**Problem Statement:**

Colloidal suspensions are a mixture of substances in which one phase is suspended in a dispersive medium. The colloid or the dispersion medium can be solid, liquid, or gas and the mixture of the two substances can occupy the same phase with the exception of gasses. Many examples of colloidal suspensions are found in the household, in industrial settings, and are studied across many academic disciplines. Products such as whipped cream, a foam created by air suspended in a liquid due to the stability of milk fat, and mayonnaise which is a stable emulsion of oil, egg yolk, and vinegar can be found in many households. Geological materials such as pumice and scoria are considered solid foams, gas suspended in a solid, and are used in industrial settings as building materials for its insulative properties. In the environmental and medical fields aerosols and sols are of notable importance. Aerosols are often described as a solid phase within a gas, such as volcanic ash from an eruption or clouds containing ice particles, but also describe liquids such as fog. Sols describe a solid dispersed phase in a liquid dispersion media. Red blood cells, white blood cells, platelets, and other dissipated compounds are dispersed in a bodily fluid and can be described as a sol. Sols of solid geological material (minerals) and biological matter (bacteria and waste matter) dispersed in liquid water are of particular interest to this study. For this study I define colloid transport and colloidal fluid in reference to sols, although portions of this work could be applied to other dispersed phases and dispersion media.

Much theoretical research has been completed in the field of colloid physical and chemical transport dynamics. Knowledge of colloid transport and collection efficiency is critical to understanding the transport of emerging contaminants and environmental pathogens. Chemical interactions and the associated resulting from these interactions between colloid, fluid, and geological materials is central to colloid transport and immobilization. Increased understanding of the physical and chemical transport properties at a sub-micron scale can be used to improve field scale hydrologic models and hydrologic model planning scenarios. Modeling tools exist that can track particles, such as colloids through the hydrological system. Hydrus1d is an unsaturated zone modeling tool which assumes one dimensional flow and applies the advection-dispersion equation with macroscopic parameters describing these processes. A statistical distribution of particles is generated based upon the advection-dispersion parameters and is returned to the user. MODPATH is a saturated zone particle tracking software to observe particle transport in a three dimensional hydrological system. This tracking tool is limited to advective flow and saturated system. No retardation, diffusion, or dispersion is considered. A small number of pore scale models have been developed to track colloid transport in porous media. These models use Lagrangian mechanics which are computationally inefficient for large numbers of colloids, can only be applied to very small fluid domains, have long modeling run times, and operate as novel approaches to modeling micro scale colloid-surface interactions. The limitations of these systems leave the interdisciplinary researcher without a practical option to gain additional insight into controlling factors driving the physical and chemical dynamics of colloid transport within their system.

Parameters such as diffusivity and dispersivity are not generally well known for most geological systems and can be time consuming and expensive to collect in the laboratory. A few studies have focused on the hydrologic unit scale description the description of these parameters, however these are rare due to limitations presented from cost and extended monitoring. Contaminant transport studies on the basin scale are generally applied to monitoring existing contaminated systems and the associated remediation process. These studies are generally have a course discretization due to a limited number of observation accessible wells, piezometers, and near surface monitoring equipment. Laboratory studies and numerical models are often used to understand the transport, distribution, and immobilization mechanisms in a hydrological system. From these studies prediction models can be generated.

