

Visualization and Modeling of Polystyrol Colloid Transport in a Silicon Micromodel

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ABSTRACT

A new experimental approach and complementary model analysis are presented for studying colloid transport and fate in porous media. The experimental approach combines high precision etching to create a controlled pore network in a silicon wafer (i.e., micromodel), with epifluorescent microscopy. Two different sizes of latex colloids were used; each was stained with a fluorescent dye. During an experiment, water with colloids was purged through a micromodel at different flow rates. Flow paths and particle velocities were determined and compared with flow paths calculated using a two-dimensional (2D) lattice Boltzmann (LB) model. For 50% of the colloids evaluated, agreement between measured and calculated flow paths and velocities were excellent. For 20%, flow paths agreed, but calculated velocities were less. This is attributed to the parabolic velocity profile across the micromodel depth, which was not accounted for in the 2D flow model. For 12%, flow paths also agreed, but calculated velocities were less. These colloids were close to grain surfaces, where model errors increase. Also, particle-surface interactions were not accounted for in the model; this may have contributed to the discrepancy. For the remaining 18% of colloids evaluated, neither flow paths nor velocities agreed. The majority of colloids in this last case were observed after breakthrough, when concentrations were high. The discrepancies may be due to particle-particle interactions that were not accounted for in the model. Filtration efficiencies for all colloid sizes at different flow rates were calculated from filtration theory. Attachment rates were obtained from successive images during an experiment. With these, attachment efficiencies were calculated, and these agreed with literature values. The study demonstrates that excellent agreement between experimental and model results for colloid transport at the pore scale can be obtained. The results also demonstrate that when experimental and model results do not agree, mechanistic inferences and system limitations can be evaluated.

COLLOIDS ARE UBIQUITOUS in many groundwater aquifers. They originate from weathering processes of the aquifer matrix, degradation of biological material, and precipitation of supersaturated solutions (Buffle et al., 1998). Under certain conditions, colloids may facilitate the transport of hazardous substances such as radionuclides (Tanaka and Nagasaki, 1997; Kersting et al., 1999), heavy metals (Karathanasis, 1999; Kretzschmar et al., 1999), and organic substances (Roy and Dzombak, 1998; Villholth, 1999). It is therefore of great interest to predict colloid transport.

Colloid transport is very sensitive to hydrochemical and hydrodynamic conditions (Roy and Dzombak, 1997; Bergendahl and Grasso, 2000; Bradford et al., 2002). Con-

ventional methods to investigate colloid transport often involve column studies. Here, colloid concentrations are measured at the column effluent or at selected points along the column length. Unfortunately, such methods do not clearly distinguish how spatial and temporal changes in hydrochemical and hydrodynamic conditions affect colloid transport. For example, breakthrough curves (BTCs) obtained from column effluent represent some average behavior of colloids in the column (Baumann et al., 2002). Since different heterogeneous realizations can contribute to such BTCs, the processes that control colloid transport in the column are obscured.

Filtration theory (Happel, 1958; Rajagopalan and Tien, 1976) is often used to evaluate colloid transport. It accounts for the hydrodynamic processes that lead to a contact between particles and filter surfaces. The attachment efficiency, α , describes the probability that a collision between a particle and a filter grain results in a permanent attachment (Elimelech and O'Melia, 1990). This parameter lumps the physical and chemical interactions between colloids and surface at the pore scale. Often the attachment efficiency is used as a fitting parameter for the inverse modeling of colloid breakthrough curves (Ren et al., 2000; Huber et al., 2000).

The boundary conditions, especially the pore topology, the local flow velocities, and the chemical heterogeneity of the surface, can vary in the pore space. In column tests, the packing density and the topology of the pore network are unknown, and local physical and chemical heterogeneities cannot be assessed (Sugita and Gillham, 1995). Also, preferential flow inside the column is obscured. Therefore, the inverse derivation of filtration parameters e.g., the attachment efficiency) are representative only for the length scale of the column. As a result, upscaling and downscaling become difficult, and experimentally derived parameters do not always conform to theory. A promising approach to study pore-scale processes involves the use of micromodels.

In groundwater and vadose zone studies, micromodels are representations of porous media etched into silicon wafers, glass, or polymers (Soll et al., 1993). Sometimes thin layers of glass beads or sand embedded between glass plates are also referred to as micromodels. The main purposes of micromodel experiments are to increase spatial and temporal resolution and to provide direct quantitative access to processes at the pore scale.

An overview of micromodel applications is documented in Table 1. Each table entry notes the experimental approach and objectives, associated references, and the type of porous media represented. Only two of the references involved study of colloid transport (Wan and Wilson, 1994b, 1996). In one study, the role of the

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Abbreviations: BTC, breakthrough curve; DDI, deionized distilled; LB, lattice Boltzmann; PTA, particle tracking algorithm; UV, ultraviolet; 2D, two-dimensional; 3D, three-dimensional.

Table 1. Selected applications of micromodels.

Class	Objective	Micromodel	Pore structure	Reference
Microbiology	Dispersion of <i>E. coli</i> Growth and mobility of biofilms	glass	homogen., cylinder homogen., triangular network cubic channel with heterog. apertures	Lanning and Ford (2002) Stewart and Fogler (2002, 2001), Kim and Fogler (2000) Dupin and McCarty (2000), Nambi et al. (2003)
Multiphase processes	Dissolution of NAPLs, determination of mass transfer rates	glass	homogen., tubes	Sahloul et al. (2002), Jia et al. (1999), Zhong et al. (2001)
	Transport of NAPLs in unsat. porous media	glass silicon wafer	monolayer of glass beads homogen., heterogen. pore structure taken from a thin section of sand stone	Kennedy and Lennox (1997) Chomsurin and Werth (2003) Keller et al. (1997)
	Soil cleanup with surfactants	glass	homogen. cubic network, heterogen. network	Jeong et al. (2000)
	Numerical modeling of three-phase flow	glass	homogen. network	Pereira et al. (1996), Pereira (1999)
	Fluid flow	glass	monolayer of glass beads homogen. network	Corapcioglu and Fedirchuk (1999) Corapcioglu et al. (1997), Soll et al. (1993)
	Capillary rise	glass	triangular network	Bernadiner (1998)
	Development of air bubbles	glass		Li and Yortsos (1995)
	Fracture-matrix interactions	glass	homogen. pore network with fracture	Haghighi et al. (1994), Wan et al. (1996)
	Cementation due to gas hydrates	glass		Tohidi et al. (2001)
	Kinetics of carbonate cementation in wells	glass		Dawe and Zhang (1997)
Oil exploration	Effects of injected polymer gels on the flow of water and oil	glass		Al-Sharji et al. (2001)
	Transport of gas condensate	glass		Jamiolahmady et al. (2000), Coskuner (1997), Wang and Mohanty (2000), Bora et al. (2000)
Colloids	Attachment at the air-water-interface	glass	homogen., heterogen.	Wan and Wilson (1994b), Wan et al. (1996)

