Irreversible Chemical Potential and Shear-Induced Diffusion in Crossflow Filtration

Albert S. Kim* and Yuewei Liu

Department of Civil and Environmental Engineering, University of Hawaii at Manoa, Honolulu, Hawaii 96822

Nonequilibrium themodynamics is used in a novel way to fundamentally investigate colloidal back-diffusion during crossflow membrane filtration. A generalized chemical potential is assumed as a superposition of equilibrium and irreversible contributions, which are proven to originate from Brownian and shear-induced diffusion, respectively. As a result, an effective drag force is derived for a particle that is simultaneously undergoing both Brownian and shear-induced diffusion in a sheared concentrated suspension.

1. Introduction

In crossflow filtration using microfiltration (MF) and ultrafiltration (UF) to remove particulate materials, colloidal back-diffusion plays an important role in mitigating particle deposition and cake formation.[1,2] When particles, ranging in size from 10 nm to 10 μm, are filtered by UF or MF membranes, their diffusion is controlled by two distinct, major factors: thermodynamic entropy for smaller particles and hydrodynamic stress for larger particles. The borderline between small and large particles is on the order of 0.1−1.0 μm, observed experimentally when studying critical flux.[3] While the significance of each diffusion mechanism was individually studied,[4,5] Sethi and Wiesner assumed the additivity of Brownian and shear-induced diffusivities and modeled the transient behavior of flux decline.[6] For large rigid particles, the lateral migration induced by the inertial lift (i.e., tubular pinch effect) can play an important role in particle transport during crossflow filtration.[7,8] However, the validity of the inertial lift is limited to the trajectory analysis of a neutrally buoyant particle and therefore was not studied together with diffusive transport mechanisms.

Brownian diffusion is a entropy-maximizing phenomenon, which originates from stochastic collisions between a particle and many solvent molecules in a fluid medium and is further influenced by particle−particle collisions.[9] Brownian motion brings forth self-diffusion of particles in dilute suspensions. Shear-induced diffusion is a factor in open flow systems of pressure-driven membrane filtration.[10,11] Macroscopic smoothness of the membrane surface in crossflow filtration provides a boundary condition that contributes to buildup of a linear shear profile near the surface, even if a flow slips on the permeable surface.[12] Because the shear-induced diffusion is ascribed to collisions between adjacent particles moving with different velocities and tumbling over each other in a shear flow, it becomes more important as the particle volume fraction increases.

Because of different origins of these three transport mechanisms of Brownian diffusion, shear-induced diffusion, and inertial lift, consilient understanding of particle transport during crossflow membrane filtration is still lacking in terms of mass transport from the membrane surface to the bulk phase. To date, effects of collisions between particles influenced by inertial lift have not been extensively studied for concentrated suspensions in crossflow membrane filtration, and Brownian and shear-induced diffusion were only presumably superpositioned at the level of the macroscopic mass balance equation.[6] Therefore, the objective of the current study is to unify two diffusion phenomena (i.e., Brownian and shear-induced) using equilibrium and irreversible thermodynamics, where the inertial lift is negligible in terms of particle size, effects of gravity, and/or crossflow velocity.

The unification provides an elegant mathematical expression of a drag force exerted on a particle in a sheared multiparticle swarm and estimates the relative significance of Brownian to shear-induced diffusion. For this research we consider an irreversible thermodynamic system using a general form of chemical potential, investigate origins of combined diffusion in a unified manner, and render practical implications on optimal operations of colloidal membrane filtration in terms of particle back-diffusion.