A fundamental understanding of the basic chemical and physical processes of colloid-surface interaction is necessary to accurately develop prediction models of colloid transport where detailed historical data is not present. *Thomas et al. 1993* performed a basin scale study of radionuclide contamination (Ra, 40K, and U) in the Carson River groundwater basin, Nevada. Their results suggest that sediment transport and a dissolution of U coatings on Fe and Mn oxides is a principal mechanism for groundwater contamination in this watershed. The co-transport of viruses through the soil environment has also been documented due to colloid transport [*Syngouna et. al. 2013*]. Breakthough curve concentrations suggested that the presence of clay particles influenced the transport of PHI X174 virus. The MS2 virus in this study showed an affinity for attaching to clay particles. Redman 2004 suggests that many bacteria can be modeled to a limited extent using colloid dynamics due to their physical size and chemical properties. Bacterial fate and transport modeling is limited using current methods, because of their ability to form communities as biofilms and their biological motility. Heavy metals and agricultural nutrients commonly sorb to colloids [*Bradford 2008*]. Heavy metals such as Arsenic, Silver, and Mercury pose an environmental and human health risk if released into surface or groundwater. Colloids provide a vector for cycling of both micro and macro nutrients important for agricultural productivity. Nutrients from Concentrated Agricultural Feeding Operations (CAFO) can be transported in such great concentrations that they pose human health risks. Elevated nitrate concentrations can be the cause of fatal ailments such as blue baby syndrome (methemoglobinemia) in young children.

The purpose of this study is to examine the physical and chemical forces of colloid transport on the micro-scale and determine controlling factors of colloid transport. A significant effort can be made to provide a dynamic and reusable mechanism for rapid generation of macroscopic colloid transport parameters that future researchers can use to apply these insights to column and field scale colloid transport prediction models. Previous modeling attempts [*Redman et. al. 2004, Gao et. al. 2010, and Qiu et. al. 2011*] have not been packaged and released as open source tools to scientific researchers. Use of these tools likely require advanced knowledge of computer science and involve steep learning curses. A need exists for a modular software suite that allows the researcher to leverage computational fluid dynamic models of geological materials and simulate colloid transport at the microscale. Customizable inputs that account for the major chemical and physical forces acting on a colloid in a porous medium should be provided along with multiple entry points of user interaction for both the regular researcher and the super user.

Physical forces describing colloid movement and settling in fluid and porous media are integral to colloid transport. Stokes settling can be applied to spherical particles with mass to describe sedimentation in an undisturbed fluid. Gravitational, buoyancy, and viscous drag forces can be used to determine a specific sedimentation velocity for particles of known density and mass. This relationship does not hold in porous media where fluid is rarely static. Drag forces can be extended to account for fluid and colloid velocity. Non dimensional colloid-surface correction factors presented in *Gao 2010* account for the structure of the porous media in calculating these forces. Fluid velocity vectors must also be accounted for in modeling colloid transport in porous media.

Physical forces alone do not describe colloid-colloid interactions or colloid-surface interactions. Development of colloid-surface interaction theory has been active since Helmholtz identified an interface between ionic solutions and a charged surface in 1853. Surface chemical potentials that define surface charge in colloid-colloid and colloid-surface interactions must be represented in colloid transport models. Significant refinement from Helmholtz initial model of surface interactions have provided a base for our modern model of colloid-surface interaction Electric double layer interaction, Lewis acid-base, and Lifshitz van der Waals forces represent the major contributors to the classical Derjaguin and Landau, Verwey and Overbeek (DLVO) interactions. Representation of these micro-scale forces can provide insight into the dispersivity of colloids in a porous media. The inclusion of random motion defined by a random walk algorithm and Brownian motion described by a random Gaussian distribution has been used to describe Dispersivity, the random diffusion of particles by heat and solute gradient or collision.

**Research Question:**

While many background studies exist that observe colloid transport as the sum of its parts, a basic research question can be explored. Simply, what are the controlling factors of colloid transport in porous media? Which physical and chemical forces dictate a colloid’s affinity to be sorbed and stored within a porous media or to be transported?

**Significance:**

A fundamental understanding of the chemical and physical forces that contribute to colloid-surface interactions at the micro-scale can aid researchers and consultants with developing more accurate field scale models of colloid transport. As noted previously laboratory and field methods can be time consuming. Although transport modeling is not a direct replacement for data collection, high quality physical models can inform experimental design, improve the efficiency of data collection by identifying data gaps, and explaining unexpected results.