gas-water interface for the transport of fluorescence latex beads, clay particles, and bacteria was investigated in an etched glass micromodel. The gas water interface turned out to be an effective sink for both hydrophobic and hydrophilic particles (Wan and Wilson, 1994b). The data was validated with column tests (Wan and Wilson, 1994a). In the other study, fluorescent colloids were used as a tracer for the flow velocities in a glass micromodel with a pore network divided by a fracture with an aperture of 1 mm.

The objective of this work is to demonstrate a new approach to study pore-scale transport mechanisms of colloids. This approach combines the power of direct observation in micromodels with a pore-scale model analysis of water flow paths and velocities. In contrast to previous experimental studies of colloids using micromodels, we used a plasma etching technique to create highly controlled 2D pore structures with vertical walls and flat bottoms. This allowed us to quantitatively compare colloid flow paths and velocities in pore bodies with those determined for water using the LB model.

MATERIALS AND METHODS

Materials

Two different sizes of spherical, fluorescent colloids (691 and 1960 nm; Duke Scientific, Palo Alto, CA) were used. They were surfactant free, and the reported particle density is 1.05 g cm^{-3} . The input pulse concentrations for the 691- and 1960-

nm colloids were 1.1×10^{12} and $4.8 \times 10^{10} \text{ L}^{-1}$, respectively. The input mass concentration was 0.2 mg L^{-1} for both types of colloids. The ζ potential of the colloids was measured using a Zetaphoremeter III (SEPHY, Paris). The values in deionized distilled water (DDI water) at a pH of 5.6 (unbuffered dispersion) were -50.2 ± 4.6 and $-26.0 \pm 2.8 \text{ mV}$ for the for the 691- and 1960-nm colloids, respectively. At pH 5.6 the surface of the micromodel also is negatively charged.

Micromodel Fabrication

Digital patterns of the micromodel pore network, and inlet and outlet channels, were created using computer-aided design software and then transferred onto a lithography mask using an electron beam lithography machine (Hitachi HL-700F, Hitachi High-Technologies Corp, Tokyo). The pattern was etched into a silicon wafer in a class 10 cleanroom environment. All silicon wafers were 10.56 cm in diameter, 500 μm thick, single sided polished, 4 to 6 Ω , N <1,0,0> crystal. They were purchased from Montco Silicon Technologies, Inc. (Spring City, PA). Each wafer was first chemically cleaned using a modified RCA cleaning method (Kern, 1983). Next, a 0.1- μm -thick silicon dioxide layer was deposited onto each silicon wafer using a dry oxidation process. The silicon dioxide served as a protective coating during wet etching. The dry oxidation was conducted in a 1000°C tube oven under O_2 -saturated conditions for 4 h.

After coating with silicon dioxide, the wafer was coated with a thin layer of positive photoresist (SPR220-7, Shipley Company, L.L.C., Marlborough, MA). Next, the lithography mask was placed on top of the wafer, and the assembly was exposed to ultraviolet (UV) light (17 mW cm^{-1} , 20 s) using