2. Nonequilibrium Themodynamics

2.1. Irreversible Chemical Potential. In thermodynamics, the chemical potential μ is generally defined as a molar Gibbs free energy, i.e., a partial derivative of Gibbs free energy $G(T,P,n)$ with respect to the mole number of particles n:

$$\left(\frac{\partial G}{\partial n}\right)_{T,P} = \mu(T,P,n) \tag{1}$$

where T is the absolute temperature and P is the pressure. For convenience, this study considers Gibbs free energy per particle $\hat{\mu}$ defined as

$$\hat{\mu}(T,P,N) \equiv \left(\frac{\partial G}{\partial N}\right)_{T,P} = \frac{1}{N_A}\left(\frac{\partial G}{\partial n}\right)_{T,P} = \frac{\mu(T,P,n)}{N_A} \tag{2}$$

where N_A is Avogadro's number. Incorporating nonequilibrium thermodynamics,[13] it is proposed that $\hat{\mu}$ consists of equilibrium ($\hat{\mu}_{eq}$) and irreversible ($\hat{\mu}_{ir}$) terms:

$$\hat{\mu} = \hat{\mu}_{eq} + \hat{\mu}_{ir} \tag{3}$$

The equilibrim term is represented as

$$\hat{\mu}_{eq} = \hat{\mu}_{eq,0} + k_b T \ln(\gamma\phi) \tag{4}$$

where $\hat{\mu}_{eq,0}$ is a reference constant, k_b is the Boltzmann constant, γ is the activity coefficient, and ϕ is the volume fraction of particles in a fluid medium.

Following Førland et al.'s and Hiemenz's approaches,[14,15] the gradient of the generalized chemical potential is assumed to be equal to the phenomenological diffusion force:

$$\nabla\hat{\mu} = \mathbf{F}_{diff} \tag{5}$$

with

* To whom correspondence should be addressed.

10.1021/ie0714403 CCC: $40.75 © 2008 American Chemical Society
Published on Web 06/28/2008

$$\mathbf{F}_{\text{diff}} = \mathbf{F}_{\text{eq}} + \mathbf{F}_{\text{ir}} \tag{6}$$

where $\mathbf{F}_{\text{eq}}$ is the equilibrium diffusion force typically due to the concentration gradient (from the viewpoint of Fick's law) and $\mathbf{F}_{\text{ir}}$ is the irreversible diffusion force stemming from the irreversible chemical potential, $\hat{\mu}_{\text{ir}}$. By considering the physical origins for the forces, one can write

$$\nabla \hat{\mu}_{\text{eq}} = \mathbf{F}_{\text{eq}} \tag{7a}$$

$$\nabla \hat{\mu}_{\text{ir}} = \mathbf{F}_{\text{ir}} \tag{7b}$$

2.2. Diffusivity Representations. A diffusion force, i.e., an effective phenomenological (fictitious) force, which causes diffusive motion of each particle under steady state conditions, may be defined as[15]

$$\mathbf{F}_{\text{diff}} = f\mathbf{v}_{\text{diff}} \tag{8}$$

where f is the friction factor and $\mathbf{v}_{\text{diff}}$ is the diffusion velocity. Equations 5 and 8 imply that the gradient of the generalized chemical potential drives diffusion of particles moving with a representative velocity $\mathbf{v}_{\text{diff}}$, and hence the diffusion force in a steady state is equal to the hydrodynamic drag force, $f\mathbf{v}_{\text{diff}}$, acting on diffusing particles. Substitution of eqs 3 and 4 into eq 5 leads to

$$\mathbf{F}_{\text{diff}} = \left[\frac{k_{\text{b}}T}{\phi}\left(1 + \phi\frac{\partial \ln \gamma}{\partial \phi}\right) + \frac{\partial \mu_{\text{ir}}}{\partial \phi}\right]\nabla \phi \tag{9}$$

