed elastic force may become significant, pulling the particle against the flow direction.

In other words, in the viscoelastic material, increasing $C$, both the Reynolds and the Weissenberg number increase proportionately to the increase of $C$, by more than an order of magnitude. Nevertheless, $Re$ remains much smaller than 1, indicating that inertia effects remain negligible, while $Wi$ becomes nearly 10, indicating very strong elastic effects. Therefore, viscoelasticity prevails over inertia and dictates the sedimentation velocity of the particle. The present analysis demonstrates that even a miniscule amount of elasticity, like in the case of human blood plasma, affects greatly the particle dynamics, and it cannot be excluded lightheadedly.

Even more impressive is the qualitatively different variation of the precipitation velocity with $C$, between blood plasma (Figure 10.2(a)) and its Newtonian counterpart (Figure 10.1): in a Newtonian solution, increasing $C$ results in a monotonic increase of the velocity, whereas in blood plasma the velocity initially decreases, and after going through a minimum, it seems to approach an asymptote at very large $C$ values. This non-monotonic variation of the velocity for all $\zeta$ results from the strong elastic effects coupled with electrokinetic phenomena. The asymptote is approached above a value of $C \approx 300000$, or $Wi \approx 15$, because the polymeric chains have become nearly fully stretched, and they cannot retard the particle motion further. Note that we have assumed that the polymeric chains can be extended finitely, having used the Giesekus model (Eq. 8.5), with a positive mobility factor, $\alpha > 0$, which controls their extensibility.

The velocity minimum is explained by closer examination of the electrokinetic phenomena. Focusing on the two largest zeta values ($\zeta = 3, 4$), the sedimentation velocity presents a sharper minimum. To elucidate this behavior, we plot the normalized electric force, $F_{el} \left( \equiv \frac{F_e}{(k_BT)^2 \zeta e^2} \right)$ versus the $C$ in Figure 10.2 (b). Note that the positive sign of the force indicates that it acts in the opposite direction of gravity. As $C$ increases, the electric force increases reaching a maximum, and then it decreases. For the larger $\zeta$ values, this behavior is amplified, resulting in stronger non-monotonic variation of the sedimentation velocity (Figure 10.2). The increase of $C$ induces a non-uniform charge density due to the distortion of the EDL. When $C$ surpasses a critical value, the EDL is sheared off to the extent that the gradients of the concentration of the counterions at the back of the particle decrease considerably, and smaller gradients of the electric potential are expected from the Poisson equation. Consequently, the electric force decreases, because it depends on the magnitude of the gradient of the electric field, which leads eventually to an increase of the sedimentation velocity. The same effect of decreased electric force is reflected in the momentum balance through the decrease of the Hartman number.
To understand better the effect of C, we present the contours of the \( T_{zz} \) component of the stress tensor in Figure 10.3 for one smaller and one larger C value, \( C = 11652, 466080 \); Table 10.5. Figure 10.3 (a) shows that, for \( C = 11652 \), the axial normal stress, \( T_{zz} \), has values smaller than one throughout, resembling the stress field of Newtonian fluids. On the contrary, Figure 10.3(b) shows that, for the much larger \( C = 466080 \), a birefringent strand develops downstream. This strand causes large alterations to the flow dynamics, as discussed in the work of Haward et al. [18] and it is responsible for the increased drag, as discussed in relation to Figure 10.2. The polymers are significantly stretched by the local extensional flow, which translates into an increase of \( T_{zz} \) by almost three orders of magnitude. Also, in these figures, we show the extent of the EDL with white dashed lines superimposed on the stress contours. These lines denote the boundary of the EDL throughout the remainder of the paper. The concentration of the anions is higher closer to the surface of the particle, and as we move away, it decreases and reaches a value equal to 0.5 at the far field. The boundary of the EDL is defined as the position where the concentration of the anions falls below 1.1 times its value at the far field. In Figure 10.3 (a), \( \text{Pe} \) is small; thus, there is no great distortion of the EDL. On the other hand, counterions are swept downstream in Figure 10.3(b), because ion convection is strong and the EDL boundary reaches downstream the value of \( Z = 6.5 \) (at the axis of symmetry), which is not shown here due to the scale of the ordinate.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure10.3.png}
\caption{Contours of \( T_{zz} \) for (a) \( C = 11652 \) and (b) \( C = 466080 \), when \( \zeta = 3 \) and \( \Phi_n = 0 \). The extent of the EDL is indicated by the white dashed lines.}
\end{figure}