Analysis of the magnitudes of each physical and chemical force, and its sensitivity to changing conditions will allow for the development of computationally efficient modeling of micro-scale interactions and the return of macroscale parameters. Rapid model return times, minutes vs. days to weeks as previous colloid transport models, allows researchers to gain simulate many more scenarios and gain a deeper understanding of their system. Releasing the proposed modeling software as a well-documented packaged that follows the Python PEP8 formatting and documentation rules will encourage collaboration and improvement in calculation and computational efficiency.

**Background:**

*Overview:*

Colloid transport in the soil environment may have significant environmental [*Gao et. al. 2009*] and agricultural impacts [*Bradford et.al 2008*]. The presence of dispersed colloids provides a vector for strongly sorbed chemicals, emerging contaminants, and agricultural amendments to be transported through the subsurface [*Qiu et. al. 2011*]. Structure, composition, and connectivity are generally considered primary mechanisms that control fluid flow in soils. In both saturated and unsaturated systems macropore flow from earthworm burrows, roots, cracks, and other heterogeneities can be described as preferential flow paths that bypass matrix flow within the subsurface [*Gerke 2006*]. Preferential flow has been identified as one of the most significant field-scale mechanisms to determine the pollution potential of chemicals [*Kung et. al. 2000*]. Field scale testing has been limited however to the use of conservative and non-conservative tracers, which may not be subject to the same suite of forces as colloids. Understanding the pore scale mechanics of colloidal transport is essential for elucidating the controlling factors of colloidal transport and for making more accurate predictions of colloidal deposition and transport on the field scale.

The attachment of colloids to geological materials and retention in constricting pores and stagnation zones is heavily influenced by the physical and chemical characteristics of the hydrological system and influence the distribution of colloids throughout a system. Changes in physical characteristics (fluid velocity, reduced porosity due to compaction) and chemical characteristics (slight changes in fluid ionic strength from a rainfall event or mixing) can alter the distribution of colloids by altering the balance of chemical and hydrodynamic forces. Most studies have focused on recovering macroscale parameters of colloid transport via laboratory analysis [cite studies] and field scale modeling. Micro-scale analysis of fluid flow domains can provide a means of identifying controlling factors for colloid-surface interactions and illustrate mechanisms of colloid retention that are not obvious in column or field scale studies. Processes such as colloid straining in pore throats or stranding in fluid stagnation zones are not visible at the field scale and play an important role in colloid retention (maybe some numbers?) {Get some refs}.

# talk about computation fluid dynamic options (level set, pore network, etc…).

Pore scale colloid transport modeling may be able to bridge a gap in the understanding and analysis of colloid transport studies. As stated previously, previous colloid modeling systems have not been released as open source tools, and as a result become limited as novel approaches. The development of an open source colloid tracking software allows for greater reproducibility of scientific studies and encourages collaboration among scientists to improve on the existing code base using shared knowledge. Collaboration between scientists becomes extremely important as academic funding becomes more limited.

*Lattice Boltzmann background:*

Lattice Boltzmann computational fluid dynamics is a refinement of the [frish]} lattice gas automata system. Due to the discretization processes and application of simple bounce back rules complex geological structures can be represented. Application of either body force of pressure boundary conditions drives flow within the system. Fluid flow is slightly compressible, and has been shown to return an approximation of the Navier-Stokes equation upon <> expansion <ref>. Lattice Boltzmann CFD models have been successfully used to represent fluid flow in both saturated systems, unsaturated systems, heat transport, and macropore fluid flow <refs>. Colloid transport has been simulated using lattice Boltzmann as a computational base for simulating colloid distribution in porous media <refs>. Two dimensional, nine fluid node lattice Boltzmann fluid CFD was selected for this study. Validation of D2Q9 lattice Boltzmann with dispersed colloid transport is prioritized, and can later be extended to a three dimensional lattice Boltzmann implementation or unsaturated flow <zho he> .