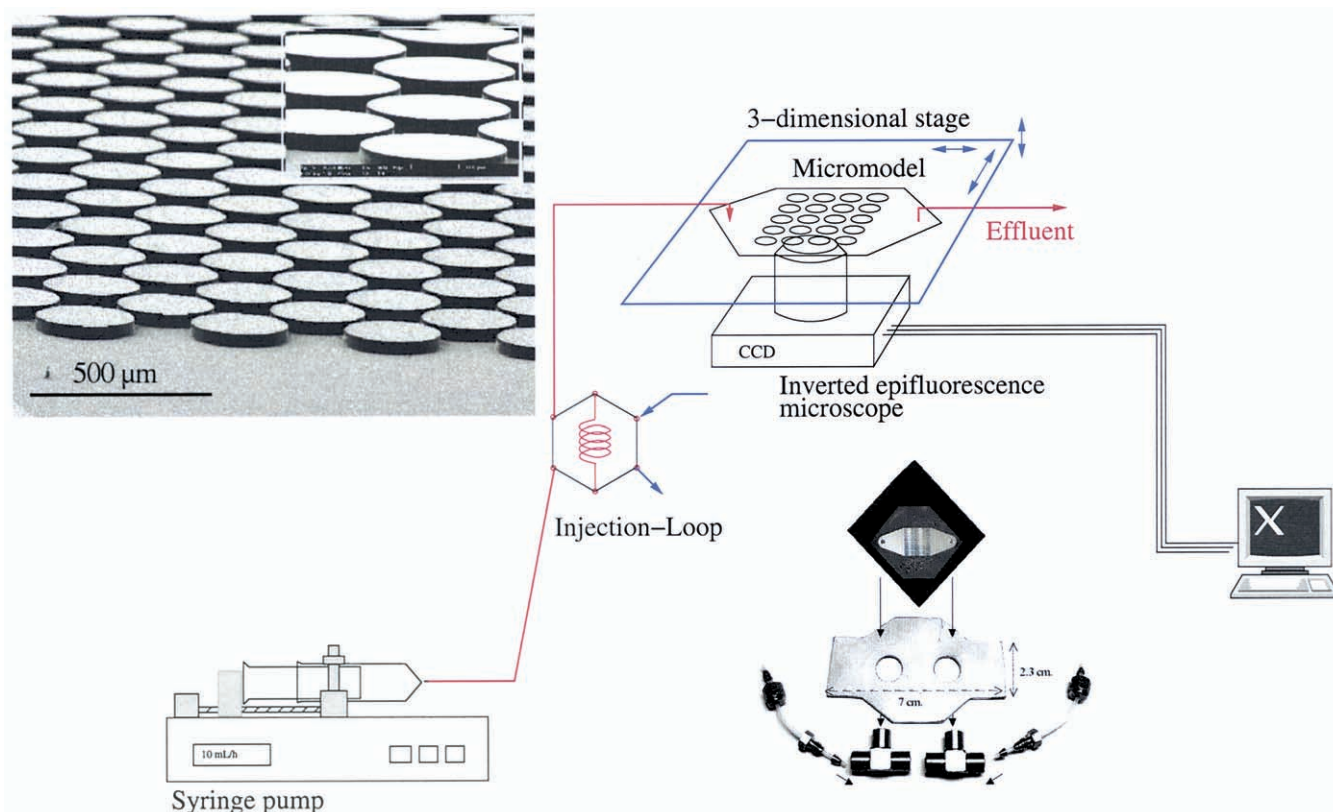


Fig. 1. Experimental setup and scanning electron microscope picture of the homogeneous micromodel.

a Karl Suss Aligner with minimum resolution of 1 μm . Photoresist exposed to the UV light was removed from the wafer surface by washing with LDD26W (Shipley Company) developer. The exposed oxide layer on the silicon surface was then wet etched with buffered hydrofluoric acid (microfabrication grade, Sigma Aldrich, St. Louis, MO), and the remaining photoresist served as an etch mask. Next, the exposed silicon surface was etched to a depth of 50 μm using a plasma-based STS Deep RIE Etcher (etching rate was 6 $\mu\text{m min}^{-1}$).

After etching, the photoresist was removed using oxygen plasma, the wafer was cleaned using sulfuric acid (95% v/v) and hydrogen peroxide (35% v/v) at a ratio of 1:9, and the remaining oxide was stripped using the buffered hydrofluoric acid. The wafer was then cleaned thoroughly with distilled water and spun dry. Last, a uniform 0.1- μm silicon dioxide layer was created on the etched pore channels using the dry oxidation process. A scanning electron microscope image of the homogeneous pore structure and a schematic of the entire micromodel assembly are shown in Fig. 1. Inlet and outlet holes were drilled at both ends of a micromodel pore network using an ultrasonic disk cutter operated with carbide slurry (0.16-cm o.d. cutting bit, Fischione Instruments Inc., Export, PA). The wafer was then cleaned with distilled water and blown dry. Next, a 0.5-mm-thick Pyrex plate (Corning 7740, standard flat double sided polished, Bullen Ultrasonics, Inc., Eaton, OH) was attached to the etched silicon wafer by an anodic bonding process. The anodic bonding is an irreversible electrochemical process. Details of electrochemical reactions and the conditions during anodic bonding are discussed in Albaugh and Rasmussen (1992).

After bonding, the micromodel was mounted on an aluminum plate for structural support. The aluminum plate dimensions were chosen so the plate fit on the stage of the fluorescence microscope during a dissolution experiment. A water-resistant

epoxy (Quick Set, Loctite Corp., Rocky Hill, CT) was used to fix 0.16-cm low dead-volume stainless-steel tees (Swagelok, Solon, OH) over the drilled holes. PTFE Teflon tubing (0.16-cm diam., Cole Parmer, Vernon Hills, IL) was connected to the tees. The different parts of a micromodel assembly are shown in Fig. 1. Last, the micromodel was incubated in an oven at 50°C for at least 3 h to strengthen the Epoxy bond before use. More details of micromodel fabrication steps are in Chomsurin (2003). Micromodel pore network information is summarized in Table 2.

Micromodel Experiment

A micromodel was initially flushed with CO_2 to facilitate gas displacement. Next, it was continuously purged with DDI water at different flow rates using a syringe pump (Cole Palmer, Vernon Hills, IL). Preliminary experiments with the syringe pump and spherical colloids showed no visual pulsations of the flow; that is, the flow of the colloids was steady. Care was taken to eliminate external vibrations and shocks, as they might influence colloidal transport. Colloid dispersions were delivered as block inputs from the bypass loop (110 μL) of a six-port valve (Upchurch Scientific, Oak Harbor, WA) at flow rates between 5 and 15 $\mu\text{L h}^{-1}$. Using $U = Q/A\epsilon$, with the flow rate Q , the cross-sectional area of the micromodel

Table 2. Micromodel pore network information.

Property	Value
Porosity	0.38
Grain size range (equiv. diameter), μm	300
Average grain size (equiv. diameter), μm	300
Average pore space, μm	173
Average pore throat, μm	35
Aspect ratio (Pore space width/pore throat width)	4.9

A , and the porosity ϵ , the average linear velocities U in the pore network can be calculated to a range between 63 and 189 cm d⁻¹. These are in the range of velocities found in a silty sand aquifer. Some deliberate increases of the flow rates up to 150 $\mu\text{L h}^{-1}$ were done to investigate fast flow phenomena. The actual flow rates are given in the text. All experiments were run at 20°C. Since a complete removal of colloids from the micromodel was not possible, a new micromodel was used for each different colloid size, or whenever the micromodel had more than 10 colloids attached in a single pore space.

Image Acquisition

Images of fluorescent colloids in micromodel pores were obtained with an inverted epifluorescence microscope (Epi-phot-200, Nikon, Melville, NY) equipped with a digital camera (8-bit, RT monochrome Spot camera, Diagnostic Instruments, Sterling Heights, MI) and motorized stage (0.1- μm resolution, Prior Scientific Inc., Rockland, MA), both controlled by Meta-morph digital software (Universal Imaging Corp., Downingtown, PA). During each experiment the micromodel was mounted glass side down on the stage and images were acquired at periodic intervals in different sections of the micromodel with either a 10 $\times$ or 20 $\times$ objective (plus a 10 $\times$ eyepiece). This corresponded to a pixel size of 0.7 or 0.35 μm , respectively. The exposure time for each image was 500 ms.