It is important to examine the distortion of the cloud of the counterions behind the particle caused by convection for representative values of C. When this distortion is stronger, it would induce a larger electric force that would impede the motion. However, as explained previously, this dependence is not monotonic. This distortion is visualized better, if we plot the spatial distribution of the concentration of the counterions (Figure 10.4) around the particle for \( C = 50845, 183254, \text{and} 466080 \), when \( \zeta = 3 \). For the smaller value of \( C \) (Figure. 10.4(a)), a nearly symmetric profile around the particle is observed. Increasing \( C \) by a factor of 3.6 to reach its intermediate value, more counterions drift to the trailing edge of the particle, as seen in Figure 10.4(b). We note that material flows from the bottom to the top of the figure while the particle remains stationary in the coordinate system we used. The mild distortion of the counterion cloud coupled with the substantial value of \( \zeta \) leads to a pronounced electric force (maximum of the electric force (Figure 10.2(b))), which hinders the motion of the particle. The EDL boundary reaches downstream to the value of \( Z = 4 \) (at the axis of symmetry), which again is not shown here due to the scale of the ordinate. For the largest value of \( C \) (Figure. 10.4(c)), the cloud of counterions is swept further away, up to \( Z = 6.5 \), so the electric force becomes weaker.
SEDIMENTATION OF A SPHERICAL PARTICLE IN AN ELECTROLYTE VISCOELASTIC SOLUTION

10.2.2 EFFECT OF THE RELAXATION TIME

The variation of $\mathcal{C}$ affects all dimensionless numbers simultaneously. Since elasticity is one novel aspect of our study, we would like to isolate its effects on particle dynamics. To do so, we select a rather small value of $\mathcal{C}$, 10593, and we vary only the relaxation time of the material, $\tilde{\lambda}$. Note that $Wi$ scales linearly with $\tilde{\lambda}$. We choose two cases for the zeta potential, namely $\zeta = 3, 4$. We pick these values due to the stronger minimum they induce; Figure 10.2. In Figure 10.5, we observe the same variation of the settling velocity as in Figure 10.2(a). As elasticity increases, the drag force increases as well, because of the birefringent strand developed at the trailing of the particle and the biaxial stretching in the front of the particle. So initially the precipitation velocity is reduced, but when elasticity becomes dominant, the velocity increases and seems to approach an asymptote, because the polymeric chains cannot be stretched any further and the electric force has decreased, as already explained. We conclude that the dependence of the settling velocity on $\mathcal{C}$ (Figure 10.2(a)) is mainly governed by the elasticity of the electrolyte solution. We examined higher values of $\mathcal{C}$, but the decrease was not as pronounced as in this case.

Figure 10.4: Distortion of the dimensionless counter ion concentration profiles for different Weissenberg numbers: (a) $\mathcal{C} = 50845$, (b) $\mathcal{C} = 183254$, and (c) $\mathcal{C} = 466080$ when $\zeta = 3$ and $\Phi_B = 0$. 

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26
10.2.3 EFFECT OF THE ZETA POTENTIAL