Now, Fick's first law can be written as

$$\mathbf{J}_{\text{diff}} = D\nabla \phi = \phi\mathbf{v}_{\text{diff}} \tag{10}$$

where $\mathbf{J}_{\text{diff}}$ is the diffusive flux caused by both equilibrium and irreversible contributions and D is the diffusivity. Here, one can calculate the generalized diffusivity using eqs 8–10 as a superposition of equilibrium and irreversible origins:

$$D = D_{\text{eq}} + D_{\text{ir}} \tag{11}$$

where

$$D_{\text{eq}} = \frac{k_{\text{b}}T}{f}\left(1 + \phi\frac{\partial \ln \gamma}{\partial \phi}\right) \tag{12a}$$

$$D_{\text{ir}} = \frac{\phi}{f}\frac{\partial \hat{\mu}_{\text{ir}}}{\partial \phi} \tag{12b}$$

indicating that the equilibrium and irreversible components of the diffusion force contribute to corresponding diffusivity counterparts. Note that in eqs 12a and 12b f is commonly included in D_{eq} and D_{ir} because it is the drag force coefficient of a particle moving with $\mathbf{v}_{\text{diff}}$ under the combined influences of $\mathbf{F}_{\text{eq}}$ and $\mathbf{F}_{\text{ir}}$.

The equilibrium part, D_{eq}, is the generalized Stokes−Einstein diffusivity:[16–19]

$$D_{\text{eq}} = D_{\text{B}}S(\phi)\,K(\phi) \tag{13}$$

with the Brownian self-diffusivity

$$D_{\text{B}} = \frac{k_{\text{b}}T}{6\pi\eta a} \tag{14}$$

and

$$S(\phi) = \frac{\partial \phi\, Z(\phi)}{\partial \phi} \tag{15}$$

where $K(\phi)$ is the sedimentation coefficient, η is the fluid viscosity, a is the particle radius, and $Z(\phi)$ $(= \Pi(\phi)/\rho k_{\text{b}}T)$ is the osmotic compressibility. (Π and ρ are the osmotic pressure and number concentration, respectively.) Especially for hard-sphere systems, the exact solution for the osmotic compressibility is known as the Carnahan−Starling equation:[20]

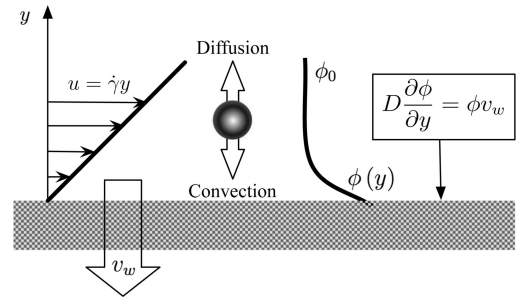

Figure 1. Schematic of crossflow membrane filtration. In the linear shear flow field, particles experience hydrodynamic drag toward the membrane due to the permeate flux being driven by applied pressure and forming a higher volume fraction than the bulk concentration ϕ_0 above the membrane surface. Axial convection due to the shear flow vanishes on the membrane surface due to the no-slip boundary conditions imposed, which generates a balance between downward convective and upward diffusive fluxes at $y = 0$. Replacing D_{ir} in eq 19 with D of eq 13 yields the general boundary condition on the membrane surface as shown above.

$$Z(\phi) = \frac{1 + \phi + \phi^2 - \phi^3}{(1 - \phi)^3} \tag{16}$$

from which $S(\phi)$ is derived as

$$S(\phi) = \frac{1 + 4\phi + 4\phi^2 - 4\phi^3 + \phi^4}{(1 - \phi)^4} \tag{17}$$

The friction factor is known as

$$f = 6\pi\eta a K^{-1}(\phi) \tag{18}$$

which represents the amount of drag force per diffusion speed. As the volume fraction increases, $K(\phi)$ decreases from $K(\phi = 0) = 1$ to $K(\phi = 1) = 0$. Therefore, particles diffusing with $\mathbf{v}_{\text{diff}}$ in the swarm of volume fraction ϕ should undergo $K^{-1}(\phi)$ times higher diffusion force than that in a dilute suspension of particles moving with the same velocity. Detailed discussion on the sedimentation coefficient can be found elsewhere, emphasizing its role in hydraulic permeability and ultrafiltration.[21,22] From eq 13, the osmotic compressibility and activity coefficient are linked by the following relationship:

$$S(\phi) = 1 + \phi\frac{\partial \ln \gamma}{\partial \phi} \tag{19}$$

of which each side converges to unity in a dilute particle suspension, because

$$\lim_{\phi \to 0} Z(\phi) = 1 \tag{20a}$$

$$\lim_{\phi \to 0} \gamma = 1 \tag{20b}$$

which connote

$$\lim_{\phi \to 0} D_{\text{eq}}(\phi) \to D_{\text{B}} \tag{21}$$

The irreversible part of the generalized diffusivity has the following relationship as described by eq 12b:

$$D_{\text{ir}}\frac{\partial \phi}{\partial y} = \frac{\phi}{f}F_{\text{ir}} = \phi v_{\text{w}} \tag{22}$$

where y is the coordinate in the direction normal to the membrane surface, as shown in Figure 1, The irreversible dissipation force of eq 7b is considered to be the Stokes drag on a single particle in a concentrated suspension, analogous to eq 8:

$$\mathbf{F}_{ir} = f\mathbf{v}_w \tag{23}$$

In the original study of shear-induced diffusion, Leighton and Acrivos[23] considered a flux balance:

$$D_{SI}\frac{\partial\phi}{\partial y} = \phi K(\phi)v_g \tag{24}$$

where v_g is the settling velocity of an isolated particle and D_{SI} is the shear-induced diffusivity. Equation 24 indicates that the gravitational flux is balanced with upward shear-induced diffusion by

$$D_{SI} = \dot{\gamma}a^2\hat{D}(\phi) \tag{25}$$

where $\dot{\gamma}$ is the shear rate (of the crossflow) and $\hat{D}(\phi)$ is a dimensionless function that indicates the dependency on the particle volume fraction:[10,11,23]

$$\hat{D}(\phi) = \frac{1}{3}\phi^2(1 + 0.5e^{8.8\phi}) \tag{26}$$

An extensive analysis of $\hat{D}(\phi)$ was conducted by Sierou and Brady for monodispersed identical spheres.[24] Other basic studies on shear-induced diffusion of unequal-sized spheres, nonspherical particles, and their timely irreversible behaviors can be found elsewhere.[25–27] Comparing eqs 22 and 24, we write the irreversible diffusivity, analogous to eq 13 as

$$D_{ir} = D_{SI}K(\phi) \tag{27}$$

as a product of the shear-induced diffusivity and the sedimentation coefficient.

With eqs 13 and 27, the generalized diffusivity is finally expressed as

$$D = D_{eq} + D_{ir} = \left[D_B S(\phi) + \dot{\gamma}a^2\hat{D}(\phi)\right]K(\phi) \tag{28}$$

where the terms in the squared brackets contribute to enhancing configurational randomness in reversible and irreversible ways, and the sedimentation coefficient contributes to the hydrodynamic hindrance proportional to the volume fraction. Shear rate linearly increases the irreversible diffusion, which may be the origin of the timely irreversibility of sheared colloidal suspensions.[27] From eqs 7b and 23 the irreversible chemical potential μ_{ir} is interpreted as energy dissipated when a particle moves from a reference point (i.e., the membrane surface) back to a certain position y away from the surface, and hence it appears as the origin of the particle back-diffusion induced by the shear flow.