THEORY

Calculation of Theoretical Attachment Efficiency

Theoretical attachment rates were calculated using filtration theory (Rajagopalan and Tien, 1976). First, the filtration efficiency η , the probability for a colloid to get into contact with a single cylinder due to gravitation, interception, or diffusion, is calculated with Eq. [1] and [2]

$$\eta = \frac{\rho_p - \rho_f}{18\mu U} g d_p^2 + \frac{3}{2} A_s \left(\frac{d_p}{d_g} \right)^2 + 0.897 \sqrt[3]{A_s} \left(\frac{k_B T}{\mu d_p d_g U} \right)^{2/3} \quad [1]$$

$$A_s = \frac{1 - \gamma^5}{1 - 1.5\gamma + 1.5\gamma^5 - \gamma^6}; \quad \gamma = \sqrt[3]{1 - \epsilon} \quad [2]$$

d_p and d_g denote the diameter of the particles and of the filter grains, respectively; ρ_p and ρ_f are the bulk density of the particle and the fluid, respectively; μ is the fluid viscosity; U is the average linear velocity; g is the gravitational acceleration; A_s is a constant specific to the porous medium; k_B is Boltzmann's constant; T is the thermodynamic temperature; and ϵ is the porosity. Second, the filtration rates are calculated by multiplying the number of colloids approaching a cylinder, obtained from the concentration of colloids and the flow rate, with the filtration efficiency η . The surface area of each collector (depth = 50 μm) is 47 124 μm^2 . Note that the surface area of a spherical collector with 300- μm diameter is 282 743 μm^2 . Thus, the filtration efficiency at a cylindrical post is one-sixth that of a spherical collector. Finally, the attachment efficiency α , the probability that a collision results in a permanent attachment (Elimelech and O'Melia, 1990), is the measured attachment rate divided by the filtration rate. The micromodel setup provides direct access to the attachment rate by counting the immobile colloids over time.

Approximation of the Colloid-Surface Interaction Energy

The interaction energy between the colloids and the surface of the micromodel was calculated using classical DLVO theory

(Verwey and Overbeek, 1948; Derjaguin and Landau, 1941). The total interaction energy is considered as the sum of the electrostatic interaction energy ΔG^{EL} and the Van-der-Waals interaction energy ΔG^{VDW} . The electrostatic interaction energy is obtained from

$$\Delta G^{\text{EL}} = 64\pi\epsilon\alpha_c \left(\frac{k_B T}{z_i e} \right)^2 \gamma_i \gamma_2 \exp(-\kappa s) \quad [3]$$

where ϵ is the permittivity of the medium, a_c is the colloid radius, z_i is the ion valance, e is the electron charge, and s is the distance between surface and colloid. γ_i is given by

$$\gamma_i = \tanh \left(\frac{z_i e \psi_{0,i}}{4k_B T} \right) \quad [4]$$

with the surface potential $\psi_{0,i}$, and κ is given by

$$\kappa = \sqrt{\frac{e^2 \sum n_{j0} z_j^2}{\epsilon k_B T}} \quad [5]$$

with the number of ions in bulk solution n_{j0} . The Van-der-Waals interaction energy is obtained from

$$\Delta G^{\text{VDW}} = \frac{A_{123} a_c}{6s} \left[1 - \frac{5.32s}{\lambda} \ln \left(1 + \frac{\lambda}{5.32s} \right) \right] \quad [6]$$

where A_{123} is the Hamaker constant. For the micromodel system (polystyrene-water-SiO₂), A_{123} is 3.79×10^{-21} J (Bergendahl and Grasso, 1999). The ζ potential was used as a proxy for the surface charge of the colloids. The experiments presented in this study were run at a low ionic strength (pure water, $I \approx 1 \times 10^{-6}$).

Water Flow Simulation

Two-dimensional water flow in the micromodel pores was previously simulated with the LB method (Knutson et al., 2001). The LB method is a computationally efficient method for simulating fluid flow with complex boundary conditions such as flow through porous media. It represents a volume element of fluid (e.g., water) with a collection of particles determined by a particle velocity distribution function at each grid point. Discrete time steps are taken and the fluid particles collide with each other during transport, in some cases under applied forces. The collision rules are defined so that the time-average motion of the particles obeys the Navier-Stokes equation. Lattice Boltzmann results from Knutson et al. (2001) are presented for water flow in a 1 by 1 pore body section of the micromodel pore network. A node spacing of 1 μm was used so that water flow was determined at a total of 474×474 nodes.

Bounce-back boundary conditions were used to impose no-slip conditions at the grain boundaries. This means that particles moving from a water node to a solid node were "bounced-back" in the opposite direction from which they came and at the same speed. Koch and Ladd (1997) showed that for bounce-back conditions the error in flow velocity between cylinders separated by 10 lattice nodes was <3% for moderate Reynolds numbers ($\text{Re} < 80$). In this work, we compare simulations at $\text{Re} \ll 1$ with measured colloid velocities. In this case, Re is defined according to Koch and Ladd (1997) as $\text{Re} = \rho U a / \mu$, with ρ and μ denoting the density and viscosity of the fluid, U the average linear velocity in the micromodel, and a the diameter of the cylinders. Details and validation of the modeling results are given in Knutson et al. (2001).

A contour plot of the calculated 2D flow field around a micromodel post at a flow rate of 10 $\mu\text{L h}^{-1}$, corresponding to an average linear velocity of 126 cm d⁻¹ (14.6 $\mu\text{m s}^{-1}$), is shown in Fig. 2. The highest flow velocities (90 $\mu\text{m s}^{-1}$) occur