We continue by assessing the effect on the particle velocity of the zeta potential, which ranges from 0 to 4.5 (Table 10.2). We select a small value of \( \mathcal{C} \) (Figure 10.6(a)), and a larger one (Figure 10.6(b)). We choose these values deliberately. The smaller value presents a symmetric distribution of counterions, and the electric force is not so strong. The larger value corresponds to the maximum effect of the electric force, because the cloud of the counterions is distorted, but not to the extent that electric effects fade away by convection. We introduce the steric effects stemming from the finite size of ions, another novel aspect of our study. We choose three values, \( \Phi_B = 0, 0.1, 0.2 \). The case of \( \Phi_B = 0 \) corresponds to point-like ions. For the smaller \( \mathcal{C} \) (Figure 10.6(a)), we find that the zeta potential affects more the sedimentation velocity (2.56 \% decrease) compared to the case of larger \( \mathcal{C} \) (1.5 \% decrease) (Figure 10.6(b)). For the latter case, the distortion of the electric double layer does not permit a considerable variation of the electric force making the dependence of the sedimentation velocity on the zeta potential milder. Also, for both cases, the finite size of the ions does not induce significant differences. A slight change appears only for larger values of the zeta potential and \( \mathcal{C} \) (Figure 10.6(b)). In Figure 10.7, we plot the electric force versus the zeta potential for \( \mathcal{C} = 105927 \) and for the three different values of \( \Phi_B \). When \( \Phi_B = 0 \), the force increases with a rate that resembles a quadratic dependence on \( \zeta \). Note that \( F_{el} \) will not reach any constant value but will keep increasing, which

Figure 10.5: Effect of the Weissenberg number on the particle velocity for \( \mathcal{C} = 10593 \), when \( \zeta = 3, 4, \Phi_B = 0 \).

Figure 10.6: Effect of the Zeta Potential on the Particle Velocity for (a) \( \mathcal{C} = 10593 \) and (b) \( \mathcal{C} = 105927 \).
is a deficiency of the assumption of point-like ions. For this case, the electric force is scaled with the term $Re_{el}/Re$, as it is written in Eq. 8.10. When we increase $\Phi_B$, the slope is smaller, and the forces will reach a plateau for large enough $\zeta$, a direct consequence of the steric effects. Still, the force variations present minimal effects on the sedimentation velocity. For this case, we have determined that the hydrodynamic force ranges from 8 to 9.4, and is much larger than the electric force.

![Figure 10.7: Effect of the Zeta Potential on the Electric Force for $\mathcal{C} = 105927$.](image)

Let us elucidate further the effect of the steric factor. The finite size of ions sets an upper bound on their concentration around the particle. To visualize it better, we plot the spatial variation of cations (Figure 10.8(a)) and anions (Figure 10.8(b)) around the spherical particle for $\mathcal{C} = 105927$. From these figures we can easily understand that the particle is positively charged, since the concentration of the anions is higher than that of cations close to the particle surface. The different ion distribution between the two values of the steric factor is apparent. The concentration of anions around the particle decreases from 12 ($\Phi_B = 0$) to 2 ($\Phi_B = 0.2$). Also, the anions are greatly packed near the surface of the particle, which creates strong concentration gradients responsible for the strength of the resulting electric force (Figure 10.7). The variation of cations is smaller for either value of the steric factor. Note that both anions and cations drift downstream because of the large value of $\mathcal{C}$, which increases their convective transport. However, the location of the EDL boundary does not change much, and only a slight variation is found upstream of the particle.
Figure 10.8: Steric Effect on Ionic Concentration for $\mathcal{C} = 105927$, when $\zeta = 3$, (a) cations, (b) anions. The left-hand side of each panel corresponds to $\Phi_B = 0.2$, and the right-hand side corresponds to $\Phi_B = 0$.  

Figure 10.9: Contours of $T_{rr}$ for $\mathcal{C} = 10593$ and for two different values of zeta potential (a) $\zeta = 2$ and (b) $\zeta = 4$.  

The velocity gives us insight into the required time for the sedimentation of the particle. However, in many biological systems, the success of a separation process is graded not only by its duration, but also by keeping the integrity of the sedimenting material intact. For example, many biopolymers that can be used as drug carriers are susceptible to degradation of their conformation when significant stresses are exerted upon them [5]. Thus, we examine the spatial variation of the $rr$ component of the stress tensor for $\zeta = 2$ (Figure 10.9(a)) and for $\zeta = 4$ (Figure 10.9 (b)). For both cases, we use $\mathcal{C} = 10593$. We observe that as the zeta potential increases, the $T_{rr}$ decreases slightly. To be more specific, the maximum value of the $T_{rr}$ falls from 0.134 to 0.122, which translates into a 8.96% decrease. Hence, although the sedimentation velocity of the particle decreases when the zeta potential increases, smaller stresses are exerted on its surface. Therefore, the presence of the electric force does not affect the integrity of fragile materials, like biopolymers, by slowing them down. The same behavior is observed for $T_{rz}$ in Figure 10.10 where the maximum value of the $T_{rz}$ component decreases from 0.142 in Figure 10.10(a) to 0.128 (Figure 10.10(b)), translating into a 9.86% decrease.