2.3. Drag Force. Using the Nernst−Einstein equation, the generalized diffusivity is linked to mobility, i.e., particle velocity per unit force applied, in the form of

$$D = D_{eq} + D_{ir} = k_b T\frac{v_w}{F_{drag}} \tag{29}$$

which implies that during the crossflow membrane filtration particles diffusing with diffusivity D undergo the countering drag force F_{drag} due to the permeate flux v_w. Particle diffusion is therefore balanced by convective transport. For monodispersed hard-sphere suspensions, Happel's cell model provides a good analytic representation of the sedimentation coefficient in a resistance form:[28]

$$H(\phi) = K^{-1}(\phi) = \frac{6 + 4\phi^{5/3}}{6 - 9\phi^{1/3} + 9\phi^{5/3} - 6\phi^2} \tag{30}$$

which is well documented for concentrated suspensions such as $\phi = O(10^{-1})$. Using the cell model for monodispersed hard spheres, the drag force is written as

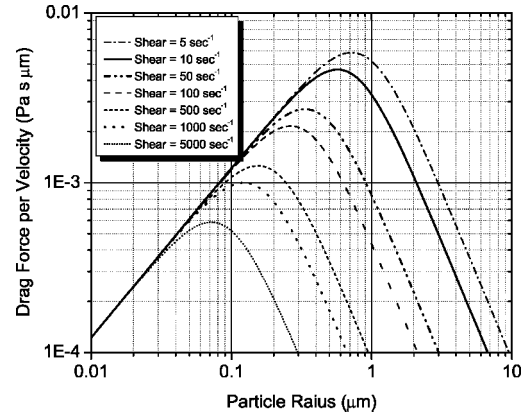

Figure 2. Inverse mobility (drag force per flow velocity) vs particle radius with different shear rates: a plot of eq 31. Parameters used are $T = 300$ K, $\phi = 0.5$, and $\eta = 10^{-3}$ Pa•s.

$$F_{drag} = \frac{6\pi\eta a v_w H(\phi)}{S(\phi) + \frac{\dot{\gamma}a^2}{D_B}\hat{D}(\phi)} \tag{31}$$

which is interpreted as the mean hydrodynamic force that a single particle experiences while undergoing both Brownian and shear-induced diffusion in a sheared multiparticle swarm. As the shear rate increases, the drag force of eq 31, which brings particles down toward the membrane surface from the bulk phase, is mitigated through enhanced shear-induced diffusion.

Results and Discussion

Figure 2 shows the dependence of the drag force, in the form of inverse mobility (i.e., resistance), on the shear rate and particle radius. It is apparent that the magnitude of the resistance decreases as the shear rate increases when the particle radius is greater than about 0.1 μm. When the particle radius is below 0.1 μm, shear-induced diffusion is found negligible in comparison to the Brownian diffusion. There is a peak of resistance for a given shear rate, at which the dominant transport mechanism changes from Brownian to shear-induced diffusion.

It is interesting to determine the particle radius that gives the maximum drag force by calculating

$$\frac{\partial F_{drag}}{\partial a} = 0 \tag{32}$$

which results in

$$\dot{\gamma}a^3 = \frac{k_b T}{12\pi\eta}\frac{S(\phi)}{\hat{D}(\phi)} \tag{33}$$

The estimation of the right-hand side of eq 33 is subject to selecting functional forms of $S(\phi)$ and $\hat{D}(\phi)$ if the particles are mutually interacting physicochemically. It is worth noting that $H(\phi)$ is not included in eq 33 as the sedimentation coefficient, $K(\phi) = H^{-1}(\phi)$, is commonly weighted in eq 28. Using the maximum volume fraction valid for the shear-induced diffusion (i.e., $\phi = 0.5$), one evaluates

$$\dot{\gamma}a^3 = 1.82\ \mu\text{m}^3/\text{s} \tag{34}$$

which is plotted in Figure 3 and indicates the minimum value of shear rate that triggers the shear-induced diffusion as significant as the Brownian diffusion. Far below the straight line in Figure 3, the drag force linearly increases with the radius of monodispersed particles primarily undergoing Brownian diffusion, but above the line the drag force decreases with