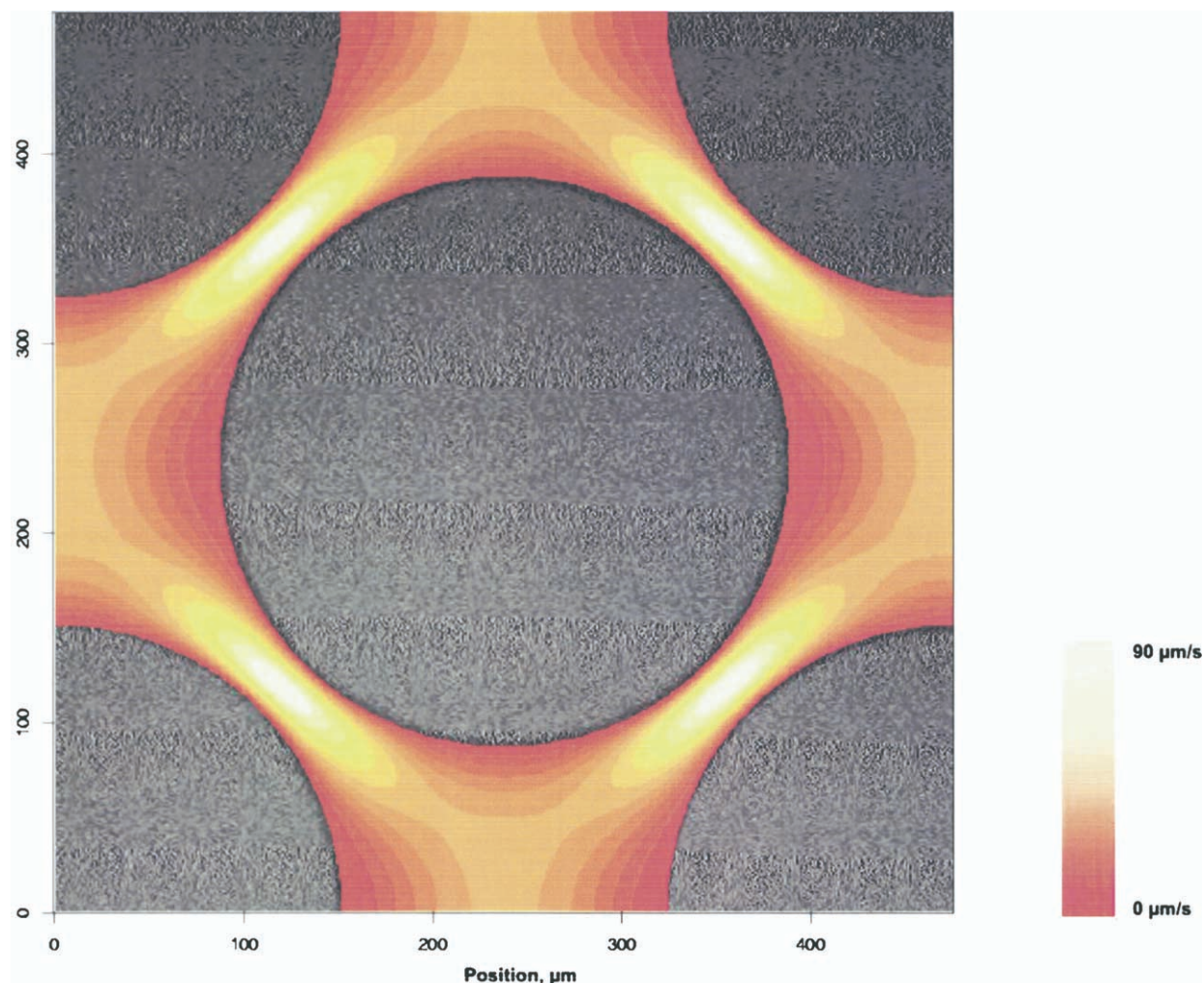


Fig. 2. Contour plot of the calculated flow velocities in the homogeneous micromodel at $10 \mu\text{L h}^{-1}$. Flow is from left to right; grid spacing is $1 \mu\text{m}$.

between pore throats, the lowest at upstream and downstream stagnation points. Flow in the micromodel is three-dimensional (3D); it is affected by no slip boundary conditions at grain surfaces and at the bottom and top of the micromodel flow channels. The velocity distribution between two parallel plates can be approximated with Eq. [7] (Wiley-VCH, 1998):

$$v = 6U \left[\frac{x}{h} - \left(\frac{x}{h} \right)^2 \right] \Big|_{x \leq h} \quad [7]$$

where v is the local velocity, U is the average linear velocity, x is the distance from the bottom of the channel, and h is the height of the channel. The parabolic flow profile between two plates $50 \mu\text{m}$ apart is shown in Fig. 3. This profile indicates that the 2D model results only approximate flow in the micromodel pores.

An interactive particle tracking algorithm (PTA) based on the LB flow field was used to calculate the theoretical flow trajectories of the colloids. For a chosen starting point, the local x and y velocities were taken from the LB model. With this data, the displacement for the particle for a given time step was calculated. Next, the new coordinates of the particle were calculated, and a line was drawn showing the movement of the particle. This procedure was repeated until the exposure time of the image was reached. The time steps of the PTA were kept short, so a typical particle needed more than five

time steps to move across one grid element of the LB model (i.e., $1 \times 1 \mu\text{m}^2$).

Most of the colloids observed were in the focal plane, the vertical center of the channel where the flow velocity is highest. The schematic in Fig. 3 demonstrates that the colloids in the vertical center move up to 1.5 times the average linear velocity. If the average linear velocity in the LB simulation is set equal to that in the experiment, only a small fraction of the velocities in the PTA and experiment will match. Therefore, average linear velocities for the LB simulations were set to 1.36 times the average linear velocities of the experiment. Thus, roughly 44% of the colloids should be within a margin of $U \pm 10\%$.

RESULTS AND DISCUSSION

Image Resolution

With a $20\times$ objective, the pixel size is $0.35 \mu\text{m}^2$. The 691-nm colloids should fit in one pixel. However, when colloids fluoresce, their image diameter is larger than their actual size. The minimum colloid diameter that we observed with the $20\times$ objective was 170 nm .