Figure 10.10: Contours of $T_{rz}$ for $\mathcal{C} = 10593$ and for two different values of zeta potential (a) $\zeta = 2$ and (b) $\zeta = 4$. 

---
10.2.4 EFFECT OF THE DEBYE LENGTH

We continue with examining the effect of the ratio of the particle diameter to the Debye length, $K = \frac{D}{l_D}$. The Debye length is inversely proportional to the bulk ion concentration, thus decreasing the concentration, increases $l_D$ and decreases $K$. In the present study, we vary the bulk ion concentration, which does not only affect $K$, but also the Hartman number, $(Ha = K^2 Re \omega / Re)$. $K$ ranges from 0 to 6, and typical values are summarized in Table 10.6. Two representative cases regarding $C$ are selected: a) $C = 10593$ (Figure 10.11(a)) and b) $C = 105927$ (Figure 10.11(b)). Note that herewith the value of $Ha$ is determined from Table 10.6 and not Table 10.5. Also, we choose three different values of the steric factor, namely $\Phi_B = 0, 0.1, 0.2$. When $K \to 0$, the solution becomes infinitely dilute, leading to a very small $Ha$ number and small electric forces. Thus, the motion of the particles is almost unaffected by the presence of ions, and we obtain the case of an uncharged particle. To rephrase it, for $K = 0$, we obtain the same results as for $\zeta = 0$. Moving away from the limiting point of $K = 0$, the variations of the concentration influence the motion of the spherical particle. The electric force increases with $K$, which impedes the motion. However, for both cases of $C$, the dependence of the sedimentation velocity on $K$ is not monotonic. A velocity minimum is predicted, after which the velocity increases again. When $K$ increases considerably, so does $Ha$. At the same time, the Debye length becomes smaller, and larger gradients of the electric potential develop because the concentration of the counterions increases around the surface of the particle. As a result, the extra stress tensor contribution from electrostatic interactions in the momentum balance, Eq. (8.3), increases greatly and influences the pressure field around the particle. This effect is more pronounced for $\Phi_B = 0$. The altered pressure field creates a force that accelerates the particle even though the electric force grows. We will investigate this argument below.

Table 10.6: Variation of $K$ and the corresponding values of ionic concentration and Hartmann number.

<table>
<thead>
<tr>
<th>$K$</th>
<th>Concentration ($M$)</th>
<th>$Ha$ ($C = 10593$)</th>
<th>$Ha$ ($C = 105927$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.09</td>
<td>$2.08 \cdot 10^{-9}$</td>
<td>0.001</td>
<td>0.0001</td>
</tr>
<tr>
<td>0.5</td>
<td>$6.42 \cdot 10^{-8}$</td>
<td>0.031</td>
<td>0.0031</td>
</tr>
<tr>
<td>1</td>
<td>$2.57 \cdot 10^{-7}$</td>
<td>0.124</td>
<td>0.0124</td>
</tr>
<tr>
<td>2</td>
<td>$1.03 \cdot 10^{-6}$</td>
<td>0.49</td>
<td>0.049</td>
</tr>
<tr>
<td>4</td>
<td>$4.11 \cdot 10^{-6}$</td>
<td>1.98</td>
<td>0.198</td>
</tr>
<tr>
<td>6</td>
<td>$9.25 \cdot 10^{-6}$</td>
<td>4.45</td>
<td>0.445</td>
</tr>
</tbody>
</table>

In the examined cases, not only do we increase $Wi$ but also $Pe$ though $C$, and the velocity minimum is moved towards larger $K$, which is observed in Figures 10.11 (a) & (b). Convection affects mainly broader electric double layers ($K < 1$) than thinner ones ($K > 1$). Thus, for $C = 105927$, where convection is strong, we need thin double layers, which can withstand the distortion from the induced flow field, so that the electric force hinders eventually the motion of the particle.