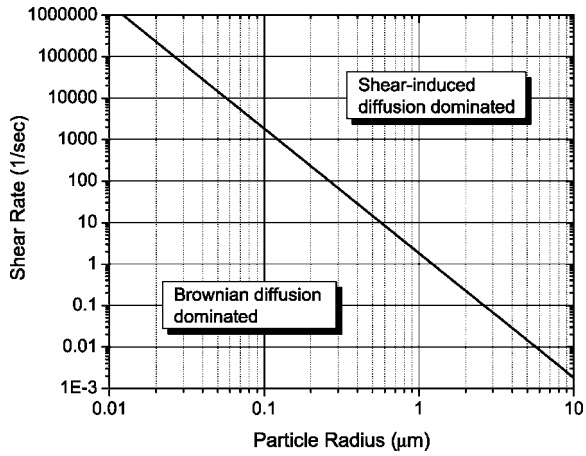

Figure 3. Shear value of maximum drag force vs particle radius: a plot of eq 34. Parameters used are $T = 300$ K, $\phi = 0.5$, and $\eta = 10^{-3}$ Pa•s.

respect to the radius of the particles primarily experiencing shear-induced diffusion. Note that the typical orders of shear rate in the crossflow, i.e., 10^1-10^3 s^{-1}, cover particle radii of about $0.1-0.5$ μm only. This implies that small variations in particle sizes in feedwater may require a remarkable change of shear rate (possibly of different orders) to maintain the influence of the shear-induced diffusion and hence the permeate flux.

Concluding Remarks

The origins of the Brownian and shear-induced diffusions are investigated by incorporating nonequilibrium thermodynamics through the generalized chemical potential equation, which consists of equilibrium and irreversible terms. In contrast to the fact that Brownian diffusion originates from the equilibrium thermodynamics of the entropic maximizing phenomena, shear-induced diffusion is ascribed to the irreversible chemical potential, where gradient is derived as being equal to (dissipative) Stokes drag acting on a particle experiencing permeate velocity above the membrane surface. Using the generalized chemical potential, the effective drag force is derived for a particle undergoing Brownian and shear-induced diffusion in a sheared, concentrated multiparticle swarm.

We unified the two diffusion mechanisms that play important roles in crossflow membrane filtration to provide a solid fundamental basis for understanding the mass transport phenomena using irreversible thermodynamics. Using the effective force of eq 31, the mean hydrodynamic force acting on particles within a concentration polarization or a cake layer is analytically calculated and further used for critical flux prediction, giving good agreements with experimental observation.[29] More fundamental studies are desired using nonequilibrium thermodynamics for complex colloidal crossflow filtration by seamlessly linking microscopic hydrodynamics and macroscopic mass balance equations.

Acknowledgment

This research was made possible by a grant from the U.S. National Science Foundation Faculty Early Career (CAREER) Development Program (CTS04-49431).

Literature Cited

(1) American Water Works Association Research Foundation. *Water Treatment Membrane Processes*; McGraw-Hill: New York, 1996.

(2) Mulder, M. *Basic Principles of Membrane Technology*; Kluwer Academic Publishers: Boston, MA, 1996.

(3) Bacchin, P.; Aimar, P.; Field, R. Critical and sustainable fluxes: Theory, experiments and applications. *J. Membr. Sci.* **2006**, *281*, 42–69.

(4) Romero, C. A.; Davis, R. H. Transient model of crossflow microfiltration. *Chem. Eng. Sci.* **1990**, *45*, 13–25.

(5) Song, L. F.; Elimelech, M. Theory of concentration polarization crossflow filtration. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 3389–3398.

(6) Sethi, S.; Wiesner, M. R. Modeling of transient permeate flux in cross-flow membrane filtration incorporating multiple particle transport mechanisms. *J. Membr. Sci.* **1997**, *136*, 191–205.

(7) Segre, G.; Silberberg, A. Radial particle displacements in poiseuille flow of suspensions. *Nature (London)* **1961**, *189*, 209–210.

(8) Chellam, S.; Wiesner, M. R. Particle transport in clean membrane filters in laminar flow. *Environ. Sci. Technol.* **1992**, *26*, 1611–1621.