The micromodel depth was $50 \mu\text{m}$. The same vertical focus plane, about $25 \mu\text{m}$ from the bottom of the micromodel, was used to capture all images. Colloids above and below this plane were out of focus. Hence, the

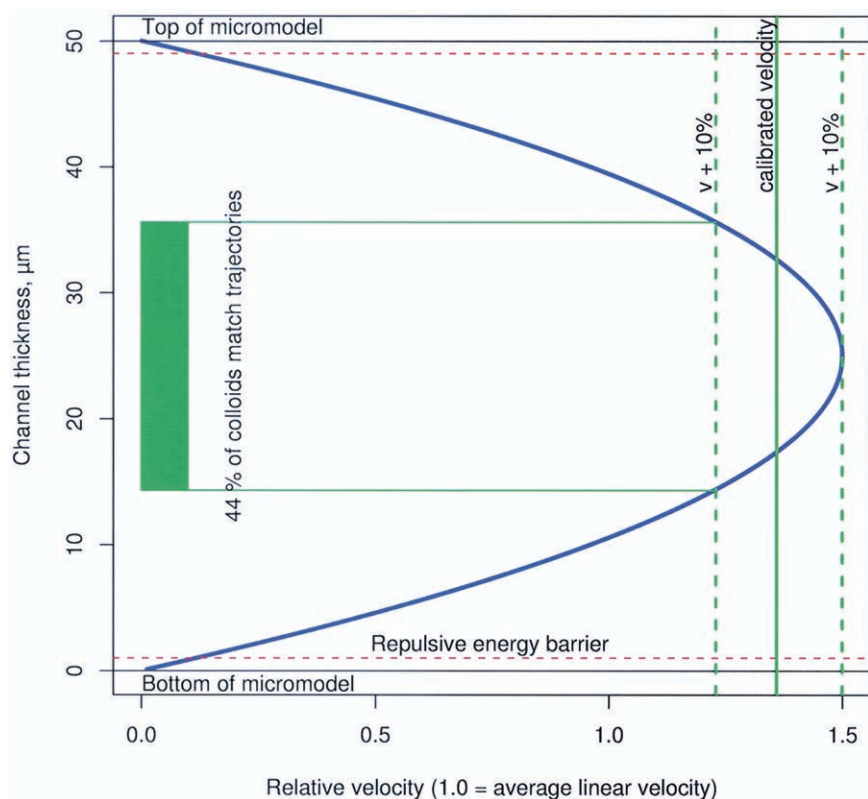


Fig. 3. Schematic of the parabolic flow profile in the micromodel channel.

vertical position of colloids moving through the micromodel could be qualitatively determined.

Flow Pathways in the Micromodel

A composite order image was constructed by overlaying four images taken 2 s apart, where colloids in each image were assigned a different color. The composite order image of 691 nm colloids at $15 \mu\text{L h}^{-1}$ in the micromodel pore network is shown in Fig. 4. Results at other flow rates and for the 1960-nm colloids were similar and are not shown. Flow is from left to right. The exposure time for each image was 500 ms, and $100\times$ magnification was used (i.e., $10\times$ objective).

Colloids appear as dots and streaks in the image. Some dots and streaks are not in the focal plane (i.e., not in the vertical center of the micromodel, and these appear blurry (e.g., c in Fig. 4). Faster moving colloids appear as streaks, where the length of each streak is proportional to the colloid velocity. The longest streaks are in pore throats, the shortest near grain walls. The flow velocities of the particles in the pore throats reach about 1000 cm d^{-1} , which is five times higher than the average linear velocity and in agreement with the calculated 2D velocity distribution.

Near grain walls there are cases where colloids appear as streaks (a and b in Fig. 4) and as dots (c and d in Fig. 4). Colloids that appear as dots did not appreciably move during the 500-ms exposure time. For these cases, the composite order image illustrates that colloids moved between images taken 2 s apart. For example, colloids at Positions c and d in the image appear as dots along

the grain wall; successive images show that these colloids move only a few colloid diameters every 2 s.

In some cases streaks appear to be closer to the grain surface than dots. This seems counter-intuitive since colloids closer to grain walls should move more slowly. However, the micromodel is not a 2D flow system. Flow across the depth of a pore channel is parabolic (Fig. 3). As a result, the water velocity near the top and bottom of a pore channel is slower than at the mid height.

The colloid at Position c is out of focus (i.e., near the top or bottom of the flow channel), whereas the colloid at Position b is in focus (i.e., in the vertical center of the micromodel). This explains why Colloid b moves faster than Colloid c. Colloid d is also in focus, and it is closer to the grain surface than Colloid b. As a result, it moves more slowly than Colloid b. From Fig. 4 it can also be seen that one colloid close to a grain surface (Position e) is not moving at all. This colloid seems to be attached to the surface. Another colloid (Position f) seems to be attached to the top or bottom of the micromodel.

Images of the 1960-nm colloids are shown in Fig. 5 after breakthrough (i.e., the concentration of the colloids equals the input concentration) at $100\times$ magnification. Also shown are calculated flow lines based on the LB model (Fig. 5b). In all cases flow is from left to right at a flow rate of $150 \mu\text{L h}^{-1}$. As in Fig. 4, the longest streaks are near the middle of pore throats and the shortest near grain walls. Also, for a given streak, the intensity is less in a pore throat than in a pore body, indicating greater flow velocities in pore throats. The