The finite size of ions also affects the sedimentation velocity here. For $\Phi_B = 0$, the ion concentration is unbounded. Thus, the velocity decrease is steeper compared with the case of $\Phi_B = 0.1$ or 0.2, and it exhibits the smallest minimum. However, this behavior changes for large $K$ and

30
now $\Phi_B = 0$ results in the largest velocity. The upper bound in the ion concentration set by the steric factor does not permit the electric, extra stress tensor contribution to grow unrestricted, and the altered pressure field around the surface of the particle is not so strong to accelerate the particle to the same extent as in the case of $\Phi_B = 0$.

Let us investigate how the pressure is affected by the variation of $K$. The sedimentation velocity of the particle is controlled via a force balance, Eq. (8.10). The second term in Eq. (8.10) can be further decomposed into two parts, the form drag, which depends on the pressure around the particle and the viscoelastic part, which depends on the developed viscoelastic stresses. In Figure 10.12(a), we plot the form drag and the viscoelastic drag for the different values of $\Phi_B$ and $\mathcal{C} = 10593$. In Figure 10.12 (a), the form drag decreases for all values of the steric factor as $K$ increases, but when $\Phi_B = 0$, the decrease is excessive. Also, it attains negative values when $K$ becomes approximately larger than four and now it facilitates particle motion. For $\Phi_B = 0$, the concentration is unbounded around the particle, which is unphysical, leading to negative values of the form drag. On the other hand, when $\Phi_B > 0$, the value of the concentration is restrained, and the form drag does not become negative. Concerning the viscoelastic drag (Figure 10.12 (b)), it decreases with respect to $K$, and the slope is greater again when $\Phi_B = 0$.

In Figure 10.13, we plot the pressure contours for different values of $K$ and $\Phi_B = 0$. Note that for the rest of the dimensionless numbers, we use $\mathcal{C} = 10593$ and $\zeta = 4$. $Ha$ is obtained from Table 10.6. We observe that even for small values of the concentration (Figure 10.13(a)), the pressure is affected slightly by the presence of ions. As we increase the concentration, the
maximum value of the pressure increases further (Figure 10.13(b)), and the pressure distribution is different from the one found earlier (Figure 10.13(a)). Finally, for the largest value of $K$, the pressure attains an even larger value all around the particle (Figure 10.13(c)). As we stated before, the form drag (Figure 10.12(a)) attains a negative value in this last case approximately and onwards, which is a consequence of the modified pressure profile. Regarding the EDL, it is much larger for $K = 0.09$ than the other ones investigated here and extends up to $Z = 17$ (on the axis of symmetry).

![Figure 10.13: Contours of the pressure field for (a) $K = 0.09$, (b) $K = 2$, (c) $K = 4$. The values of the other dimensionless numbers correspond to $\mathcal{C} = 10593$ with $\zeta = 4$.](image)

![Figure 10.14: Contours of $T_{rz}$ for (a) $K = 0.5$, (b) $K = 1$. The values of the other dimensionless numbers correspond to $\mathcal{C} = 10593$ and $\zeta = 4$.](image)

In Figure 10.14, we plot contours of the shear component of the stress tensor, $T_{rz}$, for $K = 0.5, 1$. The values of the rest of the dimensionless numbers are obtained from $\mathcal{C} = 10593$ and $\zeta = 4$. Moreover, $\Phi_B = 0$. As we discussed in Figure 10.11(a), the settling velocity decreases with $K$ for the selected range presented here. So, we expect that $T_{rz}$ should decrease slightly, which is evident from Figure 10.14(a) and Figure 10.14(b). The maximum value of $T_{rz}$ changes from 0.139 to 0.134, which translates into a 3.6% decrease.