An applied fluid is represented as a fluid distribution of a numerical density representing particles following traditional Boltzmann gas dynamics. Particles can interact and collide with one another, can collide with the solid phase and be reflected, and can stream according to a number of velocities associated with the specific direction and alignment of fluid nodes. D2Q9 lattice Boltzmann fluid velocities and eigenvectors are defined by:

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Node type | Node numbers | Lattice velocity | Eigenvector(s) | weight |
| Type 1 | 1, 2, 3, 4 | 1 |  | 1/9 |
| Type 2 | 5, 6, 7, 8 |  |  | 1/36 |
| Type 3 | 9 | 0 |  | 4/9 |

The eigenvector distribution preserves physical fluid vectors in a Newtonian system. An applied weight is given to each link type for streaming purposes and to preserve a mass balance in the system.

Non-dimensional number density is calculated from the equilibrium distribution function and defines one of three base equations that form the equation of state. Non-dimensional fluid density is simply the summation of the particle distribution function with regard to each fluid node.

Momentum density and non-dimensional fluid velocity may also be calculated similarly with the inclusion of by extending the previous equation to include the representative eigenvectors of the distribution function.

Non-dimensional fluid viscosity is applied to the model through the parametrization of a relaxation time. Adjustments to the relaxation time parameter, effectively alter the shear viscosity and control the progression of the model to equilibrium <refs>.

Non-dimensional time step and node separation are both commonly set to 1 and drop out of the equation <confirm this equation>.

Streaming and collision in the model domain is achieved using the BGK <refs> solution to the lattice Boltzmann equation. These functions are often separated in calculation, but represented as a single equation in the literature

A general form of the equilibrium distribution function closes the single relaxation time lattice Boltzmann CFD equation.

Multiple relaxation time lattice Boltzmann implementations have been presented by <Hilpert, etc..> These methods account for instability in boundary conditions from relaxation times that diverge significantly from 1. Alternative boundary conditions have been developed and can extend the stable range of the relaxation time parameter for fluids <Pan et. al.>.

Dimensionalization of lattice Boltzmann fluid domains has been covered in some detail by <Sukop, Hilpert>. The relationship between non-dimensional lattice Boltzmann and model dimensions can be derived through the non-dimensional Reynolds number:

The non-dimensional Reynolds number is assumed to be constant between lattice units and physical units, therefore we can equate a lattice calculation and physical calculation of Reynolds number and solve for the unknown mean fluid velocity in physical units.

CFD methods that rely on defining their fluid flow domain from binarized porous media thin sections and X-ray computed tomography representations may be limited by image collection and processing methodology <refs>. Segmentation algorithm choice and optimization technique between researchers has been documented as a source enormous uncertainty in the representation of the skeletal system of porous media <sources>. <et.al.> present porosity values ranging from <x> to <x> of the same porous media segmented in different laboratories using accepted techniques. Currently over 100 segmentation techniques exist, each returning slightly different interpretations of greyscale imagery based its unique optimization function. The inclusion of organic material in soil samples presents its own limitations. Dual energy X-ray CT scans and the addition of specific dopants are required to represent organic material in the image collection process. Misrepresentation of organic materials can cause severe overestimations of porosity, connectivity, and permeability. The use of synthetically generated porous media for model development therefore is preferred to reduce uncertainty in physical properties of porous media from image collection and segmentation.

*Colloid Transport background:*

aaa

**Framework:**

*Lattice Boltzmann code development:*

Work on this project will begin by researching and developing a two-dimensional, nine fluid node (D2Q9) version of lattice Boltzmann computational fluid dynamics (CFD). Lattice Boltzmann CFD has been chosen as the project base due to its ability to represent complex geometries, which is common in natural porous media, and its relative ease of programming. < x, x, and x> single relaxation time lattice Boltzmann has been shown to return an approximation of the Naiver-Stokes equation. Pan et. al. show that instability can occur near no flow boundary conditions for relaxation times that diverge from 1. For many problems, however a relaxation time of 1 is sufficient and alternative boundary condition rules could be added in the future without significant changes to the underlying computational scheme, due to the object oriented approach of the modeling code. Nine months of work is set aside to develop a user oriented version of D2Q9 lattice Boltzmann. In this time research and development will consist of three objectives.

