*Transport of Synthetic Colloids through
Single Saturated Fractures:*

A Literature Review

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TRANSPORT OF SYNTHETIC COLLOIDS THROUGH SINGLE SATURATED FRACTURES: A LITERATURE REVIEW

by

Paul W. Reimus

ABSTRACT

Colloids having the same surface charge sign as the bulk of the geologic media in a groundwater system may be able to travel through the system faster than soluble species because they will follow fluid streamlines more closely and they should have less tendency to diffuse into pores or dead spaces in the media than soluble species. Synthetic colloids with uniform, controlled properties may be ideal for serving as "worst-case" tracers that provide lower-bound estimates of contaminant travel times in hydrologic systems. This report discusses a review of the literature pertaining to colloid transport in single saturated natural fractures.

After a brief background discussion to put the literature review in perspective, the phenomenon of colloid transport in saturated fractures is divided into three major topics, each of which is reviewed in detail: (1) saturated fluid flow through fractures; (2) colloid transport by convection, diffusion, and force fields; and (3) colloid interactions with surfaces. It is suggested that these phenomena be accounted for in colloid transport models by using (1) lubrication theory to describe water flow through fractures, (2) particle tracking methods to describe colloid transport in fractures, and (3) a kinetic boundary layer approximation to describe colloid interactions with fracture walls. These methods offer better computational efficiency and better experimental accessibility to model parameters than rigorously solving the complete governing equations.

1.0. INTRODUCTION

This literature review was conducted for the C-Wells Reactive Tracer Tests Task of the Yucca Mountain Site Characterization Project being conducted at Los Alamos National Laboratory for the U. S. Department of Energy. The C-Wells are a group of boreholes located near the potential high-level nuclear waste repository site at Yucca Mountain, Nevada. The wells provide a good setting for studying flow and transport through saturated, fractured tuff. Such a setting simulates the environment that a radionuclide could encounter if it were to leak from the repository and reach the groundwater table under Yucca Mountain.

The approach in the C-Wells field experiments is to inject various tracers into the saturated zone via an injection well and then observe the appearance of these tracers in sampling wells at downgradient locations (i.e., obtain tracer breakthrough curves). The breakthrough curves observed at C-Wells will be used to validate geochemical/transport models that describe the migration of tracers through the system as well as to identify any behavior that is inconsistent with small-scale laboratory experiments. This information ultimately will be used to help characterize the transport properties of the saturated zone and to improve model predictions of radionuclide transport in this zone. More details about the C-Wells tracer tests can be obtained from the "Study Plan for Testing of the C-Hole Sites with Reactive Tracers."¹ Additional information about how the C-Wells task fits into the Yucca Mountain Site Characterization Project is available in the multivolume Yucca Mountain "Site Characterization Plan."²

The objective of this literature review is to provide background information to evaluate the potential use of synthetic colloids as tracers in the C-Wells field experiments. Colloids having the same electrical surface charge sign as the bulk of the geologic media in a groundwater system could be ideally suited for providing lower bound estimates of contaminant travel times because they will be repelled from the rock surfaces and they should follow fluid streamlines through the fractures more closely than soluble species tracers. Also, because of their larger size and lower diffusivity than soluble species, colloids should be less affected by diffusion into the pores and dead spaces of fracture walls, which can significantly retard soluble species.^{3,4} Thus, there is significant motivation to investigate the use of synthetic colloids as tracers and to understand the mechanisms of colloid transport in saturated, fractured systems.

General background information on colloids, colloid transport, and tracer experiments is provided in Sec. 2 of this report, which includes specific discussions on colloids associated with radionuclide migration and the use of colloids as tracers in laboratory and field experiments. Section 3 contains detailed information on the many diverse scientific topics that are pertinent to colloid transport through single saturated fractures. These topics are divided into three main categories: (1) saturated fluid flow through fractures; (2) colloid transport by convection, diffusion, and force fields; and (3) colloid interactions with surfaces. Particular emphasis is given to colloid-surface interactions, as these are probably the most important and the most uncertain aspects of the problem of colloid transport in fractures. Section 3 also contains two sections that address the application of colloid transport theory to (1) studies of colloid deposition onto idealized collector surfaces and (2) filtration theory. Conclusions are summarized in Sec. 4.

The reader is cautioned that this literature review focuses primarily on the open literature (journal articles and conference proceedings), so studies that have been reported only in small-circulation documents, such as government reports, may not be cited. The review is current through November 1992. The broad scope of the subject matter prevented in-depth examination of the literature on any specific topic. Thus, this report serves primarily as a starting point for obtaining a more detailed understanding of the subject matter through a more focused survey of the literature.

2.0. GENERAL BACKGROUND ON COLLOIDS, COLLOID TRANSPORT, AND TRACER EXPERIMENTS

A "colloid" is a substance in the form of finely divided particles that does not settle out of and cannot be readily filtered from the uniform medium in which it is suspended. Colloidal dispersions in air are called aerosols, and dispersions in aqueous solutions are called hydrosols. Colloid particles fall roughly within the size range of 1 nm to just over 1 μm (characteristic length scale, typically a diameter or radius). In natural systems, particle size distributions are typically normal or lognormal, and particle shapes can vary widely. Within the colloid size range, the behavior of particles is strongly influenced by surface properties (e.g., surface electrical charge density, surface chemical groups). However, colloids are small enough to also be influenced by forces generally associated with molecules (e.g., Van der Waals forces, Brownian motion/diffusion, migration in an electrical field) and large

enough to be influenced by body forces (e.g., gravity, fluid drag). Below 1 nm, the physical and chemical behavior of colloids begins to approach that of large molecular species, and above 5-10 μm , colloids are large enough that body forces begin to dominate their behavior (particulate science rather than colloid science).

For nonaerosol dispersions, the chemical behavior of colloids is generally grouped into two categories: lyophilic and lyophobic, meaning "solvent loving" and "solvent hating," respectively.⁵ Lyophilic colloids form thermodynamically stable "solutions" when introduced to a solvent; that is, only a single phase is formed. A solution of a large polymer molecule (molecular weight of 10^4 to 10^6) is an example of a lyophilic system. In contrast, a lyophobic system consists of two distinct phases and is not thermodynamically stable; that is, the colloids will ultimately flocculate and/or settle, thus separating from the "solvent." However, a lyophobic system may remain stable for a very long time because of kinetic considerations (metastability). A third category of colloids is the "micelle," which occurs in systems that behave lyophilically at low solute concentrations, but a distinct separate phase (micelles) forms as the solute concentration is increased above some critical value. The formation of micelles is generally reversible. In this report, we will be concerned primarily with metastable lyophobic colloids, as the majority of colloids in natural groundwater systems are lyophobic.

In recent years, there has been an increasing body of evidence that colloids can be an important physical/chemical form in which contaminants may be transported through groundwater systems.⁶⁻¹⁸ In such situations, it is important to distinguish between "true colloids," which consist of a polymerized or crystallized chemical form of the contaminant, and "pseudocolloids," which consist of natural colloids that have contaminants adsorbed/attached to their surface.⁶ In both cases, the system is typically lyophobic but metastable. True colloids form when chemical conditions are conducive to polymerization or crystallization of compounds containing the contaminant. Natural colloids are ubiquitous in essentially all natural groundwaters, and they can include both organic and inorganic species. Natural organic colloids include living entities, such as viruses and bacteria (although the latter are generally at the upper end of the colloid size range) as well as large organic molecules such as humic acids and other complex organic acids. Natural inorganic colloids are composed of chemical species present in geologic formations and include clays and other amorphous or crystalline mineral phases. The mechanism of formation of natural inorganic colloids is unclear (weathering/diagenesis, spallation, and precipitation of supersaturated phases are all possibilities), but the fact

that they are present is very evident.^{6,7,17,18} The concentration of natural colloids in groundwaters typically ranges from 10^8 to 10^{17} particles per liter.⁶ Depending on their concentration, natural colloids can provide a great deal of surface area for sorption of molecular contaminants. Assuming that such sorption is irreversible (or nearly irreversible), natural colloids can facilitate contaminant transport by acting as contaminant carriers.⁷

In situations where the average groundwater flow rate exceeds the transport rate of molecular contaminants (because of retardation mechanisms such as sorption to the immobile rock phase or diffusion into pores and/or dead spaces), colloids may significantly enhance the transport rates of contaminants. This enhancement arises because colloids have small diffusion coefficients relative to molecular species, so they tend to stay in fluid streamlines away from rock surfaces and out of pores and dead spaces. Even when they contact rock surfaces, colloids will not be retarded significantly if they possess a surface electrical charge of the same sign as the rock (to be expected for natural inorganic colloids because they are composed of the same material as the rock). Also, their large size can physically preclude colloids from entering pores or dead spaces in the rock. However, colloids are typically much smaller than the openings through which most groundwater flows, so physical straining by the geologic media is not expected to be a significant mechanism of retardation. Thus, if contaminants can form true colloids or are tightly bound to natural colloids, they may be transported through groundwater systems much faster than would be predicted by assuming molecular transport mechanisms.

Figure 1 is a schematic illustration of a lyophobic colloid moving through a saturated natural fracture. Fluid convection and gravitational settling forces acting on the colloid are depicted by vectors pointing in the appropriate directions. Diffusion is depicted by a randomly fluctuating vector. Diffusion will always be superimposed on the deterministic (e.g., convection, gravitation) motion of the colloid. It is important to note that the colloid never actually experiences acceleration relative to fluid flow except over extremely short time scales. This is because the force vectors shown in Fig. 1 are always balanced by hydrodynamic drag forces that the colloid experiences as it moves (discussed in more detail later). Also shown in the figure are pores and channels in the fracture wall, most of which are not large enough to admit colloids.

The insert in Fig. 1 shows schematically the forces acting on a colloid near a wall. In addition to convection, gravitational settling and diffusion, short-range

Fig. 1.
A colloid being transported through a saturated fracture (not to scale).

forces (Van der Waals attraction and electrostatic repulsion) are shown acting on the colloid. As will be discussed later, these and other forces can achieve a balance such that the colloid becomes stationary with respect to movement toward or away from

the wall. Thus, the colloid can become "attached" to the wall, or it can remain at a constant distance from the wall while translating parallel to it.

The properties of colloids that can result in enhanced transport of contaminants suggest that lyophobic colloids may serve well as "worst-case" tracers in groundwater flow systems (by "worst-case," we mean tracers that travel through the system faster than soluble species and possibly even faster than the average groundwater travel time, thus providing a lower bound estimate of contaminant travel times). A tracer experiment involves injecting a species of interest into a certain location in a groundwater system (typically either as a step function or a pulse) and then observing the concentration-vs-time profile of the species at a downstream location (the breakthrough curve). The tracer must be readily distinguishable from natural species in the system, and it should have a low analytical detection limit because downstream concentrations may be highly attenuated in field tests. A hypothetical injection pulse and breakthrough curve are shown in Fig. 2. The shape of the breakthrough curve allows the investigator to deduce information about the transport behavior of the species in the system as well as about the hydrologic characteristics of the system.

Fig. 2.
Hypothetical injection pulse and breakthrough curve for a tracer experiment.

2.1. Evidence of Colloids Associated with Radionuclide Transport

Evidence of colloidal contaminant transport in both laboratory and field studies is reasonably convincing.⁶⁻¹⁸ Although it is not the intent of this literature review to provide an exhaustive list of such studies, a few cases in which colloids have been implicated in radionuclide migration are worth mentioning. Such studies are of particular interest to the Yucca Mountain Project because this project is concerned with the movement of radionuclides from a geologic high-level nuclear waste repository.

Means et al.⁸ associated radioactive cobalt and uranium with high-molecular-weight organic material in groundwater near a disposal trench at the Oak Ridge National Laboratory. Champ et al.⁹ demonstrated rapid groundwater transport of plutonium in core column studies. Killey et al.¹⁰ associated ⁶⁰Co with large-molecular-weight anionic organic ligands in a contaminant plume at the Chalk River Nuclear Laboratory in Canada. In a series of studies, Kim et al.¹¹⁻¹⁵ established that actinides associated with colloids can be transported readily through the Gorleben (Germany) aquifer systems. Saltelli et al.¹⁶ demonstrated colloidal americium movement through saturated glauconitic sand columns. Transition-element (manganese, cobalt) and lanthanide (cerium, europium) radionuclides were associated with inorganic colloids in groundwater at the Nevada Test Site by Buddemeier and Hunt.¹⁷ Penrose et al.¹⁸ have reported that plutonium and americium associated with colloids have migrated up to 2 km in a shallow aquifer at Los Alamos National Laboratory. This distance is several orders of magnitude farther than would be predicted assuming that the plutonium and americium are soluble species. Recently, Rawson et al.¹⁹ have suspected colloidal migration of plutonium and americium from a mixed-waste disposal site through the vadose zone at the Idaho National Engineering Laboratory. Many of these studies are discussed in review articles by Kim⁶ and McCarthy and Zachara.⁷

2.2. Colloids as Tracers: Past Experience and Desirable Properties

The idea of using colloids as tracers in either laboratory or field experiments is not new. Harvey et al.²⁰ used both fluorescent-dyed polystyrene "microspheres" and fluorescently tagged natural bacteria as tracers in a field study of bacterial transport through a sandy aquifer. O'Melia and coworkers^{21,22} and Toran and Palumbo²³ also used polystyrene microspheres in laboratory studies of colloid transport through porous media in packed columns. Bales et al.²⁴ used viruses with negatively charged surfaces to study transport through sandy soil columns, fractured tuff core

samples, and a 30-m-wide wash full of natural sediments. Rosta et al.²⁵ studied the transport of laponite sols (a synthetic clay material) through columns packed with glass beads, quartz, alumina, and glaciofluvial sediments. In a Yucca Mountain Site Characterization Project study, Rundberg et al.²⁶ investigated the transport of three different sized fluorescent-dyed carboxylated polystyrene microspheres through a saturated fracture network taken from near Yucca Mountain, Nevada. In this study, it was found that only one size microsphere (0.91- μm -diam) gave a reasonable breakthrough curve, although only about 25% of these colloids eluted through the network. The other microspheres either had less than 5% elution (0.1- μm -diam) or could barely be detected in the effluent (9.55- μm -diam). For all sizes, the retention of colloids in the fracture network was significant, but the test apparatus was never taken apart to determine the disposition of the retained colloids.

The desirable properties of a colloid that is to be used as a tracer in a laboratory or field experiment are listed below.

- The tracer should be approximately spherical as this greatly simplifies the hydrodynamic motion of the colloid in a laminar flow field, and it simplifies hydrodynamic interactions with surfaces, including both fracture walls and other colloids. A spherical colloid also allows the use of established theory to predict Van der Waals and electrostatic interactions between colloids and surfaces. A significantly nonspherical colloid would introduce complexities that go far beyond the intended scope of most tracer studies.
- The tracer should be relatively monodisperse; that is, the diameters of the particles should have a small standard deviation (5% or less of the mean). This property will allow the transport behavior of all colloids to be treated the same, thus avoiding the complexity of accounting for a population of different sized particles.
- The tracer should be capable of being detected at very low concentrations. The primary reason for this is that the colloid tracers are expected to be highly attenuated in field tests (that is, there may be as much as a factor of 10^5 decrease between the inlet and outlet concentrations of a pulse). For instance, Harvey et al.²⁰ observed typical attenuations of 10^5 when injection and sampling wells were only a few meters apart. A high inlet concentration can partly compensate for large attenuations, but colloid volume fractions should be limited to much less than 1% to avoid significant

colloid-colloid interactions that can affect both dispersion flow properties and colloid transport behavior.²⁷ Thus, very good sensitivity to low concentrations of colloids may be critical to the success of field tests.

- The tracer should be easily distinguishable from natural colloids that may be present in the system.
- The tracer should be stable against flocculation and against significant attachment to rock surfaces. The latter property dictates that the tracer should be negatively charged as rock surfaces tend to be negatively charged at natural pHs. Flocculation is undesirable because it can produce colloid doubles, triples, or larger flocs that have different transport properties than individual colloids. At the very least, flocculation would produce a situation similar to that of not having a monodisperse colloid.
- The tracer should be large enough that it does not diffuse significantly into pores or side channels of the rock, yet small enough that it is not physically strained from the system or affected by gravitational forces. A large size also favors detection of the colloids. These considerations qualitatively limit the range of diameters from about 0.3 to 1.0 μm , although the actual range of acceptability will have to be determined experimentally.
- The tracer should be chemically stable in the suspending solution; that is, it should not dissolve or grow larger by dissolution or precipitation/crystallization mechanisms. If dissolution or growth were to occur, one would be faced with the problem of modeling the transport of a colloid with a time-dependent size.

The criteria listed above suggest that polystyrene microspheres are probably the best initial choice for a colloid tracer in both preliminary laboratory experiments and field experiments. These colloids (1) are naturally spherical (by virtue of the synthesis process), (2) are monodisperse with a standard deviation within 2 or 3% of the mean, (3) can be readily tagged with fluorescent dyes that allow sensitive detection and distinguishability from natural colloids, (4) can be manufactured with an assortment of surface chemical groups that allow control of surface charge, (5) are chemically stable in water, and (6) have a density of 1.05 g/cm³, which minimizes gravity effects when dispersed in water (even for relatively large particles). None of the other candidate tracers, including viruses, bacteria, laponite sols, or silica spheres, possess all of these properties.

A particularly advantageous feature of the fluorescent-dyed polystyrene microspheres is that they offer the potential of extremely low detection limits through the use of flow cytometry.^{28,29} Flow cytometers typically are used in biological applications to count particles such as cells, and they can be equipped readily to detect fluorescing particles. In fact, flow cytometers frequently are calibrated using fluorescent polymer microspheres. In principal, this instrument has the capability to count individual colloids in small samples at very low concentrations.

A variety of fallback analytical techniques can be used to determine microsphere concentrations if flow cytometry fails to meet expectations. These include particle filtration and counting under a microscope,²⁰ counting electronic pulses in a small-aperture flow counter,²¹ measurement of light extinction in a spectrophotometer,²² extraction of the microspheres into an organic phase followed by fluorometry on the organic solution,²⁶ and deducing particle concentrations from light-scattering measurements (i.e., turbidity).³⁰ These techniques are not as attractive as flow cytometry because they are either very tedious or they have little promise of matching flow cytometry's detection limits and selectivity. However, they could be adopted if flow cytometry fails to meet expectations.

The principal disadvantage of polystyrene microspheres is that they are frequently synthesized in processes that use surfactants, which, if not carefully separated from the colloids after synthesis, can drastically affect the surface properties of the colloids. Thus, the transport behavior of the microspheres could vary from batch to batch or sample to sample if surfactants are present. Care should be taken to select manufacturers that use surfactant-free processes and/or meticulously clean the microspheres before packaging and shipping. If necessary, the microspheres can be cleaned by repeatedly washing them with deionized water until the electrical conductivity and surface tension of the supernate does not change. Separation of the wash water from the microspheres can be done by centrifuging, and resuspension of the microspheres may be aided by sonification.³¹

Another potential disadvantage of the polystyrene microspheres is that they inherently have polymer chains extending from their surfaces into solution. The steric effects introduced by these chains may be difficult or impossible to quantify (to be discussed later), and the interaction between these chains and a rock surface are unknown.