As a final item, we examine the influence of the steric factor on the stresses for two values of $\Phi_B$. The cases that we investigate correspond to $\Phi_B = 0$ (Figure 10.15(a)) and $\Phi_B = 0.2$ (Figure 10.15(b)) under the following conditions: $\zeta = 4$, $\mathcal{C} = 10593$ and $K = 1$. We present contours of the shear component of the stress tensor. For $\Phi_B = 0.2$ (Figure 10.15(b)), the value of the $T_{rz}$ is higher than when $\Phi_B = 0$, (Figure 10.15(a)), which is traced back to the finite size of ions. The maximum value of the $T_{rz}$ component increases from 0.134 for $\Phi_B = 0$ to 0.139 for $\Phi_B = 0.2$, which translates in a 3.73% increase. As the steric factor increases, the opposing electric force
becomes smaller, and the settling velocity reaches a higher value. The larger settling velocity results in stronger viscoelastic forces exerted on the particle.

Figure 10.15: Contours of $T_{rz}$ for (a) $\Phi_B = 0$ (b) $\Phi_B = 0.2$. The values of the other dimensionless numbers correspond to $\mathcal{K} = 1$, for $\mathcal{C} = 10593$ with $\zeta = 4$. 
11. CONCLUSIONS

We presented a comprehensive, numerical study for the sedimentation of a spherical, charged particle in the human blood plasma, a viscoelastic electrolyte solution [2], under a centrifugal field. We used the Giesekus constitutive equation to model the viscoelastic stresses of human blood plasma, and we employed the Carnahan-Starling LDA model to account for the finite size of ions. We solved numerically the governing equations. We investigated the effect of the intensity of the centrifugal field in terms of the g-factor, which is the multiplier of gravity, on the sedimentation velocity and the developed stresses on the surface of the particle. Also, we examined the effects of the zeta potential, the ratio of the diameter to the Debye length, and the steric factor.

Furthermore, the answers to the questions posed in the introduction are summarized here. We conclude that:

- Increasing $\zeta$, the sedimentation velocity decreases via the increased viscoelastic response of the material that opposes the motion of the particle. Electrodynamic effects fade away for large values of $\zeta$, and the sedimentation velocity reaches the same limiting value for all the zeta potential values investigated here.
- Increasing the zeta potential leads to smaller sedimentation velocities, because the amplified electric force hinders the motion of the particle. For example, for $\zeta = 10593$, $Wi = 0.528$, the velocity decreases from 0.99 to 0.97 approximately.
- Regarding the ratio of the diameter to the Debye length, $K$, the sedimentation velocity depends non-monotonically on it. When $K \to 0$, the solution is infinitely dilute, and no electrostatic interaction takes place. Increasing its value, the sedimentation velocity decreases until it reaches a minimum and then increases again. This increase stems from the altered pressure field around the particle due to electrostatic interactions, and the particle accelerates.
- In all cases, introducing the Carnahan-Starling LDA model leads to the same effect. The finite size of ions imposes an upper bound for the ion concentration around the surface of the particle. The electric force decreases, and its effect is not so prominent. Thus, the sedimentation velocity increases, and so do the stresses. However, the effect of the steric factor is mainly observed when the electrodynamic effects are dominant. These cases correspond to large zeta potential values and for medium to large values of the ratio of the diameter to the Debye length.

In a forthcoming study, we will examine the sedimentation of more than one charged, spherical particle in human blood plasma and electrolytic solutions like polyelectrolyte gels [40,41]. Furthermore, when microparticles enter in the recirculation of the blood, proteins tend to bind to them, leading to the formation of the protein corona. Thus, we aim to investigate the corona effect and the variation it induces in the flow kinematics of the particle [7,42–45].
12. REFERENCES


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13. APPENDIX

We have already mentioned that to calculate the settling velocity, we use the fact that the net force acting on the spherical particle or an arbitrary volume enclosing the particle is zero when steady state is achieved. The electric force acting on the particle is defined using the Maxwell stress tensor, which is given by:

$$\tilde{T}^M = \tilde{\varepsilon}_0 \varepsilon_r \tilde{E} \tilde{E} - \frac{1}{2} \tilde{\varepsilon}_0 \varepsilon_r \tilde{E} \cdot \tilde{E} I$$  \hspace{1cm} (13.1)

where $\tilde{E}$ is the electric field which is equal to:

$$\tilde{E} = -\nabla \tilde{\psi}$$  \hspace{1cm} (13.2)