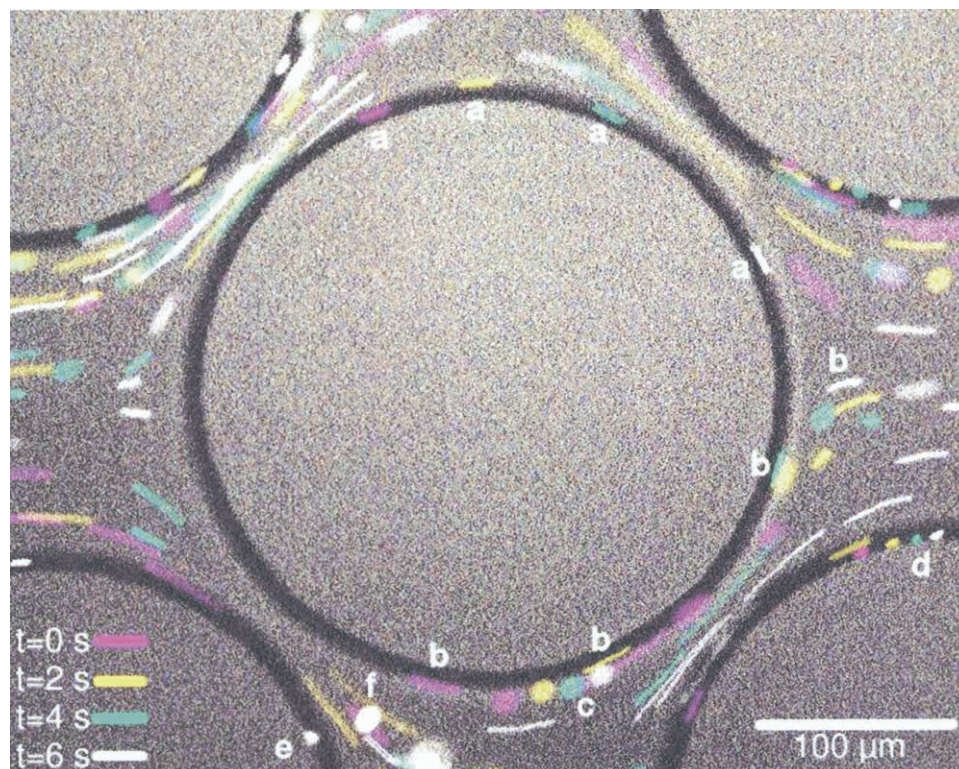


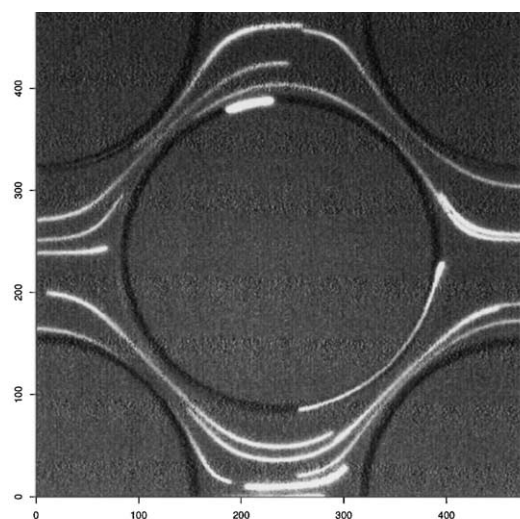
Fig. 4. A composite order image of 691-nm colloids in the homogeneous micromodel. Flow is from left to right at $15 \mu\text{L h}^{-1}$. The color code indicates the position of the colloids at time steps 2 s apart.

intensity also varies among streaks. However, it is not possible to correlate this with colloid velocity because colloids at different vertical positions (i.e., colloids that are in or out of focus) have different intensities.

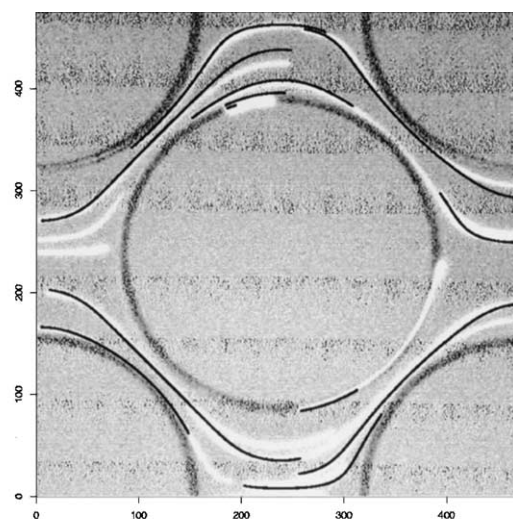
Calculated flow paths in Fig. 5b coincide well with measured streak lengths. A total of 56 individual colloid streaks from the images in Fig. 4 and 5, and from an image of the 1960 nm colloids at $150 \mu\text{L h}^{-1}$ at an earlier time during breakthrough (i.e., when the concentration was lower than in Fig. 5) were compared with model results. For about 50% of the colloids, measured streak

lengths and locations matched the calculated trajectories very well (i.e., the length of measured and calculated trajectories was within $\pm 10\%$, and the lateral deviation was within $\pm 2.5 \mu\text{m}$). This is near the maximum of what could have been expected with the 2D approximation of the 3D flow field (see Fig. 3). The result indicates that in many cases colloids move along with the calculated flow of water in the pore structure, and the model does a good job of determining colloid flow paths and velocities.

For about 20% of the colloids, measured streak loca-



a



b

Fig. 5. (a) Measured colloid trajectories and (b) an overlay of calculated and measured trajectories for the 1960-nm colloids in the homogeneous micromodel during breakthrough. Flow is from left to right.

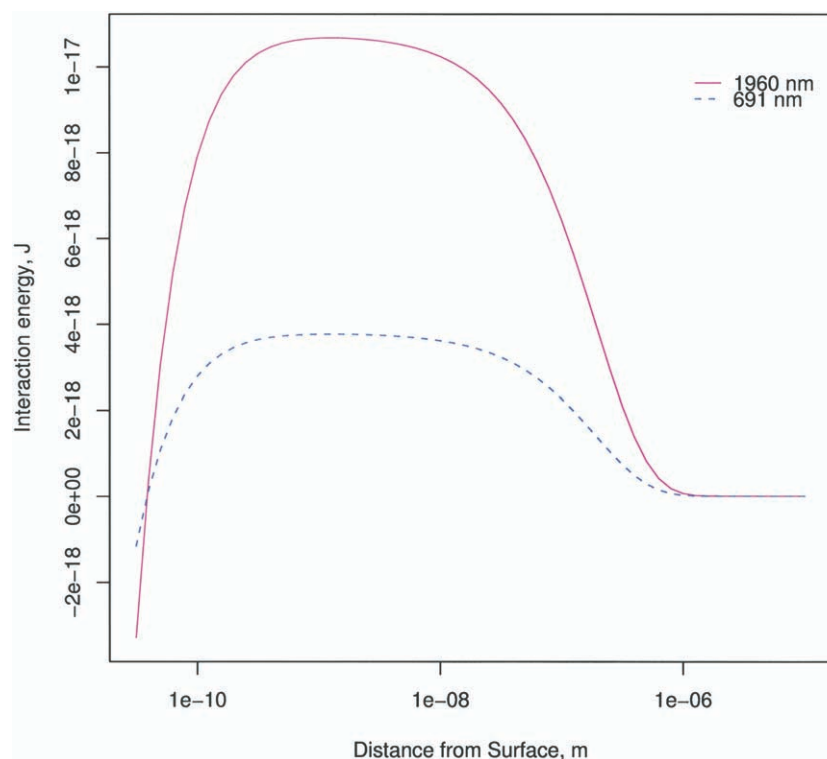


Fig. 6. Schematic of the interaction energy between polystyrol colloids of different size and the micromodel surface.

tions matched the calculated trajectories, but the measured streak lengths were shorter (i.e., characterized by a smaller velocity). Most of these colloids were out of focus (i.e., the colloids are moving at the top or at the bottom of the flow channel). These colloids were likely affected by slower flow at the top and bottom of flow channels. As previously noted, this is a limitation of applying the 2D model to the 3D micromodel.