Despite these disadvantages, polystyrene microspheres probably represent the best available colloid tracer for laboratory and field experiments. Microspheres with carboxyl surface groups should have a significant negative surface charge in the

pH range of interest, and they are widely available at reasonable prices. Polystyrene with other surface chemical groups or modified carboxylated polystyrene also could be considered. Modified carboxylate microspheres are made by copolymerizing styrene and acrylic acid to yield a surface that is more completely covered with carboxyl groups than normal carboxylated microspheres. The result is that the surfaces are more hydrophilic and more resistant to flocculation than normal carboxylated surfaces.

3.0. COLLOID TRANSPORT THROUGH SATURATED FRACTURES

The transport of colloids through saturated natural fractures is truly an interdisciplinary field of study. To understand the pertinent phenomena, one must become familiar with the following scientific/engineering disciplines: transport phenomena (specifically mass transport and fluid mechanics), chemical kinetics and thermodynamics, particle hydrodynamics, surface chemistry (especially short-range forces), geochemistry, electrochemistry, groundwater hydrology, and statistics. The problem is somewhat simplified by the fact that flow through natural fractures under reasonable pressure gradients is almost always laminar with a Reynolds number considerably less than one (i.e., creeping flow). Also, in most natural systems there are no significant temperature gradients, so the system can generally be assumed to be isothermal.

A flow chart showing one way that the various interdisciplinary scientific topics can be related for the problem of colloid transport through fractures is given in Fig. 3. Most of this section is divided into three main subsections corresponding to the three main headings shown at the top of the flow chart. Each of these general topics must be considered carefully when developing models and interpreting experiments involving colloid transport in fractures. The subtopics shown in Fig. 3 will be discussed in detail in the subsections. Figure 3 offers a convenient device to refer back to as each subtopic is discussed so that a perspective can be maintained on how the subtopics fit into the "big picture."

Before we look at the colloid transport problem in detail, we will discuss some good general references. Colloid properties are discussed at length in the authoritative colloid science texts by Hiemenz⁵ and Hunter.³² Hirtzel and Rajagopalan³³ extend the fundamentals to more advanced topics of colloid science, such as charge-regulated surfaces and filtration theory. Israelachvili³⁴ treats the topic of Van der Waals forces between colloidal particles particularly well. The

Fig. 3.

Flowchart showing interdisciplinary scientific topics as they relate to colloid transport through saturated fractures.

fundamentals of electrical double-layers are discussed in detail by Bockris and Reddy.³⁵ Happel and Brenner³⁶ provide an excellent treatment of low Reynolds number hydrodynamics, which builds on the introductory treatments of this topic provided by most fluid mechanics or transport phenomena texts, such as Bird et al.³⁷ and Landau and Lifshitz.³⁸ The hydrodynamics of colloidal dispersions are discussed by Van de Ven²⁷ and Kim and Karrila;³⁹ the latter is a much more theoretical text. The hydrology of groundwater systems is discussed in an excellent book by DeMarsily.⁴⁰ A good general treatment of the physical chemistry of surfaces is provided by Adamson.⁴¹ Finally, Stumm and Morgan⁴² provide an excellent treatment of geochemistry in groundwater systems. These references are by no means the only ones that can be obtained on the mentioned topics, but the author found them to be the most informative for the problem at hand.

Excellent reviews of the specific problem of colloid deposition from liquid dispersions onto solid surfaces are provided by Spielman,⁴³ Adamczyk et al.,⁴⁴ Adamczyk,⁴⁵ Jia and Williams,⁴⁶ Chap. 6 of Van de Ven,²⁷ Chap. 5 of Hirtzel and Rajagopalan,³³ and Chap. 8 of Probstein.⁴⁷ Van de Ven's book, "Colloidal Hydrodynamics"²⁷ serves as an excellent background text for much of the material presented in this literature review.

3.1. Saturated Flow in Natural Fractures

3.1.1. The Continuity and Navier-Stokes Equations. Because colloids tend to follow fluid streamlines, one must be able to predict or understand the flow field in a fracture before one can predict colloid transport through fractures. As with all flow problems, this involves the solution of the continuity equation in conjunction with the Navier-Stokes equations (momentum equations). In saturated groundwater systems, the flow can be assumed incompressible, isothermal, and at steady-state, so these equations become³⁷

$$\text{Continuity: } \nabla \cdot \mathbf{v} = 0 \quad \text{and} \tag{1}$$

$$\text{Momentum: } \rho \mathbf{v} \cdot \nabla \mathbf{v} = -\nabla p + \mu \nabla^2 \mathbf{v} + \rho \mathbf{g} , \tag{2}$$

where

$$\begin{aligned} \nabla &= \text{del operator (see Ref. 37, Appendix A),} \\ \nabla^2 &= \text{Laplacian operator,}^{37} \end{aligned}$$

- $\mathbf{v}$ = fluid velocity vector (cm/s),
- ρ = fluid density (g/cm³),
- μ = fluid viscosity (g/cm-s),
- p = pressure (g/cm-s² or dyne/cm²), and
- $\mathbf{g}$ = gravity vector (980 cm/s²).

The boundary conditions generally associated with a single fracture are

- $\mathbf{v} = 0$ at fracture walls,
- p = constant at fracture entrance and exit, and
- $\nabla p = 0$ along sides of fracture (no flow).

In porous media, Darcy's equation, or modifications thereof, is frequently used in place of the momentum equation(s) to describe the macroscopic behavior of the flow system. Darcy's equation is⁴⁰

$$\mathbf{v} = -\left(\frac{k\rho\mathbf{g}}{\mu}\right)\nabla H, \quad (3)$$

where

- k = intrinsic permeability (cm²),
- $\mathbf{g}$ = gravitational constant (980 cm/s²),
- $H = (p/\rho\mathbf{g} + h)$ = hydraulic head (cm), and
- h = vertical elevation (cm).

This empirically derived equation makes it relatively easy to predict macroscopic flow fields in homogeneous porous media. For a large fracture network, it often is assumed that the system can be treated as an equivalent porous medium with (frequently) a nonisotropic hydraulic conductivity tensor.⁴⁸

One cannot make such simplifications for a single fracture. However, a typical simplification is to ignore the inertial terms in the Navier-Stokes equations [the second term on the left-hand side of Eq. (2)]. This simplification is justified by noting that the Reynolds number in groundwater systems, which is defined as

$$N_{Re} = \frac{bV\rho}{\mu} , \quad (4)$$

where

b = characteristic length, for example, a fracture width (cm) and

V = characteristic groundwater velocity (cm/s),

is almost always much less than 1, which implies negligible importance of fluid inertia. Even for a relatively high groundwater velocity of 1×10^{-4} cm/s⁴⁹ and a large fracture aperture of 1 cm, the Reynolds number is only 0.01. In the experiments of Rundberg et al.²⁶ in which an artificial pressure gradient was imposed, the Reynolds number was only 0.00144. Thus, one usually is justified in dropping the inertial terms from the Navier-Stokes equations to obtain the "creeping motion" equations.

Even without the inertial terms in the equations, the flow problem is very difficult to solve because of the highly irregular boundaries corresponding to the fracture walls. One approach to solving this complicated, inherently three-dimensional problem, would be to solve the problem numerically using a finite-element discretization, which would allow approximation of the highly irregular boundaries. However, the resulting calculations would be very computationally intensive and may require innovative algorithms to efficiently achieve convergence of the velocity and pressure fields. Based on this literature search, it appears that this approach has never been attempted.

3.1.2. Parallel Plates and the Reynolds Equation. An approximation sometimes used in fracture flow problems is to assume that fractures are parallel-plate channels. In this case, a simple analytical solution for the flow field in a channel exists if laminar flow is assumed:

$$v_x(y) = \frac{4V_{max}}{b^2} (by - y^2) , \quad (5)$$

where

$v_x(y)$ = velocity in x-direction as a function of the coordinate in the direction across the channel width (y) (cm/s),

y = coordinate that varies from 0 to b (across channel),

b = channel width (cm), and

$$V_{\max} = -\left[\frac{dp}{dx} + \rho g \left(\frac{dh}{dx}\right)\right] \left(\frac{b^2}{8\mu}\right) = \text{maximum velocity (at channel centerline)}$$

(cm/s).

When integrated over the cross-section of the channel, Eq. (5) gives an expression for the volumetric flow rate in the channel as a function of pressure drop:

$$Q = -L_z \left(\frac{b^3}{12\mu}\right) \nabla P, \quad (6)$$

where

Q = volumetric flow rate (cm³/s),
 L_z = width of channel in z-direction (cm), and
 $P = p + \rho gh$.

Equation (6) is often called the cubic law, and it has the same functional form as Darcy's equation. For a rough-walled fracture, a representative value of the aperture b can be obtained by measuring the dependence of the volumetric flow rate on the pressure drop across the fracture, substituting this dependence into Eq. (6), and solving the equation for b . The value of b thus obtained is called the "hydraulic aperture."

Although simple and easy to apply, the parallel-plate approximation cannot predict the existence of alternate flow pathways having different velocities through the fracture. The only velocity variations predicted in the fracture will be a result of the parabolic velocity profile across the fracture aperture. If attempting to explain tracer breakthrough curves with such a model, it will undoubtedly be necessary to introduce a "dispersion coefficient" to account for dispersion due to pathways of different velocities.⁵⁰⁻⁵² The product of the dispersion coefficient and the average velocity in the channel then can be used in the tracer continuity equation (discussed later) as a Fickian diffusion coefficient in the axial direction. The dispersion coefficient typically is obtained by fitting the continuity equation to the observed data.

The problem with this approach is that the experimentalist has no way of knowing if the observed shape of the breakthrough curve is in fact entirely a result of dispersion or if other mechanisms (such as tracer-wall interactions or diffusion

into pores) are operative. Thus, the interpretation of the data is not unambiguous, and dispersion coefficients can be verified only by running experiments at other flow rates and/or in similar systems.

A more refined approach to approximating the flow field in a fracture is to assume that the cubic law applies locally in the fracture and that the continuity equation applies over the entire fracture domain (i.e., $\nabla \cdot \mathbf{Q} = 0$). This approach leads to the following equation:

$$\frac{\partial}{\partial x} \left[\frac{L_z b^3(x,z)}{12\mu} \frac{\partial p(x,z)}{\partial x} \right] + \frac{\partial}{\partial z} \left[\frac{L_x b^3(x,z)}{12\mu} \frac{\partial p(x,z)}{\partial z} \right] = 0 \quad , \quad (7)$$

where

$b(x,z)$ = fracture aperture as a function of x and z coordinates (cm) and
 $p(x,z)$ = pressure as a function of x and z (g/cm-s²).

Equation (7) is known as the Reynolds equation because it is a variation of the equation(s) originally derived in the late 1800s by Reynolds to describe lubrication processes. Actually, Reynolds started his derivation directly from the Navier-Stokes equations, but the result he obtained is the same as that obtained by applying the cubic law locally and imposing conservation of mass.⁵³

The Reynolds equation is a two-dimensional, elliptic, partial differential equation for the pressure field in a fracture that can be solved readily by numerical methods. The boundary conditions are constant pressures at the inlet and outlet of the fracture and zero pressure gradient at the sides of the fracture. A numerical solution yields the pressures at the midpoints of the discretized cells. The pressure at the boundary between two cells is obtained by solving for the pressure that results in an equal volumetric flow rate between the two cells (conservation of mass). When the pressures at the cell boundaries are known, the cubic law is applied from the midpoint of each cell to the cell boundaries to obtain the components of the fluid velocity vector in the four directions from the center. The components then can be added together vectorially to obtain the resultant velocity vector for each cell. Local conservation of mass provides a direct check of the accuracy of the solution (i.e., the volumetric flow rates across the cell faces must sum to zero).

The Reynolds equation has been used by many investigators to obtain the flow field in a fracture.^{49,53-58} In some cases, slight variations of the above proce-

dure have been used, but the end result is always essentially the same. Typically, finite-difference methods are used to discretize the system, and the resulting system of algebraic equations is solved using either a direct or iterative matrix solver. Recently, Thompson⁴⁹ reported significant enhancements in solution efficiency using multigrid methods. Typical results are shown in Fig. 4; the vectors indicate flow direction, and the lengths of the vectors are proportional to local volumetric flow rates.⁵³ It is obvious that axial dispersion resulting from flow pathways of different velocities will be accounted for explicitly when using the Reynolds equation model of flow in a fracture.

Fig. 4.
Flow field in a fracture obtained by solving the Reynolds equation. (From Ref. 53.)

3.1.3. Fracture Surfaces and the Fracture Aperture Distribution. To use the Reynolds equation to solve for the flow field in a fracture, the fracture aperture distribution (aperture as a function of position) must be known. For an experimental system, a fracture surface profile can be obtained using modern profiling techniques. A laser profilometer is particularly convenient as it provides three-dimensional profile information in a relatively short time.⁵⁹ Profilometers provide information on only one surface at a time; therefore, to get the aperture distribution, both fracture surfaces must be profiled, and then the profiles must be "matched" carefully so that the apertures can be deduced from the height differences between the profiles. Random errors from the profiling instrument may result in a predicted aperture distribution that is somewhat inaccurate. The absolute apertures in a fracture will be a function of the normal pressure forcing the fracture surfaces together.⁶⁰ For a given pressure, the absolute apertures can be estimated by adjusting all the apertures (obtained from the matching procedure) upward or downward by the same amount until the hydraulic aperture obtained by solving the Reynolds equation matches the experimental hydraulic aperture.

In addition to surface profiling, other techniques have been used by various investigators to obtain an estimate of the aperture distribution in a fracture. Gentier et al.,⁶¹ Billaux and Gentier,⁶² and Cox et al.⁶³ have obtained fracture aperture distributions by making casts of the fracture void space using an RTV silicone rubber. The aperture as a function of position is determined using a light-transmittance imaging technique. The procedure requires an RTV wedge of precise dimensions for calibration of the light transmittance technique. Hakami and Barton⁶⁴ made epoxy replicas of the fracture surfaces and then placed liquid drops of known (very small) volume onto one surface before joining the surfaces. Upon joining, the area occupied by the drop could be observed visually, and the average aperture at that position was calculated by dividing the volume of the drop by the area. The procedure was repeated over the entire spatial domain of the fracture. Pyrak-Nolte et al.⁶⁵ made a cast of the fracture void space using a low-melting-point metal (Woods metal) and then determined the aperture as a function of position using imaging techniques on the cast. However, Billaux and Gentier⁶² point out that this technique can suffer from tearing of the metal cast because of adhesion to the rock surfaces when the fracture is taken apart.

Mathematical techniques often are used to generate representative fracture aperture distributions. Two approaches are commonly used: a fractal method and a geostatistical method. The basis for the fractal approach is discussed by Brown and

Scholz,⁶⁶ Brown et al.,⁶⁰ and Brown.⁶⁷ Given the appropriate fractal dimension(s), a fractal surface can be generated using stochastic techniques,⁶⁸ and then two surfaces can be brought together to form a fracture.^{49,53} The two surfaces must be forced to have identical topography at the larger length scales to obtain a fracture that does not have unrealistic "gaps".⁵³ Geostatistical techniques involve the determination of a fracture aperture distribution (typically lognormal) and a correlation function that effectively correlates the apertures over short length scales but leaves them uncorrelated at large spatial separations.^{55,58,69,70} Wang et al.⁷¹ provide an interesting discussion of the aperture correlation of a fractally generated fracture, thus providing a sort of comparison of the two techniques.

3.1.4. Discussion of the Reynolds Equation. A question that naturally arises when discussing the Reynolds equation is "How much spatial resolution in the plane of the fracture is needed to get a flow field prediction that agrees reasonably well with the actual flow field?" In other words, "How fine does the finite difference grid have to be to provide an accurate solution?" Based on this literature review, these questions have not been addressed formally. However, many investigators are interested in these questions, and some are doing work to address them.⁷²

Although the Reynolds equation provides a significant and perhaps necessary simplification of the full Navier-Stokes equations, it will not provide certain information about the flow field in a fracture that may be important for colloid transport. For example, the Reynolds equation assumes parallel-plate flow locally, and thus, it cannot predict velocity components that are perpendicular to fracture surfaces. Such velocity components will exist in a real fracture when the fluid flows around bends and through narrow constrictions. These components could influence the flux of colloids toward or away from a surface, which would affect the predicted rate of collisions between colloids and fracture surfaces. As it is, the only mechanism for colloids to come into contact with surfaces when using a Reynolds equation flow field is by diffusion. Because the Reynolds equation will be used to predict flow fields in this study, it will be assumed implicitly that colloid-wall collisions resulting from convection are negligible. Some preliminary calculations by the author have indicated that this assumption is probably valid if flow rates are low, but this problem may have to be revisited if experimental evidence indicates excessive colloid deposition at bends and narrow constrictions in fractures.

3.2. Colloid Transport by Convection, Diffusion, and Force Fields

It is useful to begin a discussion of colloid transport by considering the motion of an individual spherical colloid in response to forces acting on it. Newton's second law dictates that

$$F = ma = m \left(\frac{du}{dt} \right), \quad (8)$$

where

- F = force acting on colloid (g-cm/s²),
- m = colloid mass (g),
- a = acceleration (cm/s²),
- u = colloid velocity (cm/s), and
- t = time (s).

The net hydrodynamic drag force acting on a spherical particle in a uniform flow field is given by

$$F = f(v - u), \quad (9)$$

where

- f = friction coefficient (g/s) and
- v = fluid velocity (cm/s).

For a spherical particle far away from surfaces, the friction coefficient is given by Stokes Law:^{27,36}

$$f = 6\pi\mu R, \quad (10)$$

where

- μ = fluid viscosity (g/cm-s) and
- R = particle radius (cm).

Setting Eqs. (8) and (9) equal to each other and integrating (in one dimension only), we get

$$u = (u_0 - v) \exp\left(\frac{-ft}{m}\right) + v, \quad (11)$$

where u_0 = initial velocity (cm/s). The ratio m/f in Eq. (11) is the characteristic relaxation time for the particle to attain a steady-state velocity given that a constant force acts on it at time zero. For a 1- μ m-diam spherical particle with a density of 1 g/cm³ in water at 25°C, this relaxation time is approximately 6×10^{-8} s. If one considers the velocity resulting from thermal (Brownian) motion, given by^{37,73}

$$u_t = \sqrt{\frac{8kT}{\pi m}}, \quad (12)$$

where

u_t = velocity due to thermal motion (cm/s),

k = Boltzmann's constant (1.38×10^{-16} ergs/K), and

T = temperature (K).

then the distance over which such a particle will move in Brownian motion before attaining a steady velocity will be about $u_t m/f = 3 \times 10^{-8}$ cm, or 0.3 nm.⁷³ Thus, for a particle to experience accelerations over time or length scales comparable to diffusional accelerations, an external force would have to change significantly over a time scale of 6×10^{-8} s or over a length scale of 0.3 nm. If forces do not change significantly over these scales, particle inertia can be assumed to be negligible. For colloidal particles in water, deterministic forces generally change over scales much larger than this. Thus, particle inertia usually can be ignored. (However, there may be exceptions in the vicinity of a surface, where forces can change rapidly over small length scales—this will be discussed later.) An alternative, though less general, approach to determine the importance of particle inertia is to calculate the particle Reynolds number:²⁷

$$N_{Re} = \frac{\rho u r}{\mu}, \quad (13)$$

where

d = particle diameter (cm) and

ρ = particle density (g/cm³).