*Lattice Boltzmann objective 1:* Research into binarization schemes from greyscale imagery of CT scan data and the conversion of binary images into fluid domains <sentence fragment rewrite>. A general background of the limitations and advantages of binarization schemes is necessary to understand the limitations of lattice Boltzmann CFD modeling with heterogeneous natural porous media. Limitations may exist for computed tomography data collected from porous media high in organic materials which may be of interest colloid transport modeling.

*Lattice Boltzmann objective 2:* Research lattice Boltzmann development literature and develop a computationally efficient version of D2Q9 lattice Boltzmann. Although there are existing implementations of D2Q9 lattice Boltzmann with source code available, development of a custom implementation of lattice Boltzmann is valuable to understand the numerical methods and applicable boundary conditions applied to the modeling code. Development of a custom version will allow the code to be structured in a highly extendable way. Structuring lattice Boltzmann code into a series of object oriented subroutines instead of the traditional functional code structure will allow it to be extended in the future to include more complex boundary conditions.

Dimensionalization from the non-dimensional lattice Boltzmann CFD results will be studied and subroutines added to the source code for data post processing. Dimensionalization will be implemented through the non-dimensional Reynolds number calculation.

*Lattice Boltzmann objective 3:* Create a user focused interface to lattice Boltzmann computational fluid dynamic modeling code. Creation of user focused interface will require research in software packaging and design. Two proposed entry points into the modeling software will be provided to the user. A keyword value style formatted text file will provide the regular user with a method to parameterize and run the lattice Boltzmann modeling software. The object oriented lattice Boltzmann classes will be available, and well documented for the super user to parameterize and run lattice Boltzmann models. A main advantage of the super user entry point is that it will be relatively simple to run multiple models and perform sensitivity analysis to changing parameters such as relaxation time.

*Colloid particle tracking code development:*

Work on this project will begin with research into existing colloid-surface interaction models. A general understanding of the benefits and limitations of other approaches to this problem will aid in the design and implementation of a colloid transport model. Research into other particle tracking software can provide insight into numerical methods for tracking colloids. A computationally efficient particle tracking method is planned. Two years of research and development is necessary to accomplish this goal. This goal is split into six objectives.

*Colloid code objective 1:* Research particle tracking modeling software and colloid-surface interaction models to develop a base approach to colloid transport modeling. A general understanding of the advantages and limitations of Eulerian, Lagrangian, and Newtonian modeling schemes will be necessary to begin developing a colloid transport model. Hybrid modeling approaches will also be considered to balance computational efficiency with precision. Compatibility with lattice Boltzmann computational may limit the number of modeling approaches that are suitable for this project. Development of object oriented computer code to handle model grid boundary conditions imposed by the choice of modeling scheme will be created and tested.

*Colloid code objective 2:* Research into the physical forces affecting colloid transport at the microscale will occur. Compilation of physical relationships of colloids in porous media is planned. It is expected that drag forces in a flowing fluid, buoyancy, gravity, and fluid velocity will be the dominant physical that are included in the colloid transport code. Object oriented code for each physical force will be created to allow for later changes and updates to be performed. An initial colloid transport model run will be attempted with these forces to test boundary condition update routines.

*Colloid code objective 3:* Research into chemical forces influencing colloid-surface interactions at the microscale is planned. DLVO theory will be researched thoroughly to begin developing mathematical relationships for colloid-surface interactions. Israliechev <sp> 1992 and Derjaguin<year> will provide a starting point to explore colloid-surface relationships and identify unknowns that will be provided by the user. Previous colloid transport modeling papers <Qui, Gao, ?> will be consulted and mathematical relationships from these models will be incorporated as necessary. An object oriented approach to developing colloid-surface interaction code will be developed. It is anticipated that chemistry handbooks of surface forces will need to be consulted during development to parameterize model chemistry for testing purposes. A series of initial model runs will be performed to test that boundary conditions along porous media grains are enforced by colloid-surface interaction chemistry.