The components of the Maxwell stress tensor are:

$$\tilde{T}^M = \tilde{\varepsilon}_0 \varepsilon_r \left[ \begin{array}{ccc} E_1^2 - \frac{1}{2}E_0^2 & \tilde{E}_1 \tilde{E}_2 & \tilde{E}_1 \tilde{E}_3 \\ \tilde{E}_2 \tilde{E}_1 & E_2^2 - \frac{1}{2}E_0^2 & \tilde{E}_2 \tilde{E}_3 \\ \tilde{E}_3 \tilde{E}_1 & \tilde{E}_3 \tilde{E}_2 & \tilde{E}_3^2 - \frac{1}{2}E_0^2 \end{array} \right]$$  \hspace{1cm} (13.3)

Integrating the traction vector which is the inner product of the stress tensor with the unit outward normal vector over the surface of the particle gives the electric force. The electric force is calculated as it follows:

$$\tilde{F}_{el} = \int_S \tilde{T}^M \cdot \mathbf{n} \, d\tilde{S}$$  \hspace{1cm} (13.4)

Where $\mathbf{n}$ is the unit outward normal to the particle surface.

In this work we have considered a cylindrical coordinate system and by assuming axisymmetry we are solving a 2D problem. The Maxwell stress for the two-dimensional system is given in a non-dimensional form by:

$$\tilde{T}^M = \tilde{\varepsilon}_0 \varepsilon_r \left( \frac{k_B T}{\pi \varepsilon_0} \right)^2 \left[ \begin{array}{ccc} \frac{\partial \tilde{\psi}}{\partial \rho} \frac{\partial \tilde{\psi}}{\partial \rho} - 0.5 \left( \left( \frac{\partial \tilde{\psi}}{\partial \rho} \right)^2 + \left( \frac{\partial \tilde{\psi}}{\partial \xi} \right)^2 \right) & 0 & 0 \\ 0 & \frac{\partial \tilde{\psi}}{\partial \rho} \frac{\partial \tilde{\psi}}{\partial \xi} - 0.5 \left( \left( \frac{\partial \tilde{\psi}}{\partial \rho} \right)^2 + \left( \frac{\partial \tilde{\psi}}{\partial \xi} \right)^2 \right) \end{array} \right]$$  \hspace{1cm} (13.5)

Since we are interested in the component of the force acting along the z axis, we obtain the following expression:

$$\tilde{F}_z = \tilde{\varepsilon}_0 \varepsilon_r \left( \frac{k_B T}{\pi \varepsilon_0} \right)^2 \int_S \left[ \varepsilon_r \left( \frac{\partial \tilde{\psi}}{\partial \rho} \frac{\partial \tilde{\psi}}{\partial \rho} + \left( \frac{\partial \tilde{\psi}}{\partial \xi} \right)^2 \right) - 0.5 \left( \left( \frac{\partial \tilde{\psi}}{\partial \rho} \right)^2 + \left( \frac{\partial \tilde{\psi}}{\partial \xi} \right)^2 \right) \right] n_z \, d\tilde{S}$$  \hspace{1cm} (13.6)

where that case $d\tilde{S} = 2\pi \tilde{D}^2 \tilde{r} d\tilde{z}$. So, finally we obtain:

$$\tilde{F}_z = 2\pi \tilde{\varepsilon}_0 \varepsilon_r \left( \frac{k_B T}{\pi \varepsilon_0} \right)^2 \int_S \left[ \varepsilon_r \left( \frac{\partial \tilde{\psi}}{\partial \rho} \frac{\partial \tilde{\psi}}{\partial \rho} + \left( \frac{\partial \tilde{\psi}}{\partial \xi} \right)^2 \right) - 0.5 \left( \left( \frac{\partial \tilde{\psi}}{\partial \rho} \right)^2 + \left( \frac{\partial \tilde{\psi}}{\partial \xi} \right)^2 \right) \right] n_z \tilde{F} d\tilde{z}$$  \hspace{1cm} (13.7)