If $N_{Re} \ll 1$, particle inertia can be ignored. In the example above, $N_{Re} = 4.5 \times 10^{-3}$.

This analysis of relaxation times is important because if particle inertia is not negligible, the only way one can describe a system of particles accurately is to calculate both the particle concentration and velocity distributions in time using the general Fokker-Planck equation.⁷⁴ The Fokker-Planck equation may be required in aerosol systems, as the pertinent time and length scales are much larger than in liquids because of the smaller viscosity of the medium. The Fokker-Planck equation also may be required in very concentrated particle suspensions, as the time and length scales of interparticle interactions can become comparable to the time and length scales for diffusion.⁷⁵ The Fokker-Planck equation should not be needed to describe colloid transport in aqueous solutions provided that their concentration is low enough that particle interactions can be ignored (less than 1% volume fraction).

3.2.1. Particle Trajectories. Given that particle inertia is negligible in liquids and assuming for the moment that diffusion is negligible compared with deterministic motion, a general force balance on an arbitrarily-shaped particle can be written as^{27,36,76-79}

$$\mathbf{F} = \mathbf{f} \cdot \mathbf{u} + \mathbf{c} \cdot \boldsymbol{\omega} \quad (14a)$$

and

$$\mathbf{T} = \mathbf{c}^T \cdot \mathbf{u} + \mathbf{f}_r \cdot \boldsymbol{\omega} , \quad (14b)$$

where

- $\mathbf{F}$ = force vector acting on particle,
- $\mathbf{T}$ = torque vector acting on particle,
- $\mathbf{u}$ = translational velocity vector,
- $\boldsymbol{\omega}$ = rotational velocity vector,
- $\mathbf{f}$ = translational resistance tensor,

f_r = rotational resistance tensor,
 c = coupling tensor (coupling between translation and rotation), and
 c^T = transpose of coupling tensor.

The forces on the left-hand sides of Eqs. (14) cause movement of the particle, whereas those on the right-hand sides resist movement of the particle. The coupling tensor accounts for the fact that, with an arbitrarily shaped particle, translational motion will induce rotation and vice-versa. For a spherical particle far away from surfaces, all terms of the coupling tensor are zero, and the translational resistance tensor is diagonal with the diagonal terms equal to $6\pi\mu R$ (Stokes resistance).^{27,36}

Solving Eqs. (14) for u gives

$$u = \frac{dr}{dt} = M \cdot F - M' \cdot T, \quad (15)$$

where

r = position vector,
 $M = (f - c \cdot f_r^{-1} \cdot c^T)^{-1}$ = translational mobility tensor, and
 $M' = M \cdot c \cdot f_r^{-1}$ = rotational mobility tensor.

For an arbitrarily shaped particle, a diffusion tensor is defined as^{27,36}

$$D = kTM. \quad (16)$$

For a spherical particle far away from surfaces $M = \text{diag}[1/6\pi\mu R]$ and Eq. (16) reduces to the familiar Stokes-Einstein equation:

$$D = \frac{kT}{6\pi\mu R}, \quad (17)$$

where D = diffusion coefficient (cm^2/s). From this equation, the diffusion coefficient can be seen to be inversely proportional to the radius of the colloid. Given that the radii of molecular species are typically on the order of 10^{-8} to 10^{-7} cm, it is appar-

ent that the diffusion coefficients of colloids are generally 2 to 4 orders of magnitude smaller than those for molecular species (at a given temperature in a given fluid). Thus, colloids are very slowly diffusing species compared with molecules.

Assuming that diffusion is negligible, if the forces and torques on a particle as a function of time and position are known, then the set of coupled ordinary differential equations corresponding to Eq. (15) can be solved to obtain the particle position as a function of time given some initial position. This approach, called the "particle trajectory" approach, has been used by many investigators to determine particle trajectories in the vicinity of collector surfaces.⁸⁰⁻⁸⁸ The approach has been used frequently in filtration studies to determine the trajectories that lead to particle deposition on collector surfaces. An overview of the method is provided by Van de Ven.²⁷

Some of the deterministic velocity expressions for spherical particles being acted upon by various forces are of interest. For a spherical particle far away from surfaces ($\mathbf{M} = \text{diag}[1/6\pi\mu R]$, $\mathbf{M}' = 0$), Eq. (15) reduces to

$$\mathbf{u} = \mathbf{M} \cdot \mathbf{F} = \frac{\mathbf{F}}{6\pi\mu R} . \quad (18)$$

When the force acting on the particle is gravity,

$$\mathbf{F} = (m_p - m_f)\mathbf{g} = \left(\frac{4}{3}\right)\pi R^3(\rho_p - \rho_f)\mathbf{g} , \quad (19)$$

where

- m_p = mass of particle (g),
- m_f = mass of fluid displaced by particle (g),
- ρ_p = density of particle (g/cm³),
- ρ_f = density of fluid (g/cm³), and
- $\mathbf{g}$ = acceleration because of gravity (cm/s²).

The particle velocity obtained by substituting Eq. (19) into Eq. (18) is (assuming a stagnant fluid)

$$\mathbf{u} = \left(\frac{2}{9\mu} \right) R^2 (\rho_p - \rho_f) \mathbf{g} . \quad (20)$$

Thus, the velocity as a result of gravity is proportional to the density difference between the particle and the fluid and to the particle radius squared.

In general, a force is given by the negative gradient of the potential, $-\nabla\phi$. Thus, in a potential field, the particle velocity will be given by (again, assuming a stagnant fluid)

$$\mathbf{u} = - \left(\frac{1}{6\pi\mu R} \right) \nabla\phi . \quad (21)$$

Using Eq. (17), Eq. (21) is equivalent to

$$\mathbf{u} = - \left(\frac{D}{kT} \right) \nabla\phi . \quad (22)$$

In the case of a charged particle in an electric field, Eq. (22) becomes

$$\mathbf{u} = - \left(\frac{zeD}{kT} \right) \nabla\phi_{\text{elec}} , \quad (23)$$

where z = number of electronic charges on particle (+ or -) and e = electronic charge. If the only force acting on the particle is fluid drag, given by $\mathbf{F} = f\mathbf{v}$ (where $\mathbf{v}$ = fluid velocity in cm/s), then we get the interesting result that

$$\mathbf{u} = \mathbf{v} . \quad (24)$$

This result also is obtained from Eq. (11) when $t \gg m/f$. Equation (24) is the mathematical statement that, in the absence of other forces, colloids will tend to follow fluid streamlines.

Equations (15) and/or (18) are strictly valid only if diffusion is negligible relative to other forces acting on the particle. To account for diffusion, one must modify the particle trajectory method to allow for a random diffusion force. Formally, this requires the solution of a stochastic differential equation called a Langevin equation,^{27,74} which for a spherical particle far away from surfaces is given by

$$ma = -fu + F_{det} + B(t) , \quad (25)$$

where F_{det} = deterministic force vector and $B(t)$ = random diffusion force. If particle inertia is negligible ($ma = 0$), Eq. (25) becomes

$$u = \frac{(F_{det} + B(t))}{f} \quad (26a)$$

or

$$u = u_{det} + \frac{B(t)}{f} . \quad (26b)$$

Upon integrating Eq. (26) with respect to time, it can be shown that²⁷

$$x(t + \Delta t) = x(t) + u_{det} \Delta t + Rn[0, 2D\Delta t] \quad (27)$$

where $x(t)$ = particle position vector at time t and $Rn[0, 2D\Delta t]$ represents a randomly directed vector with a normally distributed length having a mean of zero and a variance of $2D\Delta t$.

Assuming that the deterministic fluid velocity field and any other potential energy fields are known, Eq. (27) can, in principle, be used to generate stochastic particle trajectories that include the effects of diffusion. This has been done by Van de Ven⁸⁹ and Foister and Van de Ven⁹⁰ in laminar flow fields. When using this approach, one has to be careful to take small enough time steps that u_{det} does not change significantly between the particle positions at the start and end of each time step. Alternatively, if the drag force from fluid convection is the only important deterministic force (given by fv) and wall effects are ignored, Eq. (26) can be solved directly using techniques for stochastic differential equations.^{27,90}

Recently, particle trajectory techniques have been used to predict solute transport through porous media⁹¹⁻⁹⁵ and through saturated fractures.^{55-57,70,72} In these applications, a large number of solute "particles" (assumed to be completely independent) are allowed to transport individually through the flow system according to Eq. (27). The steady-state flow field typically is solved before the particle transport calculations (e.g., the Reynolds equation is used to obtain the steady-state

flow field in a variable-aperture fracture). Monte Carlo techniques are used to determine the initial position of each particle at the entrance to the flow system as well as the stochastic motion of the particle resulting from diffusion or dispersion during each time step. In some cases, an additional term is added to Eq. (27) to account for chemical interactions with the surfaces (e.g., sorption).^{93,95} Concentration profiles or breakthrough curves can be obtained at any spatial location or time by summing the contributions of all individual particles. A sufficient number of particles must be simulated to obtain representative statistics of the solute behavior in space and time. This approach, which is frequently called "particle tracking," offers certain advantages over the more traditional approach of solving the species continuity equation in space and time (see Sec. 3.2.3). For example, heterogeneities in the flow field and in the properties of the geologic media can be accounted for explicitly with minor additional computational burden when compared with algorithms that involve solving the species continuity equation. Complex phenomena such as nonlinear or nonequilibrium sorption and diffusion of particles into the rock matrix also can be accounted for with minimal additional computational burden by stochastically sampling residence time distributions that are representative of the phenomena.^{3,93,95} Because they are independent for each particle, particle tracking calculations are inherently parallelizable on multiprocessor computers. Parallelization of the species continuity equation is more difficult because communication between adjacent finite-difference or finite-element nodes is required.

3.2.2. Hydrodynamic Corrections Near Walls. A series of mathematical studies in the 1960s and early 1970s established that translation and rotation of spherical particles in the immediate vicinity of planar surfaces differs from that in an unbounded fluid because fluid motion near the surface is constrained by the no-slip boundary condition.⁹⁶⁻¹⁰² This constraint gives rise to two primary effects: (1) a coupling is established between particle translation and rotation and (2) movement toward or away from a planar surface is hindered by film thinning between the particle and the plane. These effects can be incorporated directly into the mobility tensors $\mathbf{M}$ and $\mathbf{M}'$, and then Eq. (15) can be solved rigorously to obtain particle trajectories in arbitrary flow fields and geometries. However, because one is typically interested primarily in the translational motion of a particle, the results are commonly presented in terms of dimensionless functions that correct the mobility and velocity that the particle would have in the absence of walls. Thus, the expressions for spherical particle velocities and mobilities near a wall become

$$M_{\perp} = F_1(H)M_{\infty} \quad (28)$$

$$M_{\parallel} = F_4(H)M_{\infty} \quad (29)$$

$$u_{\parallel} = F_3(H) v_{\parallel} \quad (30)$$

$$u_{\perp} = F_1(H)F_2(H) v_{\perp} , \quad (31)$$

where

- $M_{\perp}$ = mobility perpendicular to wall (cm²/s),
- $M_{\parallel}$ = mobility parallel to wall (cm²/s),
- M_{∞} = mobility far from wall (cm²/s),
- $u_{\perp}$ = particle velocity perpendicular to wall (cm/s),
- $u_{\parallel}$ = particle velocity parallel to wall (cm/s),
- $v_{\perp}$ = fluid velocity perpendicular to wall (cm/s),
- $v_{\parallel}$ = fluid velocity parallel to wall (cm/s),
- $F_1(H)$ = correction function given by Brenner⁹⁶ and Bart,⁹⁷
- $F_4(H)$ = correction function given by Goldman et al.,⁹⁸
- $F_3(H)$ = correction function given by Goldman et al.⁹⁹ and O'Neill and Stewartson,¹⁰⁰
- $F_2(H)$ = correction function given by Goren¹⁰¹ and Goren and O'Neill,¹⁰²
- H = dimensionless distance of particle from wall (h/R), and
- h = absolute separation between particle and wall (cm).

The functions $F_1(H)$, $F_2(H)$, $F_3(H)$, and $F_4(H)$ all have complicated analytical expressions. These functions are depicted graphically in Fig. 5 (from Ref. 27). When calculating particle trajectories, simple analytical approximations of these functions are frequently used (for example, see Ref. 103).

3.2.3. Species Continuity Equation. As an alternative to using the particle trajectory approach to calculate the movement of individual particles, the distribution of particles in space and time can be obtained by solving the appropriate partial differential equation(s) describing continuum particle behavior. When particle inertia is negligible, the general Fokker-Planck equation reduces to the familiar species continuity equation (also known as the convective-diffusion equation):²⁷

Fig. 5.
Hydrodynamic correction functions vs dimensionless separation distance
($H = h/R$). (From Ref. 24.)

$$\frac{\partial c_i}{\partial t} = \nabla \cdot (D \nabla c_i - c_i \mathbf{M} \cdot \mathbf{F} + c_i \mathbf{M} \cdot \mathbf{T}) + R_i, \quad (32)$$

where

c_i = concentration of species i (number/cm³) and
 R_i = rate of generation of species i by chemical reaction.

For colloids that do not dissolve, the reaction term, R_i , will be zero (except at surfaces). If we substitute Eq. (19) for the gravity force, f_v for the drag force resulting from fluid convection, and $-\nabla\phi$ for a general force, into Eq. (32) we get the following expression for transport of spherical particles (assuming that wall effects are negligible):

$$\frac{\partial c_i}{\partial t} = \nabla \cdot \left[D \nabla c_i - c_i \mathbf{v} + c_i \left(\frac{D}{kT} \right) \nabla \phi - c_i \left(\frac{2}{9\mu} \right) R^2 (\rho_p - \rho_f) \mathbf{g} \right]. \quad (33)$$

At this point, the reader should note that we do not explicitly account for a force resulting from migration in an electrical field. In general, such a force could be significant for colloids (in fact, it is crucial for determining colloid surface charge and mobility by electrophoresis), but it will not be important in tracer studies because there should be no electrical fields imposed in such studies. We also note that the general force given by $-\nabla\phi$ in Eq. (33) is typically important only very close to surfaces. The various forces that may contribute to this force are discussed in Sec. 3.3.

We can now incorporate the hydrodynamic corrections into Eq. (33). To do this, we assume that there is a single planar surface with which the particles can interact, and we use a rectangular cartesian coordinate system with the z coordinate normal to the planar surface ($z = 0$ at surface). We also assume that the general force $-\nabla\phi$ acts only in the z -direction. The component form of Eq. (33) then becomes

$$\begin{aligned} \frac{\partial c_i}{\partial t} = & F_4(H) D_\infty \left(\frac{\partial^2 c_i}{\partial x^2} \right) - F_3(H) \left[v_x + \left(\frac{2}{9\mu} \right) R^2 (\rho_p - \rho_f) g_x \right] \left(\frac{\partial c_i}{\partial x} \right) \\ & + F_4(H) D_\infty \left(\frac{\partial^2 c_i}{\partial y^2} \right) - F_3(H) \left[v_y + \left(\frac{2}{9\mu} \right) R^2 (\rho_p - \rho_f) g_y \right] \left(\frac{\partial c_i}{\partial y} \right) \\ & + D_\infty \frac{\partial}{\partial z} \left[F_1(H) \frac{\partial c_i}{\partial z} \right] \frac{\partial}{\partial z} [F_1(H) F_2(H) v_z c_i] \\ & - \left[\left(\frac{2}{9\mu} \right) R^2 (\rho_p - \rho_f) g_z \right] \frac{\partial}{\partial z} [F_1(H) c_i] + \left(\frac{D_\infty}{kT} \right) \frac{\partial}{\partial z} \left[F_1(H) c_i \frac{\partial \phi}{\partial z} \right], \end{aligned} \quad (34)$$

where

v_i = component of velocity in i direction,

g_i = component of gravity in i direction,

D_∞ = diffusion coefficient far away from wall (cm^2/s), and

H = dimensionless distance between particle and planar surface $[(z-R)/R]$.

Note that (x, y, z) are coordinates of the particle center.

Equation (34) is the most general form of the colloid continuity equation in cartesian coordinates. It reduces to the usual continuity equation when wall effects are neglected (i.e., $F_i(H) = 1$, $i = 1$ to 4).

The boundary conditions generally used when solving Eq. (34) are

$$c_i = c_\infty \text{ at } t = 0, \quad (35a)$$

$$c_i = c_\infty \text{ at } z = \infty, \text{ and} \quad (35b)$$

$$c_i = 0 \text{ at } z = 0 \text{ or } \frac{\partial c_i}{\partial z} = 0 \text{ at } z = 0. \quad (35c,d)$$

In a general problem, boundary condition [Eq. (35b)] can be time dependent. Boundary condition [Eq. (35c)] implies that particles that come in contact with the planar surface disappear from the system (i.e., a perfect sink). Boundary condition [Eq. (35d)] prevents penetration of the surface and allows particles to arrive at and leave the surface subject to the forces acting on them. Using the latter boundary condition, particles at the surface can be immobilized only if the forces acting on the particles are perfectly balanced (i.e., a net force of zero). Methods of accounting for immobilization at surfaces will be discussed in Sec. 3.3.9.

3.3. Colloid Interactions with Surfaces

3.3.1. Van der Waals Dispersion Forces. Van der Waals forces are fundamental forces experienced by all molecules and larger macromolecular bodies at small distances of separation. Israelachvili³⁴ and Hiemenz⁵ provide thorough discussions of the rather complex physics and chemistry associated with these forces. The discussion here will be brief and limited to sphere-plane interactions, which serve as a model for colloid-wall interactions.

Van der Waals forces occur as a result of dipole-dipole interactions between molecules. As discussed by Hiemenz,⁵ the total Van der Waals interaction energy is the sum of up to three contributions: (1) permanent dipole-induced dipole (Debye) interactions, (2) permanent dipole-permanent dipole (Keesom) interactions, and (3) induced dipole-induced dipole (London) interactions. In most cases, the resulting interaction energy is attractive. For molecules, this energy varies as the negative sixth power of the distance of separation; thus, the forces are very short range. For larger bodies, the pairwise interactions of individual molecules must be integrated

over both bodies to obtain the total Van der Waals interaction energy. Hamaker¹⁰⁴ was the first to perform such calculations. For the interaction between a sphere and a planar surface, he obtained

$$\phi = -\frac{A}{6} \left[\frac{R}{h} + \frac{R}{h+2R} + \ln \left(\frac{R}{h+2R} \right) \right], \quad (36)$$

where

- ϕ = interaction energy (J),
- h = distance of separation between surfaces (cm),
- R = particle radius (cm), and
- A = Hamaker constant (J).

By convention, a negative energy corresponds to attraction, and a positive energy corresponds to repulsion. The Hamaker constant, A , is an intrinsic constant that depends only on the characteristics of the materials that make up the sphere, the plane, and the medium that separates them. Hamaker constants for various organic and inorganic materials have been tabulated by Gregory¹⁰⁵ and Visser.¹⁰⁶ For a given material, the values tabulated by Gregory and Visser apply only in situations where two bodies of identical composition are brought together in a vacuum. When the bodies consist of different materials and the medium is not a vacuum, the Hamaker constant for the system is calculated as follows:⁵

$$A_{213} = (\sqrt{A_{22}} - \sqrt{A_{11}})(\sqrt{A_{33}} - \sqrt{A_{11}}), \quad (37)$$

where

- A_{213} = Hamaker constant for system,
- A_{11} = Hamaker constant for separating medium,
- A_{22} = Hamaker constant for material 2 (one body), and
- A_{33} = Hamaker constant for material 3 (other body).