For about 12% of the colloids, measured streak locations matched the calculated trajectories, but the measured streaks were faster (up to a factor of 4). These colloids were primarily located close to the surface of the posts, where the negative charges of colloids and surface lead to a repulsive energy barrier around the cylinders. The total interaction energy close to the surface is plotted in Fig. 6. The energy barrier extends approximately $1\text{ }\mu\text{m}$ into solution. This means that colloids are not able to access flow paths within a couple micrometers of the grain surface. It is difficult to align measured and calculated flow paths with accuracy better than $2\text{ }\mu\text{m}$. Next to grain surfaces, flow paths $2\text{ }\mu\text{m}$ apart vary by a factor of 2. This could account for some of the discrepancy between measured and calculated flow velocities. Alternatively, the bounce-back boundary conditions used for the LB model result in more error near the grain walls (Gallivan et al., 1997). This error likely contributes to the discrepancy as well. Last, for the remaining 18% of the colloids, measured streak lengths and locations do not match the calculated trajectories well. For these cases, the trajectory lengths are still within $\pm 20\%$, but the deviation of trajectory flow paths exceed $2.5\text{ }\mu\text{m}$ and in some cases are $>5\text{ }\mu\text{m}$. These are primarily 1960-nm colloids from the image taken when the concentration was at a maximum. It is

likely that colloid–colloid interactions cause colloid flow paths to deviate from water flow paths determined with the model.

Colloid Filtration

The homogeneous micromodel represents an ideal system for the application of filtration theory. The micromodel can be considered as a network of cylindrical collectors, each with a $300\text{-}\mu\text{m}$ diameter. Filtration efficiencies were calculated for both sizes of latex spheres at different flow velocities; these are presented in Table 3.

The theoretical filtration efficiencies decrease with increasing flow velocity and increasing colloid diameter. This indicates that diffusion is the predominant process for the transport to the poles. Gravitational transport is of minor importance because the densities of colloids and fluid are similar.

The number of colloids approaching each of the 20 cylinders across a micromodel pore network ranges from 3 s^{-1} (1960 nm, $5\text{ }\mu\text{L h}^{-1}$) to 230 s^{-1} (691 nm, $15\text{ }\mu\text{L h}^{-1}$). From the number of colloids approaching the cylinders, the number of collisions of colloids with the surface due to gravitation, interception, and diffusion can be calculated using filtration theory. Assuming that every collision results in a permanent attachment (attachment efficiency $\alpha = 1$), the maximum attachment rates are

Table 3. Calculated filtration efficiency for the homogeneous micromodel.

Flow volume	691 nm	1960 nm
$5\text{ }\mu\text{L h}^{-1}$	0.020	0.016
$10\text{ }\mu\text{L h}^{-1}$	0.0130	0.0097
$15\text{ }\mu\text{L h}^{-1}$	0.0095	0.0072

between 0.05 s^{-1} (1960 nm, $5 \mu\text{L h}^{-1}$) and 2.2 s^{-1} (691 nm, $15 \mu\text{L h}^{-1}$).

The actual attachment rates were lower, since not every collision resulted in an attachment. The observed values, calculated from counting the attached colloids per cylinder for a period of at least 4 h, are between one and three colloids per hour. This makes sense because of the repulsive forces between the negative surface charge of colloids and the negative charged silicon surface. There was no significant difference between the 1960- and the 691-nm colloids. During the high flow rates experiments, no attachment was observed at all. The attachment efficiency thus is in the range of 1×10^{-4} to 1×10^{-6} , which is close to data cited in literature (Huber et al., 2000). However, with two orders of magnitude, the variation of the attachment efficiency determined during our micromodel experiments is rather high compared with conventional experiments. This may be due to the limited number of collector grains provided in the micromodel, resulting in a statistically limited number of actual attachment observations. As noted above, diffusion is the predominant process for a collision between colloids and surface. At the pore scale, diffusion processes introduce a randomness, which does not level out due to a high number of collector grains as in conventional column tests. In other words, the size of the pore network in the micromodel is less than a representative elementary volume with respect to colloid-surface interactions.

CONCLUSIONS

A new approach to analyze fundamental colloid transport mechanisms in porous media was presented. We combined microscopic observation of colloid transport in a well-controlled pore structure etched into a silicon wafer (i.e., micromodel) with flow paths determined from a pore-scale flow model based on the LB technique. In many cases agreement between measured and calculated flow paths and velocities were excellent. When deviations occurred, these were used to interpret mechanisms of colloid transport that were not accounted for in the model, or limitations in either the LB model or the micromodel experiment. For example, micromodel pores were only $50 \mu\text{m}$ deep. Flow across this depth was parabolic, and velocities determined for colloids moving near the bottom and top of the micromodel did not agree with the 2D model. Also, velocities determined for colloids moving near silicon posts deviated from the model, possibly because of small misalignment of model and calculated flow lines or from errors in the LB results near solid boundaries.

The etching method and LB model can readily be applied to more complex 2D geometries (Chomsurin, 2003; Kang et al., 2002). Hence, colloid transport in high precision pore networks can be combined with pore-scale modeling to investigate fundamental transport mechanisms in more complex porous media, both saturated and unsaturated. Also, in this work fluorescence microscopy was used to observe colloids stained with a fluorescent dye. Reflected differential interference con-

trast (DIC) microscopy will be used in ongoing work to observe nonfluorescent colloids such as clay minerals and humic substances. These detailed studies at the pore scale will help to create a more robust link between real world observations and the underlying theoretical framework.

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