(9) Einstein, A. *Investigation on the Theory of the Brownian Movement*; Dover Publications: New York, 1956.

(10) Leighton, D.; Acrivos, A. Measurement of the shear induced coefficient of self-diffusion in concentration suspensions of spheres. *J. Fluid Mech.* **1987**, *177*, 109–131.

(11) Leighton, D.; Acrivos, A. The shear-induced migration of particles in concentrated suspensions. *J. Fluid Mech.* **1987**, *181*, 415–439.

(12) Chellam, S.; Liu, M. Effect of slip on existence, uniqueness, and behavior of similarity solutions for steady incompressible laminar flow in porous tubes and channels. *Phys. Fluids* **2006**, *18*, 083601.

(13) Eu, B. C. *Generalized Thermodynamics: Thermodynamics of Irreversible Processes and Generalized Hydrodynamics (Fundamental Theories of Physics)*; Kluwer Academic Publishers: New York, 2002.

(14) Førland, K. S.; Førland, T.; Ratkje, S. K. *Irreversible Thermodynamics: Theory and Applications*; John Wiley and Sons: New York, 1988.

(15) Hiemenz, P. C. *Principles of Colloid and Surface Chemistry*; Marcel Dekker: New York, 1986.

(16) Batchelor, G. K. Brownian diffusion of particles with hydrodynamic interaction. *J. Fluid Mech.* **1976**, *74*, 1–29.

(17) Hansen, J. P.; McDonald, I. R. *Theory of Simple Liquids*; Academic Press: London, 1976.

(18) Hunter, R. J. *Foundations of Colloid Science*; Oxford University Press: New York, 1986.

(19) Russel, W. B.; Saville, D. A.; Schowalter, W. R. *Colloidal Dispersions*; Cambridge University Press: New York, 1989.

(20) Carnahan, N. F.; Starling, K. E. Equation of state for nonattracting rigid spheres. *J. Chem. Phys.* **1969**, *51*, 635–636.

(21) Kim, A. S.; Stolzenbach, K. D. The permeability of synthetic fractal aggregates with realistic three-dimensional structure. *J. Colloid Interface Sci.* **2002**, *253*, 315–328.

(22) Bhattacharjee, S.; Kim, A. S.; Elimelech, M. Concentration polarization of interacting solute particles in cross-flow membrane filtration. *J. Colloid Interface Sci.* **1999**, *212*, 81–99.

(23) Leighton, D.; Acrivos, A. Viscous resuspension. *Chem. Eng. Sci.* **1986**, *41*, 1377–1384.

(24) Sierou, A.; Brady, J. F. Shear-induced self-diffusion in non-colloidal suspensions. *J. Fluid Mech.* **2004**, *506*, 285–314.

(25) Zarraga, I. E.; Leighton, D. T. Shear-induced diffusivity in a dilute bidisperse suspension of hard spheres. *J. Colloid Interface Sci.* **2001**, *243*, 503–514.

(26) Lopez, M.; Graham, M. D. Shear-induced diffusion in dilute suspensions of spherical or nonspherical particles: Effects of irreversibility and symmetry breaking. *Phys. Fluids* **2007**, *19*, 073602.

(27) Pine, D. J.; Gollub, J. P.; Brady, J. F.; Leshansky, A. M. Chaos and threshold for irreversibility in sheared suspensions. *Nature (London)* **2005**, *438* (15), 997.

(28) Happel, J. Viscous flow in multiparticle systems: slow motion of fluids relative to beds of spherical particles. *AIChE J.* **1958**, *4*, 197–201.

(29) Kim, A. S.; Liu, Y. Critical flux of hard sphere suspensions in crossflow filtration: Hydrodynamic force bias monte carlo simulations. *J. Membr. Sci.*, submitted.

Received for review October 24, 2007
Revised manuscript received May 7, 2008
Accepted May 19, 2008

IE0714403