Because Van der Waals forces are a manifestation of electromagnetic interactions resulting from dipole vibrations, they are subject to retardation effects when the distance of separation approaches that of the characteristic wavelength of the

interaction. Under these circumstances, a time lag or phase difference develops between the vibrations of interacting dipoles.⁵ Hamaker's original calculations implicitly assumed that there was no such retardation. In reality, retardation becomes important when bodies are separated by more than about 10 nm.

A rigorous approach to dealing with retardation effects is to apply the Dzyaloshinskii, Lifshitz, and Pitaevskii theory of molecular interactions (see Refs. 32 and 34). In this theory, the Hamaker constant becomes a function of the distance of separation and of the frequency dependence of the dielectric permittivity of the particles and the separating medium. The theory is difficult to apply because of its complexity and the fact that the necessary data are seldom available.

As an alternative, Overbeek¹⁰⁷ used the results of Casimir and Polder's¹⁰⁸ analysis of the time-dependent Schrodinger wave equation to show that the dependence of molecular interactions on separation distance could be empirically corrected (from an inverse sixth power dependence to a slightly different dependence) to account for retardation. Using such corrections, the Hamaker approach of integrating over macroscopic bodies can be applied to obtain expressions for retarded interaction energies between bodies. Some results for a sphere-plane system, from Ho and Higuchi,¹⁰⁹ Gregory,¹¹⁰ and Czarnecki,¹¹¹ are presented in Table I. Each of these expressions has limitations on its range of applicability because the empirical corrections are valid only over a certain range of separation distance relative to the characteristic wavelength (which typically is assumed to be about 100 nm). Figure 6 provides a comparison of the interaction energies as a function of separation distance using Eq. (36) and the expressions in Table I (over their range of applicability). The Hamaker constant for all these curves was 1×10^{-20} J, and the sphere radius was 0.5 μm . Except for Eq. (36), which does not take into account retardation, the expressions are in very good agreement. Although not presented here, Clayfield et al.¹¹² derived more complicated, but presumably more accurate, expressions for retarded interactions by performing exact integrations of Casimir and Polder's results.

All of the expressions provided so far apply only when the sphere and planar surfaces are assumed to be perfectly smooth. Czarnecki and Dabros¹¹³ and Czarnecki¹¹⁴ discuss corrections to classical calculations to account for surface roughness. When the length scale of surface irregularities is small compared with the particle radius, they showed that the interaction energy at small separations can be decreased by 2 to 3 orders of magnitude as compared with the case where the surfaces are smooth.¹¹³ Thus, Van der Waals forces are very sensitive to small-scale surface roughness.

TABLE I
EXPRESSIONS FOR RETARDED VAN DER WAALS INTERACTION ENERGY
FOR SPHERE-PLANE SYSTEMS USING HAMAKER-TYPE INTEGRATIONS
(AFTER REF. 46)

If $h > \lambda/4\pi$, and $h < R$,

$$\phi = -\frac{AR}{6h} \left[\frac{2.45}{10\pi} \left(\frac{\lambda}{h} \right) - \frac{2.17}{60\pi^2} \left(\frac{\lambda}{h} \right)^2 + \frac{0.59}{280\pi^3} \left(\frac{\lambda}{h} \right)^3 \right] \quad (\text{Ref. 109})$$

If $h < \lambda/4\pi$, and $h \ll R$,

$$\phi = -\frac{AR}{6h} \left[1 + 3.54\pi \left(\frac{\lambda}{h} \right)^{-1} \right]^{-1} \quad (\text{Ref. 109})$$

If $h \leq R/5$,

$$\phi = -\frac{AR}{6h} \left(1 + \frac{14h}{\lambda} \right)^{-1} \quad (\text{Ref. 110})$$

If $h > \lambda/4\pi$,

$$\begin{aligned} \phi = A \left[\frac{2.45\lambda}{60\pi} \left(\frac{h-R}{h^2} - \frac{h+3R}{(h+2R)^2} \right) - \frac{2.17\lambda^2}{720\pi^2} \left(\frac{h-2R}{h^3} - \frac{h+4R}{(h+2R)^3} \right) \right. \\ \left. + \frac{0.59\lambda^3}{5040\pi^3} \left(\frac{h-3R}{h^4} - \frac{h+5R}{(h+2R)^4} \right) \right] \quad (\text{Ref. 111}) \end{aligned}$$

where

- A = Hamaker constant (J),
- λ = characteristic wavelength (cm),
- h = separation distance (cm), and
- R = particle radius (cm).

Fig. 6.
Van der Waals interaction energy (sphere-plane) vs separation distance using Eq. (36) and the expressions in Table I. See text for assumptions.

In addition to requiring perfectly smooth surfaces, the expressions above assume that the materials are perfectly homogeneous. Vincent and co-workers^{115,116} have estimated Van der Waals interaction forces between surfaces having one or more adsorbed layers. In essence, they concluded that for single adsorbed layers, the interaction energy at a given surface separation distance can increase or decrease depending on the Hamaker constants of the particle, the surface layer, and the medium. Their analysis was done only for interactions between identical spheres with adsorbed layers of a common material. However, their result is qualitatively valid for sphere-plane interactions of different materials with adsorbed layers on one or both surfaces. Depending on the size of the sphere(s), the thickness of the layers, and the values of the Hamaker constants, the effect can be rather dramatic (causing changes in the interaction energy of nearly an order of magnitude relative to the energy without adsorbed layers).

To explicitly account for the effect of Van der Waals forces on the motion of particles, the negative gradient of the appropriate interaction energy expression [Eq. (36) or an expression from Table I] must be substituted into either Eqs. (26) or (33) as one component of the net deterministic force F acting on the particles. It is obvious from Fig. 6 that this component will be significant only when a particle is less than one radius from the wall.

3.3.2. Electrostatic Forces. Colloids generally have a surface electrical charge resulting from ionic equilibria occurring between surface chemical groups and the suspending solution. Surface charge also can arise from electrodic phenomena,³⁵ lattice imperfections, atomic substitutions in lattices, and from nonionic adsorption of surfactant ions,⁴² but these mechanisms will not be discussed here because they are expected to be of secondary importance in natural systems. However, atomic substitutions can be important in determining the surface charge of clays, if present in the rock.

As an example of surface charge originating from ionic equilibria, if the material of interest is an oxide, the surface typically will hydrate in water to form surface OH groups. Depending on the pH of the solution, these groups can either dissociate to form O^- groups or accept hydrogen ions to form OH_2^+ groups. Thus, the surface can act as both an acid or a base, depending on the pH. If O^- groups predominate, the surface will be negatively charged; if OH_2^+ groups predominate, the surface will be positively charged. Similar behavior occurs for carbonates, silicates, and phosphates, all of which contain functional groups of weak polyprotic acids. Polystyrene microspheres can be manufactured with such functional groups on their surfaces to provide specific surface charge characteristics. Most minerals tend to have negatively charged surfaces at the pH's encountered in groundwater systems.

The charge on a surface tends to attract oppositely charged ions from solution, which congregate at the surface to achieve local charge neutralization. The negatively charged surface and the positively charged layer of counterions are often referred to as the electrical double layer. In its simplest form, the double layer can be thought of as a double-plate capacitor with equal and opposite charges on both plates.³⁵ However, in reality, the oppositely charged ions are never all located exactly in the plane of the "second plate." Instead, some counterions tend to be located at some distance from the surface. Thus, neutralization does not occur until some finite distance into solution (the so-called "diffuse" double layer). This phenomenon gives rise to an electrical potential field in the vicinity of the surface that

starts out at some specified potential in the plane of the primary layer of counterions and decays to zero (neutralization) as the distance from the surface increases.

In an ideal situation, where the surface charge is determined by a single ion that comes from the surface (e.g., Cl^- from an AgCl surface), the Nernst equation can be applied to determine the potential at the surface:⁵

$$\psi_o = \left(\frac{RT}{zF} \right) \ln \left(\frac{c}{c_{\text{pzc}}} \right), \quad (38)$$

where

ψ_o = surface potential (V),

R = gas constant (J-equiv K),

T = temperature (K),

z = charge on potential-determining ion,

F = Faraday's constant (96500 C/equiv)

c = concentration of potential-determining ion (mole/L), and

c_{pzc} = concentration of potential-determining ion at the point of zero surface charge (mole/L).

This equation also can be written in a form that is more appropriate for oxides in groundwater:¹¹⁷

$$\psi_o = \left(\frac{2.303RT}{F} \right) (\text{pH}_{\text{pzc}} - \text{pH}), \quad (39)$$

where $\text{pH}_{\text{pzc}} = \text{pH}$ at the point of zero surface charge.

In Eq. (39), it is assumed that H^+ is the potential-determining ion, which is often valid for simple oxides and simple groundwater chemistries. In these situations, the surface potential can be estimated by successive titrations (with a strong acid or base) at different ionic strengths to determine the pH at the point of zero charge and then applying Eq. (39) (for example, see Ref. 42).

However, for many oxides and other materials of interest in groundwater systems, there is frequently not a single potential-determining ion. In these cases, the surface potential is determined by a combination of ionic equilibria and adsorption of counterions from solution. The result is that the surface potential cannot be

predicted easily, as when the Nernst equation applies; instead, it must be measured experimentally. For lyophobic colloids, the surface potential probably is best measured by electrophoresis.⁵ This method, which will not be described in detail here, involves observing the movement of colloids in an electric field and inferring the potential at the surface of shear from the measured mobility of the particles. The potential at the surface of shear, or the zeta potential, is assumed to be approximately equal to the surface potential.

An alternative approach to estimate surface potential is to determine the surface charge by conductometric titration and then relate this charge to surface potential using an analytical solution to the Poisson-Boltzmann equation.^{5,46} This approach may pose difficulties because the surface area of the surface whose potential is being determined must be known and no other acid-base reactions can interfere with the measurement.

Given the surface potential, the potential as a function of distance from the surface is determined by solving the Poisson-Boltzmann equation with the boundary conditions that $\psi = \psi_0$ at the surface and $\psi = 0$ at large distance from the surface. The Poisson-Boltzmann equation is

$$\nabla^2 \psi = -\left(\frac{e}{\epsilon}\right) \sum_i z_i n_{i0} \exp\left(\frac{-z_i e \psi}{kT}\right), \quad (40)$$

where

- e = electron charge (C),
- ϵ = dielectric constant of the solution (C²/J-m),
- z_i = charge on species i ,
- n_{i0} = concentration of species i in bulk solution (number/L), and
- k = Boltzmann's constant (J/K).

For a planar surface (one-dimensional geometry), Eq. (40) can be expressed as⁵

$$\left(\frac{d\psi}{dx}\right)^2 = \left(\frac{2kT}{\epsilon}\right) \sum_i n_{i0} \left[\exp\left(\frac{-z_i e \psi}{kT}\right) - 1 \right], \quad (41)$$

which must be integrated over the boundary conditions given above.

When the surface potential is low, the solution to Eq. (40) is given by the Debye-Huckel theory:⁵

$$\psi = \psi_0 \exp(-\kappa x) , \quad (42)$$

where

$$\kappa = \sqrt{\left(\frac{e^2}{\epsilon kT}\right) \sum_i z_i^2 n_{i0}} , \text{reciprocal Debye length, m}^{-1} .$$

Alternatively, when the potential is not low and when the electrolyte is symmetrical (same magnitude charge on positive and negative ions), the Gouy-Chapman theory predicts⁵

$$\Psi = \Psi_0 \exp(-\kappa x) , \quad (43)$$

where

$$\Psi = \frac{\exp(ze\Psi / 2kT) - 1}{\exp(ze\Psi / 2kT) + 1} .$$

The phenomenon of interest for colloids interacting with fracture walls is the interaction energy that results when a charged sphere interacts with a charged planar surface. The starting point for deriving such an interaction energy is a force balance for parallel plates that generally is attributed to Bell and Peterson:¹¹⁸

$$F_R(d) = nkT \left[2 \cosh(y) - \kappa^{-2} \left(\frac{dy}{dx} \right)^2 - 2 \right] , \quad (44)$$

where

$F_R(d)$ = repulsive force or pressure between plates when they are separated by distance (d),

n = number of counterions per unit volume,

$y = ze\Psi / kT$ (reduced potential),

κ = reciprocal Debye length (m^{-1}) [see Eq. (42)], and

d = separation distance between plates (m).

The interaction energy as a function of separation distance then is given by

$$\phi(d) = - \int_{\infty}^d F_R(x) dx , \quad (45)$$

where

$\phi(d)$ = interaction energy at a separation distance (d).

Using this approach, the problem reduces to that of obtaining the potential and the potential gradient at some point between the parallel plates as a function of the separation distance (knowledge of these values at any single point is sufficient to allow calculation of the force). Formally, this requires a solution of the Poisson-Boltzmann equation for the potential between the plates with the appropriate boundary conditions. The parallel plate solution then is transformed to a sphere-sphere or sphere-plane solution using the method of Derjaguin.¹¹⁹ The boundary conditions on electrostatic potential are worthy of further discussion as the results can be very sensitive to these and it is not always obvious what they should be.

Several situations can arise at a solid-solution interface when two surfaces are brought into close proximity: (1) the potential at both interfaces can remain constant (as a function of separation distance), (2) the charge at both interfaces can remain constant, (3) the potential at one interface can remain constant while the charge remains constant at the other interface, and (4) the potential and charge at one or both interfaces can change as a function of separation distance. Significantly different interaction potentials (often with sign differences) can result when these different boundary conditions are applied.

The appropriate boundary conditions to use for each surface in a given situation depend on several factors. First, it is important to know whether surface charge adjustment during the interaction occurs as a result of charge transfer across the double layer or dissociation of acidic and/or basic sites on the surface. If the latter is true, the boundary conditions generally are assumed to be dictated by the constraint that the ionic equilibria for surface reactions must be maintained at all times. This is the so called "charge regulation" boundary condition. Ninham and Parsegian¹²⁰ appear to be the first to use such an approach for solving the electrostatic potential of interaction, but the method has been used since by several other investigators.¹²¹⁻¹²⁹ Appendix I of Ref. 121 provides a good summary of this approach.

If charge transfer across the double layer is the dominant mechanism of charge adjustment, then the appropriate boundary conditions for the problem depend on the characteristic times for (1) relaxation of the double layer (movement of ions within the double layer in response to movement of the surfaces), (2) collision between the surfaces, and (3) surface charge adjustment across the double layer:

$$\text{Double Layer Relaxation Time: } t_{DL} = \kappa^2/2D_i ,$$

$$\text{Brownian Collision Time: } t_{Br} = \kappa^2/2D_p , \text{ and}$$

$$\text{Charge Adjustment Time: } t_{Ch} = \sigma/i_o ,$$

where

D_i = diffusion coefficient of ions (cm^2/s),

D_p = diffusion coefficient of particles (cm^2/s),

σ = surface charge density (C/cm^2), and

i_o = exchange current density across double layer ($\text{C}/\text{cm}^2\text{-s}$).

More discussion of these relaxation times and alternative expressions for them are provided by Lyklema^{130,131} and Lyklema and Van Leeuwen.¹³² As discussed by Rajagopalan and Kim,¹³³ if t_{Ch} is much less than t_{DL} and t_{Br} , the interaction will occur at constant potential, whereas if t_{Ch} is much greater than t_{DL} and t_{Br} , the interaction will occur at constant charge (we note that t_{DL} is typically much less than t_{Br} , so the comparison is generally between t_{Ch} and t_{Br}). If t_{Ch} and t_{Br} are approximately equal, the interaction will occur at neither constant potential nor constant charge.

Unfortunately, values for t_{Ch} are not well known and can vary over many orders of magnitude. For instance, Rajagopalan and Kim¹³³ give a range of 10^{-6} to 10^4 s for t_{Ch} , which makes it plausible to have either constant potential or constant charge interactions (t_{Br} is typically about 10^{-5} to 10^{-4} s when hydrodynamic interactions are taken into account¹³²). Thus, it is difficult to determine *a priori* whether a surface will remain at constant potential or constant charge during an interaction.

The approach taken in most colloid flocculation or deposition studies is simply to assume that interactions between surfaces take place at either constant potential or constant charge. To facilitate calculations, an analytical solution to the Poisson-Boltzmann equation typically is used to describe the electrostatic potential as a function of separation distance. Table II provides a variety of expressions that

TABLE II
EXPRESSIONS FOR ELECTROSTATIC INTERACTION ENERGY FOR
SPHERE-PLANE SYSTEMS (VALID FOR 1:1 ELECTROLYTES,
 $|\Psi| < 50 \text{ mV}$, $KR > 10$, AND SI UNITS) (AFTER REF. 133)

Both Surfaces at Constant Potential (LPBE) - Ref. 117:

$$\phi = \frac{\epsilon R (\psi_1^2 + \psi_2^2)}{4} \left\{ \left(\frac{2\psi_1}{\psi_2} \right) \left[1 + \left(\frac{\psi_1}{\psi_2} \right)^2 \right] \ln \left[\frac{1 + \exp(-\kappa h)}{1 - \exp(-\kappa h)} \right] + \ln[1 - \exp(-2\kappa h)] \right\}$$

Both Surfaces at Constant Charge (LPBE) - Ref. 134:

$$\phi = \frac{\epsilon R (\psi_1^2 + \psi_2^2)}{4} \left\{ \left(\frac{2\psi_1}{\psi_2} \right) \left[1 + \left(\frac{\psi_1}{\psi_2} \right)^2 \right] \ln \left[\frac{1 + \exp(-\kappa h)}{1 - \exp(-\kappa h)} \right] - \ln[1 - \exp(-2\kappa h)] \right\}$$

One Surface at Constant Potential, Other at Constant Charge (LPBE) - Ref. 135:

$$\phi = \frac{\epsilon R (\psi_1^2 + \psi_2^2)}{4} \left\{ \left(\frac{2\psi_1}{\psi_2} \right) \left[1 + \left(\frac{\psi_1}{\psi_2} \right)^2 \right] \left[\frac{\pi}{2} - \tan^{-1} \sinh(\kappa h) \right] - \frac{(\psi_2^2 - \psi_1^2)}{\psi_2^2 + \psi_1^2} \ln[1 + \exp(-2\kappa h)] \right\}$$

Both Surfaces Constant Charge, Compression Method (Non-LPBE) - Ref. 136:

$$\phi = \frac{\epsilon R \kappa^2 T^2}{2e^2} \int_H^\infty \left\{ (y_1 + y_2) \ln \left[\frac{B + 0.5(y_1 + y_2) \coth(0.5x)}{1 + 0.5(y_1 + y_2)} \right] - \ln[0.25(y_1 + y_2)^2 + \cosh(x) + B \sinh(x)] + x \right\} dx$$

Linear Superposition (Any Case) (LPBE) - Ref. 133:

$$\phi = \frac{16\epsilon R \kappa^2 T^2}{e^2} \tanh\left(\frac{y_1}{4}\right) \tanh\left(\frac{y_2}{4}\right) \exp(-\kappa h)$$

where

LPBE = linear Poisson - Boltzmann equation,

H = h/R,

y_i = zeψ_i/kT,

B = $\sqrt{[1 + 0.25(y_1 + y_2)^2 \csc^2(0.5x)]}$.

describe interaction potentials between spheres and planar surfaces for various boundary conditions (adapted from Ref. 133). A plot showing interaction potentials as a function of separation distance using these expressions is provided in Fig. 7 (with the exception of the constant charge, nonlinear Poisson-Boltzmann expression of Ref. 136, which contains a complex integral that must be evaluated numerically). In all cases, the surface potential on the plane was assumed to be 20 mV (at infinite separation), the surface potential of the sphere was 30 mV, the solution was 0.001 M NaCl, and the sphere radius was 0.5 μm . It is apparent from Fig. 7 that the boundary conditions (i.e., constant potential or constant charge surfaces) can affect the interaction energy profile significantly.