*Colloid code objective 4:* Colloid-colloid chemical interactions will be studied and integrated into the colloid modeling software. Colloid-colloid chemical interactions differ from colloid-surface interaction based upon the assumed geometries and changing positions of multiple surfaces. An additional tracking colloid tracking scheme will be necessary to account for surfaces changing position. Interactions between many colloids will need to be simplified as feedback mechanisms between colloid chemical interaction fields may be challenging to represent and may not be computationally efficient.

*Colloid code objective 5:* Create a user focused input structure to the colloid particle tracking code. Creation of a user focused interface that interacts with lattice Boltzmann will require research into scientific code packaging and design. Two entry points will be provided to users. A formatted text file that contains block style entry structure similar to other scientific software is proposed for regular user interactions. This block style entry structure will use keyword, value notation for the user to easily adjust boundary conditions, physical parameters, chemical parameters, and output controls. The object oriented nature of the proposed code will allow for the super user to run multiple models with relative ease.

*Colloid code objective 6:* Documentation of all code using PEP8 style guide for python and creating user documentation will be necessary for packaging. Code documentation will include doc-strings for all custom python objects and any included compiled code. These doc-strings will inform the user documentation for both the super user and regular user. A set of user documents will be included with the packaged product. A technical note or academic paper will be drafted detailing the development, assumptions, and perceived limitations of the initial version of the colloid particle tracking software. Any other collected data or insights gained during the development process will be considered for academic publication.

*Lattice Boltzmann Colloids model validation:*

Model validation will be performed using a limited number of laboratory collected breakthrough curves. Multiple synthetic media thin sections will be generated digitally that approximate the physical structure and properties of the laboratory porous media. Simulated results will be compared to laboratory breakthrough curves in non-dimensional time. Many potential challenges are foreseen during the validation period and some may be addressed using optimization schemes or model independent parameter estimation software. Chemical property information may be difficult to find for some colloids or mineral assemblages. Bulk surface properties will have to be relied upon for heterogeneous porous media if spatial distribution of mineralogy is not known. Nine months of work is projected to complete this goal. Validation consists of <x number> of objectives.

*Model validation objective 1:* Obtain quality break through curve data from laboratory experiments for model validation purposes. Collaborative work will be planned with other researchers to obtain relevant chemical and physical properties of the geological media that laboratory studies were performed on and the colloids.

*Model validation objective 2:* A statistically significant number of artificial porous media, which approximate the physical properties of the laboratory media, will be generated. These porous media will be modeled with lattice Boltzmann and fluid velocity of the lattice Boltzmann domain will be compared to the calculated mean fluid velocity of laboratory samples during breakthrough experiments. Synthetic porous media will be regenerated in an iterative process until lattice Boltzmann CFD results are within a pre-defined tolerance of laboratory measurements.

*Model validation objective 3:* Simulations of colloid transport will be performed using the calibrated lattice Boltzmann CFD domains. Results of initial colloid transport simulations will be recorded and reported. An iterative process of altering chemical parameters will be performed as sensitivity analysis and to aid in identifying any gaps or limitations in the modeling software.

*Model validation objective 4:* Colloid transport models will be optimized using either an iterative approach with evaluation or model independent parameter estimation software if appropriate. Optimization will provide a means to identify gaps in the modeling software and assist in evaluating the rigor of the lattice Boltzmann colloid particle tracking system.

*Model validation objective 5:*  The colloid transport model validation process will be documented through the drafting of an academic article prepared for submission to a peer reviewed journal.

**Other Information:**

*Proposed timeline and deliverables:*

**References:**