It is important to recognize that all of the expressions in Table II are restricted to 1:1 electrolytes, surface potentials less than 50 mV, and κR greater than 10. The constant charge expression of Wiese and Healy¹³⁴ and the linear superposition expression given in Table II are also strictly valid only for relatively large distances

Fig. 7.
Electrostatic interaction energy (sphere-plane) vs separation distance using expressions in Table II. See text for assumptions.

of separation, and the constant charge expression of Gregory¹³⁶ is valid only when the surfaces have charges of the same sign. Many investigators have calculated interaction potentials with some of these restrictions removed, particularly for the constant potential case.¹³⁷⁻¹⁴⁰ However, these results have not been widely used because of the unwieldy analytical expressions or inconvenient numerical solutions that were generally obtained. The linear superposition approach, which has not been discussed previously, assumes constant potential surfaces and involves making the approximation that the potential distributions from both surfaces are linearly additive. This is the approach typically presented in colloid science texts (e.g., Ref. 5), but it provides good approximations only at relatively large separation distances.

As suggested by Table II, a simple analytical expression is not available for the case where the surface potential and charge are regulated by ionizable surface groups. Unfortunately, this situation is probably the relevant case for both polystyrene microspheres and the oxide surfaces that are likely to be present in natural fractures. However, it is likely that a simple analytical expression from Table II can serve as an acceptable approximation given the many nonidealities and uncertainties that are present in natural systems.

As in the case of Van der Waals forces, electrostatic forces are expected to be affected by surface roughness and adsorbed surface layers. However, this literature review did not turn up any work addressing these phenomena. Intuitively, it seems that electrostatic forces, like Van der Waals forces, should be considerably attenuated by surface roughness, and they probably will have a complicated dependence on surface layers.

To explicitly account for the effect of electrostatic forces on the motion of particles, the negative of the gradient of the appropriate expression from Table II must be substituted into either Eq. (26) or (33) as one component of the net deterministic force F acting on the particles. It is obvious from Fig. 7 that, as with Van der Waals forces, the electrostatic component of force will be significant only when a particle is less than one radius from the wall.

3.3.3. Electronic (Born) Repulsion. It is well known that, on an atomic scale, two surfaces cannot come into direct physical contact with each other because the overlap of electrons from surface atoms causes extreme repulsion at very short separations. This repulsion, also known as "Born repulsion," is the origin of the negative 12th power dependence of atomic interaction energies on separation distance in the well-known Lennard-Jones potential.⁵ Ruckenstein and Prieve¹⁴¹

used the following expression to describe Born repulsion between a sphere and a planar surface as a function of separation:

$$\phi_B = \frac{A\sigma^6}{7560} \left[\frac{8R+h}{(2R+h)^7} + \frac{6R-h}{h^7} \right], \quad (46)$$

where

- ϕ_B = Born repulsion interaction energy (J),
- A = Hamaker constant (J),
- σ = collision diameter (cm),
- R = radius of particle (cm), and
- h = minimum separation distance between surfaces (cm).

Because of the extreme short range of the forces (operative at less than 1 nm), Born repulsion is not important in determining colloid behavior in most systems of practical interest. Generally, we can assume that when two surfaces have overcome electrostatic or steric repulsive forces, they essentially come into contact as a result of attractive Van der Waals forces. Therefore, Born repulsion is not discussed further. However, it is important to recognize that Born forces must be considered to predict the existence of a primary energy minimum at some finite distance of surface separation (to be discussed later). Without Born forces, one would predict that there is an infinite attraction energy at very short separation distances, and thus two surfaces, once in contact, would never separate.

3.3.4. Steric Forces and Chemical Bonds. If a lyophobic colloid is coated (one complete monolayer or more) by an adsorbed polymer that hydrates easily, its surface will have a "fuzzy" appearance because of the polymer chains extending into solution. Bringing two such colloids into close proximity such that the polymer chains begin to overlap will result in an increase in the free energy of the system.⁵ This increase in free energy is generally attributed to a decrease in the volume fraction of water in the overlap region, which opposes the natural tendency of solutions to become more dilute by osmotic processes. Thus, the surfaces tend to repel each other, and the adsorbed polymer provides a means of stabilizing the colloid against flocculation. However, the adsorbed polymer also can have other effects on stability, such as the modification of Van der Waals forces (see Sec. 3.3.1), the modification of electrical double layer forces by changing ionic mobility or

dielectric permittivity near the surface, and entropy effects that tend to generate a repulsive force as the polymer chains on the surfaces are "squeezed" together during an interaction.¹⁴² Polymer layers also can affect hydrodynamic resistance during an interaction, thus modifying the hydrodynamic correction functions presented in Sec. 3.2.2.¹⁴³ These phenomena, taken collectively, are usually called steric stabilization, as they almost always tend to stabilize colloidal dispersions.

Vincent¹⁴⁴ provides a good, albeit somewhat dated, overview of the theory of steric stabilization. A very good recent treatment of the subject, particularly as it applies to sphere-plane interactions, is given by Warszynski.¹⁴² Warszynski developed expressions for what he considered to be the two principal components of steric stabilization forces during sphere-plane interactions. These components are the "osmotic term," which accounts for the osmotic phenomena mentioned above, and the "elastic term," which accounts for entropy effects as the polymer layers are squeezed together. He provides complicated integral expressions for the dimensionless interaction energies associated with these terms as a function of dimensionless separation distance [Eqs. (7) and (8) from Ref. 142]. These expressions are not duplicated here, but Fig. 8, which is taken from Warszynski's paper, shows how the interaction energies are expected to vary with separation distance for a particle of 0.47- μm radius and for a specific set of parameter values (which, unfortunately, Warszynski does not completely provide). The upper three curves in Fig. 8 correspond to the osmotic term with different values of the "polymer-solvent interaction parameter," χ (see Ref. 142). The lower curve corresponds to the elastic term under the same conditions as the upper three curves. Noting that the axes of Fig. 8 have log scales, it is obvious that the steric stabilization interaction energy can greatly exceed typical values of the electrostatic and Van der Waals interaction energies over a finite range of separation distances (especially less than a separation distance of $H = 0.01$, or $h = 5$ nm). Thus, steric stabilization forces could be significant, and even dominate, in the interaction between surfaces.

It is important to recognize that the curves in Fig. 8 were generated assuming that both surfaces were coated with polymer. Although not calculated here or in Warszynski's paper, the curves for a polymer-coated sphere interacting with a non-coated plane are expected to be significantly lower. This situation would be applicable to an experimental system involving polymer-coated colloids and natural rock surfaces (there should be no polymers on the rock). It would not be difficult, in principle, to extend Warszynski's development to analyze this situation.

Fig. 8.
Steric interaction energy (in units of kT) vs dimensionless separation distance.
(From Ref. 141.) See text for discussion.

Warszynski's model¹⁴² was used to interpret the experimental data of Tadros et al.,¹⁴⁵ and reasonable agreement was found between predicted and observed deposition rates in stagnation point flow. A simple model for describing hydrodynamic interactions between polymer-coated surfaces¹⁴² was invoked to help explain the results.

Adsorbed polymers on colloid surfaces also have been suspected of forming chemical bonds with other surfaces.¹⁴⁶ Van de Ven et al.¹⁴⁶ deduced such a mechanism by observing that polystyrene colloids that had attached to a smooth, non-coated surface appeared to oscillate or "dance" about the surface in a way that suggested that the colloids were "tethered" to the surface by long, flexible connections.

They also made the interesting observation that such bonds readily formed even when experimental conditions were such that repulsive electrostatic forces should have prevented deposition. Thus, the possibility of bond formation involving long polymer chains may actually negate the classical prediction that deposition will be insignificant if repulsive electrostatic forces are strong.

Although it not advisable to introduce steric stabilization into systems where colloids are used as tracers, it may not be possible to entirely eliminate the phenomenon if polystyrene microspheres are used because these particles always have some polymer chains extending a finite distance into solution. However, if the microspheres have a tendency to flocculate under test conditions, it may be advantageous to introduce steric stabilization by modifying the preparation procedure for the microspheres or by adsorbing polymers onto their surfaces.

3.3.5. Structural or Hydration Forces. Although not commonly discussed in most classical treatments of colloid stability theory, structural forces have been theorized for decades,¹⁴⁷ and they have gained increasing attention in the past 15 yr, mainly as a result of direct observation of such forces between macroscopic surfaces at submicron separations.^{34,148-156} Structural forces are not fully understood, but they are generally attributed to changes in the orientation and ordering of solvent molecules between two surfaces as the surfaces approach each other. Water molecules are normally highly ordered very near a hydrophilic surface because of their affinity for the surface. This ordering can extend out to several molecular diameters from the surface.³⁴ However, when two hydrophilic surfaces approach each other, the water molecules between them are forced to become disordered to allow the approach to continue. Because this disordering is energetically unfavorable, a repulsive force develops between the surfaces. The structural force in aqueous systems is frequently attributed to bound waters of hydration on the surfaces, and the force is therefore called a "hydration" force.

Chureav and Derjaguin¹⁵⁷ provide a good overview of the theory of structural forces and discuss their inclusion in colloid stability theory. They note that the structural force per unit area between parallel plates typically has been observed to decay exponentially with surface separation; i.e., $F_s \propto \exp(-h/L)$, where h is the surface separation and L is a correlation length. If we integrate this force to obtain the interaction energy as a function of separation distance and then use the Derjaguin method¹¹⁹ to convert the plane-plane interaction to a sphere-plane interaction, we obtain the following expression for the interaction energy:

$$\phi_s = 2\pi RKL^2 \exp\left(\frac{-h}{L}\right), \quad (47)$$

where

- ϕ_s = structural interaction energy (J),
- K = proportionality constant (N/m²),
- h = separation distance (m),
- R = sphere radius (m), and
- L = constant corresponding to a correlation length (m).

Structural forces are typically very short range with a correlation length (L) on the order of 1–3 nm. However, in some systems, L can be greater than 10 nm (e.g., water on quartz, as observed by Pashley and Kitchener¹⁵⁸). For aqueous systems, the values of K and L can depend on the concentration and species of ions in solution because these affect the local ordering of water molecules. Also, K and L are quite sensitive to the specific adsorption of ions on the surfaces.¹⁵³ Some investigators have made a distinction between the molecules in immediate contact with a surface, which are supposedly less influenced by electrolyte concentration, and those further out into solution, which are influenced more strongly by the electrolyte. Thus, Pashley¹⁵⁹ suggested using a two-term formula in which there are two correlation lengths for the interaction energy:

$$\phi_s = 2\pi R \left[K_1 L_1^2 \exp\left(\frac{-h}{L_1}\right) + K_2 L_2^2 \exp\left(\frac{-h}{L_2}\right) \right]. \quad (48)$$

Israelachvili¹⁶⁰ and Israelachvili and Pashley¹⁶¹ have shown that the interaction energy can actually exhibit oscillations as a function of separation distance. They attribute this behavior to the layering of water molecules near a surface because the oscillations roughly coincide with the diameter of water molecules (a peak in the energy occurs at each molecular diameter).

When solvent molecules have a negative affinity for a surface (e.g., a hydrophobic surface in water), the value of K in Eq. (47) can be negative, which implies an attractive structural force. Such attractive forces have been observed experimentally by Israelachvili and Pashley¹⁵⁵ and Rabinovich and Derjaguin,¹⁶² who measured the force between hydrocarbon-coated surfaces in water. Rabinovich

and Derjaguin¹⁶² noted a correlation length of 12 to 13 nm for silica surfaces coated with dimethyl dichlorosilane, which suggests that attractive structural forces may be of considerably longer range than repulsive forces in some cases. However, relatively few data exist to corroborate this finding.

The literature does not address structural forces between one hydrophilic surface and one hydrophobic surface. One exception is the experiments of Elimelech,¹⁶³ in which it was deduced that a repulsive structural force was acting between polystyrene latex colloids and glass surfaces. This situation is particularly relevant to experiments in which polystyrene microspheres will be used as tracers in natural fractures. However, because of the heterogeneities in natural systems, it should not be concluded that structural forces will necessarily be repulsive in such experiments. In light of the sketchy evidence of structural forces, it is considered prudent to attempt to explain observed colloid-wall interactions without invoking structural forces. Structural forces should be considered as a possible explanation for anomalous behavior only if this approach fails.

3.3.6. Hydrodynamic Detachment Forces. As discussed in Sec. 3.2.1, colloidal particles in flowing liquids are always subjected to hydrodynamic drag forces. These forces can affect colloid interactions with surfaces in the same way as Van der Waals, electrostatic, and steric forces. The principal difference between hydrodynamic forces and other surface forces is that hydrodynamic forces typically have small components perpendicular to surfaces. In fact, for laminar flow between parallel plates, there is no component of hydrodynamic drag perpendicular to the surfaces.

Thus, immobilization of a rigid spherical particle on a perfectly smooth surface exposed to parallel flow theoretically cannot occur. In reality, immobilization occurs because of at least two factors: (1) all surfaces have some degree of roughness, which results in peaks and valleys on the surface that can act to block the translation of the sphere (surface forces then can have components that oppose particle motion) and (2) many particles have significant elasticity, which allows them to deform or flatten under the influence of surface forces, thus creating a surface that must be deformed further or rotated from the wall if the particle is to continue to translate. Surface chemical heterogeneities also theoretically can give rise to forces acting parallel to the bulk surface (i.e., an upstream portion of the surface may be attractive to the particles, whereas a downstream portion is repulsive, thus causing immobilization). However, this has not been discussed in the literature or observed experimentally, and it is probably a relatively minor effect compared with roughness and deformation.

Hubbe¹⁶⁴ proposed a "torque balance" model to describe detachment of rigid spherical particles from a rough surface in simple shear flow as a result of hydrodynamic forces. The model is depicted in Fig. 9. Surface roughness is approximated by ridges of characteristic height H upon which particles can get "caught." For a particle to remain stationary, the torque resulting from hydrodynamic drag on the particle must be balanced exactly by specific surface forces (Van der Waals, electrostatic, steric) that tend to keep the particle in near contact with the flat surface upstream of the ridge. This hydrodynamic torque was first calculated by Goldman et al.⁹⁹ in the same study that yielded the hydrodynamic correction function, $F_3(H)$, discussed in Sec. 3.2.2. The torque is given by¹⁶⁴

$$T_z = 43.92R^3\mu\left(\frac{dv}{dy}\right)_{y=0}, \quad (49)$$

where

T_z = hydrodynamic torque,

R = radius of spherical particle (cm),

μ = liquid viscosity (g/cm-s), and

dv/dy = velocity gradient normal to surface (surface at $y = 0$) (s^{-1}).

Fig. 9.

Illustration of Hubbe's torque balance model to describe hydrodynamic detachment. (From Ref. 164.)

When a particle is in a situation such as in Fig. 9, the torque can be thought of as a force acting through the particle center multiplied by a moment arm, which is the distance between the particle center and the point of contact (i.e., the particle radius). This force is directed perpendicular to the moment arm. Using Eq. (49), the magnitude of the force acting through the center must be

$$43.92R^2\mu\left(\frac{dv}{dy}\right)_{y=0},$$

and its component in the direction perpendicular to the bulk surface, F_y , must be

$$F_y = (\sin\beta) 43.92R^2\mu\left(\frac{dv}{dy}\right)_{y=0}. \quad (50)$$

If the particle is to remain stationary at the surface, the force given by Eq. (50) must be balanced exactly by an attractive force acting toward the bulk surface, shown as F_{ads} in Fig. 9. Using the Pythagorean theorem and elementary trigonometry to solve for $\sin\beta$, it can be shown that the force acting to pull the particle away from the surface is given by

$$F_y = \sqrt{R^2 - [R - (H - h)]^2} 43.92R\mu\left(\frac{dv}{dy}\right)_{y=0}, \quad (51)$$

where

H = height of surface asperity (cm) and

h = separation distance between particle and bulk surface (cm).

Equation (51) gives the hydrodynamic detachment force for a specific surface asperity height H and separation distance h . This force will always be repulsive. If $H \leq h$, then $(H-h)$ should be set equal to zero, and the resulting hydrodynamic detachment force will be zero. It should be noted that Eq. (51) is strictly valid only when the particle is very close to being in contact with the surface because the torque expression obtained by Goldman et al.⁹⁹ was derived for particles assumed to be touching the surface. However, the error associated with using Eq. (51) will never be greater than about 6% at any separation distance.⁹⁹

A hydrodynamic detachment force also can be postulated for particles that deform on perfectly smooth surfaces (no asperities). In this case, the moment arm is assumed to originate at the furthest downstream point of "contact" between the flattened particle and the surface. Sharma et al.¹⁶⁵ have done considerable work describing the detachment of deformed particles from planar surfaces, and the interested reader is referred to their work to obtain a better understanding of how the deformation area can be estimated or deduced from experimental data.

Conceptually, it is possible to add the hydrodynamic detachment force to other surface forces to obtain the net force (attractive or repulsive) acting on a particle normal to the surface. Thus, the hydrodynamic force given by Eq. (51) becomes a component of the overall normal deterministic force F in either Eq. (26) or Eq. (33), which are used to determine particle trajectories [Eq. (26)] or particle concentrations in space and time [Eq. (33)], respectively.

3.3.7. Dynamic Forces. The magnitudes of the surface forces discussed in Secs. 3.3.1 through 3.3.6 depend primarily on surface separation and geometry; they do not depend on colloid motion (i.e., they are "static" forces). In the past 15 yr, it has been recognized that surface forces arising from the dynamics of colloid-surface interactions may be important under certain circumstances. The theories associated with these dynamic forces are less mature than those for "static" forces, and there are relatively few experimental data available to validate the theories. Nevertheless, there is sufficient evidence that dynamic forces exist and that they may be significant under certain conditions.

Although no one has previously classified dynamic forces, we make a distinction here between at least three different types of dynamic forces that have been discussed in the literature.

1. Forces resulting from the relative motion of charged surfaces and the electrolyte solution that surrounds them.
2. Forces resulting from incomplete relaxation of the double layer as a result of slow lateral charge transfer along the solid-solution interface or slow adsorption/desorption of potential determining ions between the surface and the bulk solution.
3. Forces resulting from nonequilibrium charge transfer across the solid-solution interface or within the solid itself.

The first type of dynamic force is a manifestation of electrokinetic phenomena, where the relative motion between the electrolyte and the double layer(s) generates a repulsive "streaming potential."⁵ For a single charged spherical particle in Brownian motion, Van de Ven²⁷ has shown that the streaming potential always gives rise to a decreased effective diffusion coefficient relative to an uncharged particle. This decrease is a result of the shearing of counterions from the double layer by fluid motion. The double layer thus becomes asymmetric, with an excess of counter charge trailing the particle and exerting a force in the opposite direction of the motion of the particle relative to the fluid. Van de Ven²⁷ has predicted that this decrease in effective diffusion coefficient is greatest when the double layer width (κ^{-1}) is approximately equal to the particle radius (i.e., κR approximately 1). According to Van de Ven's theory, if κR is much less than 1 or much greater than 1, the diffusion coefficient rapidly approaches that of an uncharged particle. This theoretical conclusion was confirmed by the experimental results of Schumacher and Van de Ven.¹⁶⁶ In colloid tracer studies, the double-layer width should always be on the order of 10 nm, and the particle radius will be on the order of 500 nm, so κR will be on the order of 50, which is large enough that the diffusion coefficient of the particles should not be affected significantly by surface charge.

When considering the interaction of two charged surfaces, essentially two cases of relative motion have been investigated in detail. Van de Ven and coworkers¹⁶⁷⁻¹⁶⁹ and Muller¹⁷⁰ have independently addressed the case where two surfaces come together such that the electrolyte is "squeezed" out of the gap separating the surfaces, and Prieve and Bike^{171,172} have looked at the case where a cylindrical or spherical surface slides tangentially past a planar surface. In both cases, the analyses start from the same set of governing equations, which include the continuity equation for fluid flow [Eq. (1)], the continuity equations for ions in solution [analogous to Eq. (32), with F consisting of convective and electrical forces], Poisson's equation, and the equation(s) of fluid continuity and momentum minus the inertial terms (i.e., the creeping motion equations). Poisson's equation is

$$\nabla^2 \psi = -\frac{\rho}{\epsilon} , \quad (52)$$

where

ψ = potential in solution,

$$\rho = \text{charge density in solution} = \sum_i c_i z_i e N_A,$$

$$\epsilon = \text{dielectric constant of solution,}$$

$$c_i = \text{concentration of ion } i,$$

$$z_i = \text{charge on ion } i,$$

$$N_A = \text{Avogadro's number, } 6.02 \times 10^{23}, \text{ and}$$

$$e = \text{charge on an electron.}$$

The creeping motion equations in the presence of an electrical field are¹⁶⁹

$$\mu \nabla^2 \mathbf{v} - \nabla p = \rho \nabla \psi, \quad (53)$$

where $\rho \nabla \psi$ represents the electrical body force per unit volume as a result of the ions in solution. This term, which does not normally appear in the creeping motion equations, accounts for a coupling between the electrical field and fluid motion. This coupling is the fundamental basis of all electrokinetic phenomena. After the appropriate boundary conditions are imposed, the above equations are solved simultaneously. However, because of the complexity of these equations, several simplifying assumptions generally are made (e.g., symmetrical monovalent electrolyte, certain terms are negligible relative to other terms, etc.). After $\mathbf{v}$ and ψ are obtained as a function of position, the forces acting on the surfaces can be calculated using the relationship¹⁶⁹

$$\mathbf{F} = \int_S \boldsymbol{\sigma} \cdot d\mathbf{S}, \quad (54)$$

where

$$\begin{aligned} \mathbf{F} &= \text{force vector acting on the particle surface,} \\ \boldsymbol{\sigma} &= \text{stress tensor,} \\ S &= \text{surface area of particle, and} \\ d\mathbf{S} &= \text{vector normal to surface with magnitude equal to differential surface area.} \end{aligned}$$

The stress tensor, $\boldsymbol{\sigma}$, is given by¹⁶⁹

$$\boldsymbol{\sigma} = -p\mathbf{I} + \mu(\nabla \mathbf{v} + \nabla \mathbf{v}^T) - \frac{\epsilon}{2} \mathbf{E}^2 \mathbf{I} + \epsilon \mathbf{E} \mathbf{E}, \quad (55)$$

where

p = pressure,

$\mathbf{E} = \nabla\psi$, and

$\mathbf{I}$ = unit diagonal tensor.

The first two terms on the right-hand side of Eq. (55) are the familiar hydrodynamic components of the stress tensor. These are integrated in Eq. (54) to determine the forces that give rise to the hydrodynamic correction factors discussed in Sec. 3.2.2 when uncharged surfaces interact. The last two terms in Eq. (55) are associated with the stresses resulting from the electrical field. When integrated in Eq. (54), these terms give rise to what have been termed "electroviscous" forces. These forces are always repulsive because they involve the expenditure of energy to move counterions out of their energetically favored positions in the normally symmetrical double layers near the surfaces.

Warszynski and Van de Ven¹⁶⁹ have estimated the electroviscous forces associated with disc-disc (large radius relative to separation) and sphere-sphere ($\kappa R = 50$) interactions when both surfaces have equal charges in a monovalent electrolyte. Recognizing that electroviscous forces act to retard motion in the same way that hydrodynamic forces do, they present their results relative to hydrodynamic forces that would act in these situations. For the case of constant potential surfaces, their results indicate that the electroviscous force reaches a maximum at separation distances anywhere from about 2 to 5 κ^{-1} , and the maximum magnitude depends strongly on the surface potential(s). For surface potentials less than about 50 mV, the electroviscous force is never more than about one-half the hydrodynamic force (for both discs and spheres). Even for potentials of 100 mV, the electroviscous force is never greater than about 1.5 times the hydrodynamic force. However, for potentials of 150 mV and higher, the electroviscous force can exceed the hydrodynamic force by more than a factor of 7. If the surfaces are at constant charge, the electroviscous force is predicted to be much greater, with the calculations indicating that the force tends to infinity at separations approaching zero. For surfaces that are initially at 50 mV, the electroviscous force will not exceed the hydrodynamic force significantly until the separation distance is less than about κ^{-1} . As the initial surface potential is increased, the electroviscous forces dominate over hydrodynamic forces at progressively larger separation distances ($2\kappa^{-1}$ for 100 mV

and $4\kappa^{-1}$ for 150 mV). The reader should consult the article by Warszynski and Van de Ven¹⁶⁹ for more details.

Although no calculations were reported specifically for a sphere approaching a planar surface, the above results indicate that electroviscous forces may indeed offer significant resistance to the approach of a colloid to a wall. Van de Ven¹⁶⁷ and Warszynski and Van de Ven¹⁶⁹ used the electroviscous theory to successfully predict the effect of counterion size on the critical coagulation concentration (CCC) of As_2S_3 and AgI sols. That is, they predicted that the CCC tends to increase as counterion size increases, which was in agreement with experimental results. However, their theory was unable to account for the observed dependence of the "critical deposition concentration" (CDC) on counterion size. The CDC is the ion concentration necessary for charged colloids to deposit on a macroscopic surface, which is more applicable to colloid-wall interactions than the CCC. The electroviscous theory predicted an increase in CDC of only a few per cent when the counterion was changed from K^+ (small) to Li^+ (large), whereas the experimental data of Boluk and Van de Ven¹⁷³ suggested at least a 100% increase for these two ions. Clearly, other mechanisms such as specific adsorption of counterions (which would affect surface charge) must be invoked to explain such phenomena.

Using the governing equations described above but with different boundary conditions, Bike and Prieve¹⁷² obtained the following approximate expression for the normal electroviscous force acting on a charged sphere sliding tangentially past a charged planar surface:

$$F_z = -\frac{\epsilon^3 \pi U^2 R}{K^2 h^3} \left[0.3840 \zeta^2 + 0.1810 \zeta \Delta \zeta + 0.0242 (\Delta \zeta)^2 \right], \quad (56)$$

where

- F_z = normal electroviscous force (N),
- U = velocity of translation of sphere (m/s),
- R = radius of sphere (m),
- K = specific conductance of fluid (1/ohm-m),
- h = separation distance between sphere and plane (m),
- ζ = zeta potential of sphere (V), and
- $\Delta \zeta$ = difference in zeta potential of sphere and plane (V).

This force is not expressed as a fraction of a hydrodynamic force because there is ordinarily no component of hydrodynamic force acting normal to the planar surface. It should be noted that in deriving Eq. (56), it was assumed that the sphere was sliding rather than rolling (rolling is more realistic). This assumption should result in overestimation of the force because there will be more relative motion between surfaces during sliding than rolling. Bike and Prieve¹⁷² also assumed that the sphere and plane were almost touching and that their relative motion was slow enough that lubrication theory could be used to approximate the pressure and flow fields between the surfaces. In a recent paper, they have relaxed the lubrication approximation in a more general analysis of the electrohydrodynamics of charged surfaces in motion.¹⁷⁴ They have a forthcoming paper that will specifically address the normal electroviscous force that arises when a charged sphere moves parallel to a charged plane in a linear shear flow field, a situation that is applicable to the problem of colloid transport near planar walls.

Prieve and Bike¹⁷¹ and Bike and Prieve¹⁷² point to the experiments of Alexander and Prieve^{175,176} for evidence a normal electroviscous force in a real system. In these experiments, micron-sized spheres were allowed to translate in laminar flow tangential to a horizontal planar surface. Alexander and Prieve^{175,176} noted that the spheres moved at a fixed distance from the surface in aqueous solutions, but there was a tendency for the spheres to move away from the surface in ethylene glycol solutions. This anomalous behavior was attributed to "electrokinetic lift," which is the name given by Prieve and Bike¹⁷¹ to the force given by Eq. (56). This "lift" is observed in glycol solutions but not in water because the specific conductance of the glycol is several orders of magnitude less than that of water. Bike and Prieve¹⁷² concluded that unless the specific conductance is very low or the velocity is very high, electrokinetic lift should be negligible compared with other forces. Warszynski and Van de Ven^{168,169} tried to invoke Eq. (56) to explain the anomalous deposition behavior observed by Boluk and Van de Ven,¹⁷³ and they found that the calculated electrokinetic lift was 4 orders of magnitude too small to explain the observations. Using parameter estimates that are consistent with polystyrene microspheres and natural rock surfaces in aqueous systems, we can easily show that the electrokinetic lift should always be at least 3 orders of magnitude less than electrostatic or Van der Waals forces (see Sec. 3.3.8).

The second and third types of dynamic forces mentioned at the beginning of this section are more speculative and have not been investigated in as much detail as electrokinetic forces, primarily because these forces are difficult or nearly impos-

sible to experimentally distinguish from other forces. The second type of force has been discussed by Lyklema and co-workers,¹³⁰⁻¹³² who have speculated that slow lateral movement of surface charge and/or slow counterion adsorption kinetics may give rise to additional repulsive forces during the approach of two surfaces. Interactions under these conditions would be at neither constant potential nor constant charge, but they would differ from the charge-regulated interaction discussed in Sec. 3.3.2 (where ionic equilibria are always maintained at the surface). Under conditions of slow adsorption kinetics or slow lateral movement of surface charges, the ionic distribution between the surface and the solution during the interaction will always lag behind the equilibrium values, and thus, there will always be a force resisting the continued approach of the surfaces. Recently, Dukhin and Lyklema¹⁷⁷ have developed a simple but illustrative mathematical model to show that the resistive force between approaching disks as a result of slow lateral movement of surface charge can be of the same order of magnitude as hydrodynamic forces. Thus, in theory, these forces can be comparable to electroviscous forces, but direct experimental evidence is lacking.

The third type of dynamic force (that resulting from nonequilibrium charge transfer across the solid-solution interface) has only been postulated by Van de Ven.²⁷ The rationale for suspecting such a force is that any electrical current across the solid-solution interface or within the solid itself will dissipate energy, and as with all electrical currents, the energy dissipated will resist the force causing it (in this case, the approach of two surfaces). Van de Ven²⁷ estimates that such a resistive force may approach Van der Waals and electrostatic forces in magnitude; however, in making this estimate, he assumes that the entire surface charge moves across the solid-solution interface in a nonequilibrium manner at the exchange current density. Clearly, this type of calculation provides only a conservative upper bound of the energy dissipation during an encounter between surfaces.

It is important to recognize that, other than by the mechanism of slow adsorption of ions onto the surface(s), the dynamic forces mentioned in the last two paragraphs are expected to be significant only when the solid is a conducting or semiconducting material. Nonconducting materials, such as polystyrene, are essentially incapable of accepting or donating charge across the interface, and surface charge groups on polystyrene are prevented from significant lateral movement because they are attached to the polymer matrix. Thus, there are qualitative reasons to believe that these types of dynamic forces will not be operative if polystyrene microspheres are used as colloid tracers.

3.3.8. Interaction Energy Profiles Near a Surface. In principle, all of the forces discussed in Secs. 3.3.1 through 3.3.7 can be added together to obtain the surface force contribution to the deterministic force vector used in particle trajectory calculations or in particle concentration-time calculations [F_{det} in Eq. (26) or F in Eq. (32)]. In general, each of the surface forces has a different dependence on surface separation, and none are important at separations exceeding about 1 μm . The Van der Waals and electrostatic forces discussed in Secs. 3.3.1 and 3.3.2 represent the classical colloid stability theory advanced by Derjaguin and Landau¹⁷⁸ and Verwey and Overbeek,¹⁷⁹ which also is known as the DLVO theory. Born repulsion forces also are sometimes lumped into the DLVO theory, although they are not of practical importance except to determine the separation distance associated with the primary minimum. In theory, the remaining forces (steric, structural, hydrodynamic detachment, and dynamic) can all be added in linear fashion to the classic DLVO theory; indeed, this is the manner in which they have been treated historically.

In the classic DLVO theory, the interaction energy profile (energy vs separation distance) obtained by summing Van der Waals, electrostatic, and Born repulsion forces can take on a variety of shapes depending on the relative magnitudes of the forces and the assumptions used to calculate the interaction energies (see Refs. 5 and 32). Figure 10 shows three situations of practical significance that can result when these forces are combined to yield the interaction energy profile between two surfaces. In curve (a), the repulsive electrostatic forces dominate at all but the shortest separations, and thus, contact between the two surfaces is prevented. This situation results in a "stable" system with respect to flocculation of colloids or deposition of colloids onto surfaces. In curve (b), attractive Van der Waals forces dominate at all but the shortest separations; thus, when two surfaces come into contact, they tend to remain in contact. This situation results in "rapid" flocculation of colloids or rapid deposition of colloids onto surfaces, where "rapid" refers to a mass-transport-limited situation.⁵ We note that in curve (b) there is an energy minimum, called the "primary minimum," at some short separation distance between the surfaces. At this minimum there is no net force on the colloid(s) ($d\phi/dz = 0$) because the Van der Waals forces are exactly balanced by Born repulsion forces. The surfaces will tend to remain at this separation distance rather than coming in intimate contact because this represents the lowest energy state for the system. However, the separation distance is so small (on the order of 1 nm or less) that the surfaces can be assumed to be in contact. Curve (c) represents an intermediate situation in which Van der Waals forces and electrostatic forces are of approximately the same order of

Fig. 10.

Idealized interaction energy curves showing three situations of practical significance: (a) always repulsive (no minima or maxima), (b) strong attraction (deep primary minimum with no maximum), and (c) two energy minima separated by a maximum. Curves are not necessarily to scale.

magnitude. In this case, two minima and one maximum can be present in the potential energy curve. The outer minimum is generally called the "secondary minimum" and the maximum is called the "energy barrier." The primary minimum is generally much "deeper" energetically than the secondary minimum, so two surfaces will be much more tightly held together in the primary minimum. However, if the energy barrier between the primary and secondary minima is sufficiently high, very few collisions will result in the surfaces reaching the primary minimum. In this case, the surfaces will be held loosely together in the secondary minimum, and relatively little energy will be required to separate the surfaces.

When additional forces are lumped into the DLVO theory, the shapes of the interaction energy curves will change, but the qualitative discussion of the previous paragraph will still be valid. That is, the question of whether flocculation or deposition is favorable will be determined by the location and depth of the energy minima and the existence and height of any energy maxima. To provide some perspective on the relative importance of the various forces in determining the shape of the overall interaction energy curve, the individual interaction energies associated with each of the forces discussed in Secs. 3.3.1 through 3.3.7 (with the exception of steric forces) are shown as a function of separation distance in Fig. 11 for a hypothetical set of parameter values. In this figure, all the interaction energies except those associated with Van der Waals forces are repulsive. The curves were calculated for a sphere interacting with a smooth planar surface. The following assumptions and parameter values were used in the calculations.

Fig. 11.
Individual interaction energy curves associated with the various surface forces discussed in sections 4.6.1 through 4.6.7 (with the exception of steric forces).

- The sphere diameter is 1 μm .
- Gregory's expression¹¹⁰ (from Table I) was used to calculate the retarded Van der Waals interaction energy.
- The Hamaker constant is 1×10^{-20} J.
- The characteristic retardation wavelength is 100 nm.
- The expression of Hogg et al.¹¹⁷ (from Table II) was used to calculate the electrostatic interaction energy with the assumption that both surfaces are at constant potential.
- The surface potential of both surfaces = - 25 mV.
- The solution is a 0.001 M 1:1 electrolyte with a viscosity of 0.01 g/cm-s.
- The dielectric constant is $(78.54)(8.85 \times 10^{-12})$ C²/J-m.
- Equation (46) was used to calculate the Born repulsion interaction energy.
- The collision diameter is 0.5 nm.
- Equation (47) was used to calculate the structural interaction energy with $K = 10^6$ N/m², and $L = 1$ nm.
- Equation (51) was integrated numerically to obtain the hydrodynamic detachment interaction energy as a function of separation distance.
- The characteristic height of surface asperities is 0.2 μm .
- The sphere is in a laminar flow field between parallel plates with aperture = 100 μm and a maximum velocity = 0.1 cm/s. (The shear rate at the wall is 40 s⁻¹.)
- Equation (56) was integrated to obtain the dynamic (electrokinetic lift) interaction energy as a function of separation distance.
- The specific conductance of the fluid is 0.001 ohm⁻¹m⁻¹.
- Gravity forces were not calculated. (The sphere has the same density as the fluid.)

These assumptions, with the possible exception of those for structural forces, are not unreasonable for a polystyrene microsphere and natural rock system. However, Fig. 11 is intended only to provide a qualitative perspective on the magnitude and spatial extent of the various forces; it should not be interpreted quantitatively. Steric forces were not included in the calculations because good estimates of the necessary parameter values were not available. The steric interaction energies shown in Fig. 8, as calculated by Warszynski¹⁴², are probably much greater than can be expected in polystyrene-rock systems because Warszynski assumed a relatively large polymer coating density, a long polymer chain extension into solution, and coating of both

surfaces. Nevertheless, it is apparent from comparing Figs. 8 and 11 that steric forces could be important if polymer coatings are present in the system.

It is worthwhile to note that "electrokinetic lift" is the only dynamic force from Sec. 3.3.7 that has been included explicitly in Fig. 11. Electroviscous forces resulting from the normal approach of two surfaces have not been included because these normally are taken into account by adjusting the hydrodynamic correction factors of the spheres as a function of separation distance (see Secs. 3.2.2 and 3.3.7) rather than by taking the forces into account explicitly. Also, electroviscous forces take on widely different values depending on whether the surfaces are at constant charge, constant potential, or neither constant charge nor potential (see Sec. 3.3.7).

The hydrodynamic detachment and electrokinetic lift potential energy curves of Fig. 11 were calculated by integrating Eqs. (51) and (56) with respect to h . For hydrodynamic detachment, the boundary condition was zero interaction energy at a separation distance corresponding to the asperity height ($0.2\ \mu\text{m}$). For electrokinetic lift, the boundary condition was assumed to be zero interaction energy at an infinite separation distance.

Based on Fig. 11, the following conclusions can be drawn with regard to the relative importance of the various surface forces.

- Electrokinetic lift is unlikely to be an important normal force at any surface separation in aqueous solutions. Electrokinetic lift will be important only if the specific conductance of the solution is decreased significantly, the viscosity is increased significantly, or the translation speed of the sphere is increased significantly.
- Born repulsion is important only at separation distances of $0.2\text{--}0.3\ \text{nm}$ or less. At distances less than $0.2\ \text{nm}$, it is the dominant interaction energy.
- Structural forces can be important at separation distances on the order of $5\ \text{nm}$ or less. They are of minor importance at greater separation distances.
- Van der Waals and electrostatic forces are longer range than all other forces except hydrodynamic detachment, and they tend to dominate the interaction energy profile at separation distances from 0.3 to $30\ \text{nm}$.
- Hydrodynamic detachment is relatively unimportant at short separation distances (where the energy minima are expected), but it can be the dominant force at larger separation distances. Depending on the characteristic

height of surface asperities, hydrodynamic detachment forces may decay more slowly with distance than any other force.

The manner in which overall interaction energy curves are used to account for colloid interactions with surfaces under flow conditions is discussed in the next section.

3.3.9. Boundary Conditions to Account for Colloid Interactions with Surfaces in Transport Equations. Sections 3.3.1 through 3.3.8 provide the background necessary to understand the various types of interactions known or speculated to occur between colloids and surfaces. The question now is: How do we use the overall potential energy vs separation distance curve to account for colloid interactions with surfaces under flow conditions?

One "brute-force" way to approach this problem is to simply calculate the force at each location near the surface by taking the negative gradient of the total potential energy curve and then substitute this force directly into Eq. (26) if particle trajectories are calculated or into Eq. (33) if particle concentrations in space and time are calculated. The presence of Born repulsion forces at very short separations effectively dictates a zero flux boundary condition at all surfaces. Although this approach is clearly the most general approach, it is not attractive because it requires a numerical solution with an extremely fine spatial resolution at distances very near the surfaces where the potential gradients are steep relative to gradients in the bulk solution. Nevertheless, several investigators have adopted this approach using simplified geometries (generally one spatial dimension) to calculate both transient and steady-state particle concentrations in the vicinity of a surface and fluxes to/from the surface given a set of initial and/or boundary conditions.^{44,103,180-197} In essentially all of these studies, only Van der Waals and electrostatic forces were assumed to contribute to the interaction energy profile. All of the investigators used finite-difference numerical techniques with compressed grids near the surface to obtain solutions. In cases where transient solutions were obtained, various schemes were used to gradually increase the time-step size as the concentration profiles approached steady-state.¹⁸⁷

Ruckenstein and Prieve¹⁹⁸ and Spielman and Friedlander¹⁹⁹ independently derived an analytical expression for the flux of particles to a surface assuming that particle motion is influenced only by diffusion and surface forces (negligible particle convection near the surface) and that a quasi-steady state can be assumed for particle

flux near the surface. The starting point for their development was the expression for particle flux normal to the surface under these conditions:

$$J(z) = -D(z)\frac{\partial c}{\partial z} - \frac{D(z)c}{kT}\left(\frac{\partial \phi}{\partial z}\right), \quad (57)$$

where

$J(z)$ = particle flux (particles/cm²-s),

c = particle concentration (particles/cm³),

z = dimension perpendicular to surface ($z = 0$ at surface),

ϕ = interaction energy (J or ergs), and

$D(z)$ = diffusion coefficient as a function of z [$= D_{\infty}F_1(z)$] (cm²/s).

When this equation is integrated with the boundary condition $c = 0$ at $z = 0$, the result is¹⁹⁸

$$J_0 = -K_{\delta}c_{\delta}, \quad (58)$$

where

J_0 = particle flux to the surface (negative sign indicates flux toward the surface);

K_{δ} = a constant related to the shape of the interaction energy curve and, specifically, the height of the energy barrier;¹⁹⁸ and

c_{δ} = concentration of particles at a distance δ where the surface forces have essentially decayed to zero.

If the diffusion boundary layer (i.e., the layer in which fluid convection can be neglected in calculating particle flux) is thick compared with δ , the concentration c_{δ} can be related to the concentration at the outer edge of the diffusion boundary layer, c_B , by equating the surface flux [Eq. (58)] with the flux in the diffusion layer.¹⁹⁸

When c_{δ} is eliminated, an expression for the flux to the surface in terms of c_B can be obtained:

$$J_0 = -K_{BC}c_B, \quad (59)$$

where

$$K_B = \text{a new constant given by } \left(\frac{1}{K_\delta} + \int_{\delta_F}^{\delta_D} \frac{dz}{D(z)} \right)^{-1},$$

δ_F = distance over which surface forces act, and

δ_D = distance over which diffusion coefficient depends significantly on z .

Thus, a kinetic-type boundary condition is obtained that can be applied directly to the continuity equation to account for particle deposition on a surface. This type of approach greatly simplifies the calculations necessary to describe simultaneous transport and deposition, as all the phenomena occurring near the surface are accounted for by a simple boundary condition. Accordingly, the approach often has been referred to as the "Surface Force Boundary Layer Approximation." Several investigators have used this approximation either to interpret experimental data^{197,200-202} or as a starting point for developing variations of deposition theory.²⁰³⁻²⁰⁵

Prieve and Ruckenstein²⁰⁶ and Dabros and Adamczyk¹⁸⁴ determined that the Surface Force Boundary Layer Approximation can be applied only when (1) the diffusion boundary layer is thick compared with the surface force boundary layer, (2) there is a significant energy barrier (greater than about 5-10 kT) between the bulk solution and the primary minimum, and (3) there is a very shallow or nonexistent secondary minimum. The first requirement ensures that the assumption of negligible particle transport by convection is valid. The second requirement arises because of the integral in the expression for K_δ . If a significant energy barrier is not present or a relatively deep secondary minimum exists, the value of this integral becomes sensitive to the value chosen for δ (which is selected arbitrarily), and thus, the approximation becomes subjective. When the energy barrier is sufficiently low and the primary minimum is deep, it probably is appropriate to simply use a perfect sink boundary condition ($c = 0$ at the surface) rather than a kinetic boundary condition because the deposition rate likely will be mass transport limited.

Ruckenstein and Prieve later refined the Surface Force Boundary Layer Approximation to account for particle detachment from a surface in addition to deposition.^{141,207} Their approach still involved application of Eq. (57), but they now assumed the presence of a significant secondary minimum in which particles could accumulate. To deal with the secondary minimum, they (1) assumed a Boltzmann

distribution of particles in both the primary and secondary minima, (2) used the particle concentrations in the minima as boundary conditions to solve Eq. (57) for the flux, and (3) related the particle concentration at the outer edge of the surface force boundary layer to the bulk concentration by equating the inner flux with the flux in the diffusion boundary layer. Using this approach, they obtained the following expression for the overall flux to/from the surface:

$$J_0 = -K_f c_B + K_r n_s , \quad (60)$$

where

K_f = deposition rate constant (an expression containing an integral) (cm/s),

K_r = detachment rate constant (the ratio of K_f and another integral) (1/s),
and

n_s = particle concentration on the surface (actually in the primary minimum) (particles/cm²).

Ruckenstein²⁰⁸ later refined the approach further by explicitly accounting for particle accumulation in both the primary and secondary minima. The resulting expressions for the time derivatives of particle concentrations in the primary and secondary minima are²⁰⁸

$$\frac{dn_2}{dt} = K_m(c_B - Hn_2) + K'n_1 - K''n_2 \quad \text{and} \quad (61a)$$

$$\frac{dn_1}{dt} = -K'n_1 + K''n_2 , \quad (61b)$$

where

n_1 = particle concentration in primary minimum (particles/cm²),

n_2 = particle concentration in secondary minimum (particles/cm²),

K_m = mass transfer coefficient (cm/s),

H = constant (consisting of an integral) relating n_2 to the concentration of particles at the outer edge of the surface force boundary layer (1/cm),

K' = rate constant (consisting of an integral) for movement of particles from the primary to the secondary minimum (1/s), and

K'' = rate constant (consisting of an integral) for movement of particles from the secondary to the primary minimum (1/s).

We note that these time derivatives have the same units (particles/cm²-s) as the fluxes in Eqs. (57)–(60). From Eq. (61), the flux from the bulk solution to the surface (secondary minimum) is given by

$$J_0 = -K_m(C_B - Hn_2) . \quad (62)$$

This equation would be the boundary condition to use in a transport calculation. Equations (61a) and (61b) then would be used to calculate the distribution of particles between the primary and secondary minima. Prieve and Lin¹⁸⁵ and later Albery et al.^{209,210} used modified (refined) Surface Force Boundary Layer Approximations to calculate both deposition and detachment rates from surfaces.

In parallel with the work of Ruckenstein and Prieve, Dahneke^{73,211} addressed the detachment of particles from a surface under the conditions of a negligible secondary minimum and a significant energy barrier. Using techniques similar to Ruckenstein and Prieve but with some modifications, he developed a rate expression for detachment that could be combined with earlier rate expressions for deposition^{198,199,203} to obtain a surface flux expression analogous to Eq. (60). However, K_r was calculated in a slightly different way and the concentration gradient in the diffusion boundary layer was not accounted for explicitly (see Ref. 211). It is worthwhile to note that in his first paper on particle detachment,⁷³ Dahneke provides an excellent discussion of the kinetic theory of detachment in both gases and liquids, and he describes some applications of the Fokker-Planck equation when particle inertia over energy barriers cannot be neglected (in gases).

The refinements of the Surface Force Boundary Layer Approximation by Ruckenstein and Prieve,¹⁴¹ Ruckenstein,²⁰⁸ and Dahneke²¹¹ are subject to the same restrictions as the original theory; namely, the diffusion boundary layer thickness must be large relative to the surface force boundary layer thickness, and the height of the energy barrier must be at least 5-10 kT. Zimmer and Dahneke²¹² discussed the range of validity of Dahneke's expressions for deposition and detachment. Their discussion agrees qualitatively with the conclusions of Prieve and Ruckenstein²⁰⁶ and Dabros and Adamczyk¹⁸⁴ regarding the limitations of the Surface Force Boundary Layer Approximation.

Although it originally was assumed by Ruckenstein and Prieve¹⁴¹ that particles in the primary minimum would be immobilized at the surface, this is not necessarily the case if there are significant hydrodynamic forces acting parallel to the surface (i.e., the particles could remain in the primary minimum while translating parallel to the surface). Therefore, one final refinement of the Surface Force Boundary Layer Approximation (suggested by Ruckenstein²⁰⁸ and Adamczyk and Van de Ven¹⁹³) is to account for a reversible immobilization reaction at the surface explicitly:

$$\frac{dn_s}{dt} = K_i n_1 - K_e n_s , \quad (63)$$

where

n_s = concentration of mobile particles on the surface (in the primary minimum) (particles/cm²),

n_1 = concentration of mobile particles in the primary minimum (particles/cm²),

K_i = rate constant for immobilization of particles (1/s), and

K_e = rate constant for mobilization of particles (1/s).

In general, the rate constants K_i and K_e can be expected to depend in a complex manner on a large number of system variables, including flow rate and flow-rate fluctuations near the surface, deformability of particles, surface roughness, surface chemical heterogeneities, ability of surfaces to form chemical bonds, blocking of sites by previously deposited particles, etc. Some of these factors will be discussed in the next section. In general, there is not an established body of theory available to predict K_i and K_e from first principles, but their dependence on some of the above factors is understood at least qualitatively.

If Eq. (63) is incorporated into the approximations given by Eqs. (61) and (62), we obtain the following expressions for (1) particle flux from the bulk solution to the surface region, (2) accumulation of particles in the secondary and primary minima (mobile), and (3) accumulation of immobilized particles on the surface:

$$J_0 = -K_m(c_B - Hn_2) , \quad (64a)$$

$$\frac{dn_2}{dt} = K_m(c_B - Hn_2) + K'n_1 - K''n_2, \quad (64b)$$

$$\frac{dn_1}{dt} = -K'n_1 + K''n_2 - K_in_1 + K_en_s, \text{ and} \quad (64c)$$

$$\frac{dn_s}{dt} = K_in_1 - K_en_s. \quad (64d)$$

These equations represent the most general form of the Surface Force Boundary Layer Approximation. If a secondary minimum does not exist, Eq. (64b) can be eliminated and the other equations can be modified accordingly using Dahneke's rate expression for detachment in the absence of a secondary minimum.²¹¹ It is interesting to note that if the rate constants are all large relative to the flow velocities and diffusion coefficients in the bulk solution, the boundary conditions represented by Eq. (64) will effectively reduce to time-independent equilibrium expressions (algebraic equations) relating concentrations in the minima to bulk concentrations (see, for example, Ref. 213). If the energy barrier is low or nonexistent and the primary minimum is deep, it may be best to use a perfect sink boundary condition ($c = 0$ at the surface) in lieu of Eq. (64). On the other hand, if the energy barrier is extremely high and/or there is not a significant primary minimum, it may be best to assume that all particles can come no closer to the surface than the distance to the barrier. In this case, a reflective boundary condition in which flux to the surface is set equal to flux from the surface could be used to solve the transport equations.

3.3.10. Complications for "Real" Colloids and "Real" Surfaces. In developing the expressions for potential energy or force as a function of separation distance for sphere-plane interactions (Secs. 3.3.1 through 3.3.7), it generally was assumed that the sphere and the plane were perfectly smooth, nondeformable, and chemically homogeneous. (An exception was the hydrodynamic detachment force, where it was necessary to assume deformation or surface roughness in order for the normal force to occur.) In reality, surfaces are neither smooth nor homogeneous, and they are often deformable. These realities help explain why there has often been disagreement between theory and experiment when surface forces have been investigated. Indeed, without surface roughness, heterogeneity, and deformation, it would be difficult to account for the observed phenomenon of particle attachment to surfaces when there is a component of flow parallel to the surface. The roughness,

heterogeneities, and deformation all give rise to components of surface forces that oppose particle motion, which makes it possible for immobilization to occur even when the flow field would tend to keep particles translating parallel to the surface. Particle deposition and detachment also can be affected by aging of particle-surface bonds and by the blocking of favorable attachment sites by already deposited particles.

In recent years, many researchers have attempted to quantify the effects of the phenomena mentioned in the previous paragraph. Prieve and Lin²¹⁴ were the first to investigate the effect of heterogeneity in surface potential. They calculated stability ratios for dispersions of particles having normally distributed surface potentials. (Stability ratio is the ratio of flocculation rate in the presence of repulsive energy barriers to flocculation rate in the absence of barriers; see Ref. 5.) They found that for a given mean surface potential, flocculation rates increased as the standard deviation in surface potential increased. Adamczyk et al.²¹⁵ calculated deposition rates to a rotating disk in the presence of a surface energy barrier that had sinusoidal fluctuations with time. Both their approximate analytical calculations and their numerical calculations indicated that deposition rates could be enhanced significantly relative to the rate obtained for a nonfluctuating barrier if the period of the fluctuations was greater than the relaxation time for diffusion of the particles across the electrical double layer. Recognizing that fluctuations in barrier height could occur as a particle translates over a surface, they concluded that surface potential heterogeneities could enhance deposition rates significantly.

Czarnecki and Warszynski²¹⁶ investigated the magnitude of the tangential component of Van der Waals and electrostatic forces that can occur as a result of surface roughness. In their model, they simulated a heterogeneous surface by randomly scattering spheres of random radii (0 to 0.1 μm in diameter) and random surface potentials over a planar surface. These spheres were assumed to be permanently attached to the surface and hence gave the surface a stochastic roughness and potential distribution. A 1- μm -diam sphere of a given surface potential then was stepped (in very small increments) across the surface, and the interaction energy at each step was estimated by calculating the Van der Waals and electrostatic potential between the large sphere and each of the smaller spheres. The interaction energy between the large sphere and the bulk surface was not calculated because it does not have a tangential component. From the change in the tangential component of the interaction energy at each position, the gradient of the tangential potential (i.e., the tangential force) could be calculated at each location on the surface. Czarnecki and

Warszynski²¹⁶ found that, for the parameters they used, the tangential force resulting from Van der Waals and electrostatic interactions could be easily of the same order of magnitude as the hydrodynamic force causing particles to translate along the surface. Therefore, they concluded that tangential forces resulting from surface roughness and surface potential heterogeneity could account for particle immobilization in flow fields.

Dabros and Van de Ven^{217,218} developed a general theory to account for aging of particle-surface bonds as well as the blocking of attachment sites by already deposited particles on surfaces. Referring back to Eqs. (64c) and (64d), essentially what these two phenomena do is make the rate constant K_i dependent on the number of particles immobilized on the surface (blocking) and the rate constant K_e dependent on the time since a particle was immobilized (aging). Accounting for these phenomena, the final expression for the net flux to the surface obtained by Dabros and Van de Ven is²¹⁸

$$J(t) = J_o(t) \left[1 - A \int_0^t J(x) dx \right] - \int_0^t J_o(t) \left[1 - A \int_0^\tau J(x) dx \right] P(t-\tau) k_e(t-\tau) d\tau, \quad (65)$$

where

$J(t)$ = net flux to surface (particles/cm²-s),

$J_o(t)$ = deposition (immobilization) flux to particle-free surface (particles/cm²-s),

A = area blocked per deposited particle (cm²/particle),

$P(t-\tau)$ = probability that a particle deposited between time τ and $\tau + d\tau$ is still attached to the surface at later time t ; this probability can be shown²¹⁸ to be equal to:

$$P(t-\tau) = \exp \left\{ - \int_0^{t-\tau} k_e(x) dx \right\},$$

$k_e(t-\tau)$ = detachment rate constant as a function of time since particle attachment (1/s), and

τ = time of particle attachment (s).

The first term on the right-hand side of Eq. (65) accounts for immobilization on the surface, and the second term accounts for detachment from the surface. Equation (64d) dictates that

$$J_o(t) = K_i n_1(t) . \quad (66)$$

Using this expression and recognizing that $\int_0^t J(x)dx = n_s(t)$, the effective immobilization flux, $J_{im}(t)$, is given by

$$J_{im}(t) = K_i [1 - A n_s(t)] n_1(t) . \quad (67)$$

K_i and A are assumed to be time-invariant, but this clearly would not be the case if certain surface sites are preferred for immobilization over others.

Because of the dependence of k_e on the length of time that particles have been immobilized, it is not possible to obtain an effective detachment rate constant in terms of the number of particles currently deposited, $n_s(t)$. Rather, the detachment flux at any given time is related to the number of particles that were deposited at earlier times, τ . We recognize this by noting that the inner integral of the second term on the right-hand side of Eq. (65) is equal to $n_s(\tau)$. Therefore, the detachment flux, $J_{det}(t)$, must remain an integral expression, which can be written as

$$J_{det}(t) = \int_0^t J_o(t) [1 - A n_s(\tau)] k_e(t - \tau) \exp \left\{ - \int_0^{t-\tau} k_e(x) dx \right\} d\tau . \quad (68)$$

Obviously, evaluation of this integral requires a functional form for $k_e(t - \tau)$. At the present time, there is no theoretical basis for any particular form, and it is expected that the function for k_e will depend strongly on system-specific parameters.

By mass balance, the net immobilization flux is given by

$$J_{net}(t) = \frac{dn_s(t)}{dt} = J_{im}(t) - J_{det}(t) . \quad (69)$$

To account for the effects of blocking and aging in the Surface Force Boundary Layer Approximation, we can substitute Eq. (69) for Eq. (64d) and can modify Eq. (64c) accordingly:

$$\frac{dn_1}{dt} = -K' n_1 + K'' n_2 - J_{net}(t) . \quad (70)$$

This clearly introduces complexity into the boundary layer calculations because of the necessity of evaluating the integrals in the expression for the detachment flux.

If attractive forces between a particle and a flat surface cause the particle to deform (i.e., flatten), the interaction energy between the surfaces can deviate significantly from that expected if no deformation occurs. As discussed in Sec. 3.3.6, deformation can result in the particle becoming immobilized on the surface when it would otherwise translate parallel to the surface. Sharma et al.¹⁶⁵ have analyzed this phenomenon, and they have estimated particle deformation based on the magnitude of hydrodynamic detachment forces required to remove particles from surfaces. Detailed discussions of the theory of deformation of elastic bodies near surfaces and the resultant effect on surface forces are provided by Johnson et al.,²¹⁹ St. John and Montgomery,²²⁰ Dahneke,²²¹ Derjaguin et al.,²²² and Muller et al.²²³ Deformation is more likely to occur in larger bodies (Sharma et al. investigated spheres with diameters ranging from 10 to 40 μm), so it is possible that the relatively small colloids that would be considered as tracers in natural hydrologic systems would not deform significantly. However, polystyrene has a relatively high elasticity, so deformation could occur if polystyrene microspheres are used as tracers.

In colloid tracer experiments, the diluteness of the dispersions and the expected repulsive nature of the colloid-wall interactions will help to minimize blocking effects. Aging and deformation, if they occur, will be very difficult to distinguish from other effects. For instance, aging also could be explained by chemical heterogeneities on the rock surface, which could result in different detachment kinetics on different parts of the surface. Deformation will alter the apparent shape of the interaction energy profile; thus, it could be described equally well by modifying parameters in the interaction energy expressions to "fit" the observed behavior (e.g., a different value of the Hamaker constant).

One advantage of using the Surface Force Boundary Layer Approximation to describe colloid-wall interactions is that the complex effects associated with surface roughness, chemical heterogeneity, and, to some extent, aging and deformation, can all be accounted for indirectly by using experimentally obtained estimates of the kinetic parameters in Eq. (64). Experimental methods that can be used to estimate these kinetic parameters are discussed in Sec. 3.4. As a computational example, Adamczyk et al.²¹⁵ showed that a simple kinetic expression with a single deposition rate constant could be used to describe deposition onto a surface with a distribution of repulsive surface potentials. This indirect method of accounting for surface phenomena by "lumping" effects into kinetic parameters is very attractive for

studies involving natural systems where heterogeneities and nonidealities may very well dominate colloid-surface interactions.

3.4. Colloid Deposition onto Idealized Collector Surfaces

Numerous investigators have conducted experimental and/or modeling studies of colloid deposition from liquid dispersions onto various collector surfaces in various flow fields. Although it is not the intent of this literature review to describe these studies in detail, many papers are cited here for reference. A number of these references were also cited in Section 3.3.9 (e.g., Refs. 44, 103, 180-197, 200-202, 204, 209, and 210). The aerosol literature was excluded from this literature survey because there are many differences between deposition from aerosols and liquid dispersions (turbulent transport with significant inertia rather than viscous transport without inertia) and also because there is a sufficiently large body of literature for liquid dispersions. Filtration from liquid dispersions in porous media, a special case of colloid deposition, is discussed in Sec. 3.5.

In modeling colloid deposition onto idealized collector surfaces, most investigators have taken the following approach.

1. A steady-state analytical or numerical solution of the flow field near the collector is obtained.
2. The fluid velocity as a function of position then is substituted directly into the species continuity equation [Eq. (33)].
3. The continuity equation is reduced to only those terms that are needed for the problem of interest. Frequently, the time derivative is eliminated because only a steady-state solution is desired.
4. Boundary conditions are defined for the problem. This step includes the assumption or calculation of an energy profile (interaction energy vs separation distance) near the solid-liquid surface. Any of the forces discussed in Secs. 3.3.1 through 3.3.7 can be considered.
5. The investigator decides whether to account for the surface forces explicitly in the continuity equation (i.e., solve the continuity equation over the entire distance between the bulk solution and the primary minimum) or to lump the effects of surface forces into a mathematical boundary condition such as the Surface Force Boundary Layer Approximation, the perfect sink boundary condition, or a reflective boundary condition.

6. If surface forces are included in the continuity equation, a numerical solution is required. The discretization of the spatial domain must be much finer near the solid-liquid surface to account for the effects of the short-range forces properly.
7. If surface forces are lumped into a mathematical boundary condition, the continuity equation will contain only terms for diffusion, convection, and gravity. In some cases, a limiting analytical solution can be obtained.

In contrast to this approach, the particle trajectory method, discussed in Sec. 3.2.1 [see Eqs. (26) and (27)] has been used only when the geometry and/or flow field are complicated enough that the continuity equation becomes impractical to solve. However, because of its inherent flexibility, the particle trajectory method has recently gained popularity in modeling transport through complex systems such as heterogeneous porous media⁹¹⁻⁹⁵ and variable aperture fractures.^{55-57,70,72} In these applications, a large number of stochastically moving particles must be simulated to obtain a valid statistical distribution of the behavior of the transporting species.

Adamczyk et al.,⁴⁴ Adamczyk and Van de Ven,¹⁹³ Adamczyk,^{45,224} Van de Ven,²⁷ and Jia and Williams⁴⁶ all provide good general discussions of approaches that have been taken to calculate particle deposition on idealized collectors (as well as experimental results for such systems). In the work of Adamczyk, Van de Ven and co-workers, the results of deposition calculations typically are presented in terms of a dimensionless flux called the Sherwood number, N_{Sh} :

$$N_{Sh} = \frac{J_o a}{D_{\infty} c_{\infty}}, \quad (71)$$

where

- J_o = particle flux to surface (particles/cm²-s),
- a = particle dimension (radius or diameter) (cm),
- D_{∞} = bulk diffusion coefficient (cm²/s), and
- c_{∞} = bulk concentration (particles/cm³).

This quantity allows meaningful flux comparisons between systems having different-sized particles or different bulk concentrations.

Experimentally, the rotating disk frequently has been studied as a collector surface because the flow field has been solved analytically by Cochran²²⁵ and Levich²²⁶ and because the disk is a uniformly accessible surface, meaning that the flux of species to the surface is independent of position. Early experimental studies of colloid deposition on rotating disks were conducted by Marshall and Kitchener,²²⁷ Hull and Kitchener,²²⁸ and Clint et al.²²⁹ Many investigators have obtained solutions describing steady-state deposition of colloids onto rotating disk surfaces, including Dabros and Czarnecki,²³⁰ Dabros et al.,¹⁸¹ Adamczyk and Dabros,¹⁸² Adamczyk et al.,^{183,194} Dabros and Adamczyk,¹⁸⁴ Prieve and Lin,¹⁸⁵ and Rajagopalan and Kim.¹³³ Adamczyk^{186,187} has obtained transient solutions of particle flux to the rotating disk surface.

In recent years, the stagnation point or wall-jet flow collector has become increasingly popular for colloid deposition studies because it allows deposition to be observed in real time on a uniformly accessible surface. (With a rotating disk, the disk must be stopped and removed from the dispersion to observe particle deposition.) Real-time observation of deposition and detachment allows direct estimation of kinetic parameters for the Surface Force Boundary Layer Approximation. This approach is superior to indirect back-calculation of parameters, which can be ambiguous (that is, there may be more than one combination of parameter values that describe the observed behavior equally well). The wall-jet apparatus consists of a laminar "jet" issuing from a tube onto a transparent planar surface oriented perpendicular to the axis of the tube and very close to the tube exit. The apparatus originally was applied to colloid deposition studies by Dabros and Van de Ven.¹⁹² Glauert²³¹ obtained an approximate analytical solution of the flow field associated with the wall jet, and Deshpande and Vaishnav²³² and Dabros and Van de Ven¹⁹² subsequently obtained more exact numerical solutions. These solutions indicate that for a small region near the center of the jet, where the impingement of fluid on the planar surface results in stagnation point flow, the surface is essentially uniformly accessible.¹⁹² The deposition of particles on the surface can be observed in real time using a microscope or, more recently, using an evanescent wave technique, which is also called total internal reflection microscopy.^{209,210,233-236} Investigators that have conducted studies using the wall-jet apparatus include Dabros and Van de Ven,^{192,196} Adamczyk et al.,^{237,238} Boluk and Van de Ven,¹⁷³ Varennes and Van de Ven,²³⁹⁻²⁴¹ Dijt et al.,²⁴² and Albery et al.^{209,210,243} Theoretical calculations for stagnation point flow have also been done by Chari and Rajagopalan¹⁰³ and Peters et al.²⁴⁴

Smooth parallel-plate flow channels also have been used as collectors in experimental colloid deposition studies.^{197,202,245,246} Like the stagnation point flow collector, these types of flow cells can be designed to allow direct observation of deposition and detachment processes, thus allowing direct estimation of kinetic parameters.^{197,202,246} Deposition calculations for these types of systems have been done by Bowen et al.,²⁰⁴ Bowen and Epstein,²⁴⁵ and Adamczyk and Van de Ven.¹⁸⁸

Other collectors for which deposition calculations have been done include cylindrical channels,^{188,204,247} cylinders in uniform flow,¹⁸⁹ flat plates in uniform flow,¹⁹⁰ and continuously moving surfaces.¹⁹¹ Experimental studies with these systems are not prevalent in the literature, probably because the collector surfaces are difficult to observe directly. However, deposition in beds of fibers is a situation for which cylindrical collector calculations may apply. Spherical collectors are discussed in Sec. 3.5, as they are applicable to filtration theory.

3.5. Colloid Transport in Porous Media: Filtration Theory

Transport of colloids in porous media is a subject that has been studied for many years, primarily because of the practical interest in the filtration of particulate contaminants from liquid and gaseous streams. Although the subject is of limited applicability to the problem of colloid transport through fractures, any discussion of colloid transport in groundwater systems would seem incomplete without at least a brief summary of filtration theory.

Because of the complex porous structure in an assemblage of fine grains, an exact microscopic description of the flow field in a granular bed is, even today, impossible. Instead, Darcy's equation [Eq. (3)] typically is used to describe flow through porous media. The one-dimensional continuity equation with only the convection term and a term accounting for deposition onto the porous medium generally is used to describe the movement of particles through a filtration bed:

$$\epsilon \left(\frac{dc}{dt} \right) = -v \left(\frac{dc}{dx} \right) - \frac{SA}{V} \left(\frac{ds}{dt} \right), \quad (72)$$

where

ϵ = porosity of bed,

c = concentration of particles in solution (particles/cm³),

s = concentration of particles on surface of grains (particles/cm²),

v = fluid velocity in bed (cm/s), and
 SA/V = surface area to volume ratio (1/cm).

Based on slow sand filter data, Iwasaki²⁴⁸ proposed the following empirical expression to describe the concentration profile in a filter bed:

$$\frac{dc}{dx} = -\lambda c, \quad (73)$$

where λ = filtration coefficient (1/cm). Other more complicated expressions have been proposed, primarily in an attempt to account for the apparent change in λ as a function of particle accumulation in the filter bed. Some of these expressions are summarized by Tien and Payatakes.²⁴⁹ However, Eq. (73) still is used widely, particularly for describing deposition at low particle accumulations in the porous media.

Substituting Eq. (73) into Eq. (72) and assuming that dc/dt is zero (as it is typically when λ is measured), we obtain

$$\frac{ds}{dt} = \left(\frac{V}{SA} \right) v \lambda c. \quad (74)$$

Thus, the local deposition rate is described by a simple first-order irreversible kinetic rate expression. In principle, Eqs. (72) and (74) can be solved simultaneously with appropriate initial and boundary conditions to obtain the concentration distribution and particle accumulation in space and time in a packed bed.

A great deal of effort has been expended over the past 30–40 yr in trying to predict λ from first principles. Using the approach of Payatakes et al.⁸³ as summarized by Tien and Payatakes,²⁴⁹ the filtration coefficient is given by

$$\lambda = -B \ln(1-\eta), \quad (75)$$

where

η = a dimensionless collection efficiency factor that accounts for the fraction of particles deposited per unit element length of the filter bed (i.e., the length of an average grain) and

B = a geometric factor that varies slightly depending on the model used to describe the microstructure of the porous medium.

Because η is typically small, $-\ln(1-\eta)$ usually is approximated as η . If the porous media is assumed to be an assemblage of spheres, each of which has a flow field around it given by the sphere-in-cell model of Happel,²⁵⁰ it can be shown⁸⁷ that

$$B = \frac{3(1-\varepsilon)}{2D_p},$$

where D_p is a characteristic or average diameter of the porous medium grains. Thus,

$$\lambda = \left[\frac{3(1-\varepsilon)}{2D_p} \right] \eta. \quad (76)$$

The problem of determining the filtration coefficient now boils down to determining the collection efficiency, η . Numerous investigators have addressed this problem.^{80,81,83-88,180,251-253} Many of these studies have been summarized by Tien and Payatakes²⁴⁹ and Spielman.⁴³ In essentially all these studies (except for the one by Prieve and Ruckenstein¹⁸⁰), a "limiting trajectory" approach was used to determine η . In this approach, a particle is placed in the downstream stagnation point of the collector sphere and then the trajectory equation [e.g., Eq. (26)] is integrated backwards until the particle is at a position well upstream of the sphere. The collection efficiency is determined by the ratio of the upstream cross-sectional area enclosed by the limiting trajectory to the cross-sectional area of the collector. In these calculations, diffusion is ignored (no stochastic force), but surface forces and gravity typically are included. The studies mentioned above include various combinations of surface forces, flow fields, and collector configurations (spheres or constricted tubes). Rather than using the limiting trajectory approach, Prieve and Ruckenstein¹⁸⁰ obtained a solution of the continuity equation (including the diffusion term) to estimate deposition rates on spherical collectors.

The results from trajectory calculations are not easily condensed into simple expressions relating the various model parameters to η . However, Rajagopalan and Tien⁸⁷ obtained an empirical expression that fit their numerical results reasonably well for the case of spherical collectors in the flow field calculated by Happel.²⁵⁰

They explicitly included only the effects of fluid convection, Van der Waals forces, and gravity in their calculations, but they added a term derived by Cookson²⁵⁴ from the earlier work of Natanson²⁵⁵ and Levich²²⁶ to account for diffusion to spherical collectors. The resulting expression for the filtration coefficient, as presented by McDowell-Boyer et al. in their review article, is²⁵⁶

$$\eta = \left[4A_s^{1/3} \left(\frac{U d_m}{D_p} \right)^{-2/3} + 0.56A_s \left(\frac{A}{\mu d_p^2 U} \right)^{1/8} \left(\frac{d_p}{d_m} \right)^{15/8} + 0.0024A_s \left(\frac{v_s}{U} \right)^{1.2} \left(\frac{d_p}{d_m} \right)^{-0.4} \right], \quad (77)$$

where

- U = interstitial fluid velocity (cm/s),
- D_p = particle diffusion coefficient (far from surfaces) (cm²/s),
- d_m = characteristic diameter of porous media grains (cm),
- d_p = particle diameter (cm),
- A = Hamaker constant (ergs),
- v_s = gravitational settling velocity of particle [see Eq. (20)] (cm/s),
- $A_s = \frac{1 - P^5}{1 - 1.5P + 1.5P^5 - P^6}$, and
- $P = (1 - \epsilon)^{1/3}$.

The three terms in brackets account for diffusion, interception resulting from Van der Waals attraction, and gravity, respectively. Obviously, the expression for η will be different if other forces are included in the model or other collector geometries are assumed.

Since the late 1970s, filtration theory has made incremental advances along several fronts. O'Melia and coworkers have done careful experimental studies in an attempt to elucidate the dependence of the collection efficiency on various factors affecting surface interactions.^{21,22,30,257} Matijevic and co-workers have contributed to the understanding of particle deposition and detachment in porous media through a series of experimental studies in packed beds.²⁵⁸⁻²⁶⁵ Particle detachment has been formally accounted for in packed-bed filtration models by including a first-order kinetic term for detachment in the model equations [i.e., an additional term, $-k'c$, on the right-hand side of Eq. (74)].^{266,267} More sophisticated models of the porous medium, such as models consisting of tube networks,^{268,269} also have been

introduced. Some of these models have features that attempt to account for roughness of the grains.²⁷⁰ Song and Elimelech²⁷¹ have extended the work of Prieve and Ruckenstein¹⁸⁰ by developing a boundary condition for the species continuity equation that can be used to obtain estimates of the collection efficiency for diffusive particles at low flow rates when Happel's sphere-in-cell porous media model is used. Vitthal and Sharma²⁷² have calculated particle trajectories using mobility tensors for interactions between multiple spherical bodies to explicitly account for the effects of previously deposited particles on the movement and deposition of new particles entering an assemblage of collector spheres that represent a porous medium.

4. CONCLUSIONS

Many studies have linked accelerated transport of contaminants in groundwater systems to association of the contaminants with colloids. Synthetic colloids have been used successfully as tracers in both laboratory and field transport experiments. This experience base, as well as a knowledge of the fundamental properties of colloids, suggest that synthetic colloids having the same surface charge sign as the bulk of the media in a geologic system could prove to be excellent "worst-case" tracers in field experiments because (1) they should closely follow fluid streamlines and (2) they will have less tendency to diffuse into pores or dead spaces in the media than soluble-species tracers. Polystyrene microspheres are probably the best initial choice for a synthetic colloid tracer because of their narrow and controllable size distribution, controllable surface properties, sphericity, low detection limit (potentially), and distinguishability from background colloids.

The transport of colloids through saturated natural fractures is a very diverse field of study that, in this review, was divided into three main areas of study: (1) saturated fluid flow through fractures; (2) colloid transport by convection, diffusion, and force fields; and (3) colloid interactions with surfaces. For modeling saturated fluid flow through natural fractures, it is suggested that lubrication theory (the two-dimensional Reynolds equation) be used to approximate the flow field in a fracture given an aperture distribution. Compared with models that assume idealized geometries (e.g., parallel plates), this approach has the advantage of explicitly accounting for multiple flow pathways through the fracture, which eliminates the need for an empirical parameter (the dispersion coefficient) to account for flow-field

dispersion. Solving the lubrication equations is also computationally more feasible than solving the full governing equations in three dimensions.

Given a flow field solution, particle tracking methods probably offer the best approach to modeling the transport of colloids through saturated fractures provided the dispersions are dilute enough that the particles move independently. Particle tracking methods can account for flow field heterogeneities, heterogeneities in the properties of the geologic media, particle interactions with surfaces, and diffusion into the rock matrix with more flexibility and less computational burden than traditional continuity equation methods. Particle tracking calculations are also inherently parallelizable on multiprocessor computers.

A kinetic boundary layer approximation in which colloid interactions with surfaces are assumed to follow first-order kinetics is the most convenient method of accounting for surface interactions in a colloid transport model. It is not practical or feasible to explicitly account for each of the various surface forces that can contribute to colloid-surface interactions in a natural system. The kinetic boundary layer approximation effectively lumps the effects of all the important surface forces into a few empirical parameters that, in principle, can be determined experimentally.

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