

Non-equilibrium Monte Carlo Simulations for Critical Flux of Hard Sphere Suspensions in Crossflow Filtration

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Abstract

Non-equilibrium (irreversible) thermodynamics is used to investigate colloidal back-diffusion during crossflow membrane filtration. The chemical potential is generalized as a superposition of equilibrium and irreversible contributions, originating from Brownian and shear-induced diffusion, respectively. As a result, an effective drag force is derived using the irreversible thermodynamics for a particle undergoing both Brownian and shear-induced diffusion in a sheared concentrated suspension. Using the drag force, a hydrodynamic force bias Monte Carlo method is developed for crossflow membrane filtration to determine the critical flux of hard sphere suspensions. Effects of shear rate and particle size on the critical flux are studied, and results show a good agreement with experimental observations reported in the literature.

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1 Introduction

In crossflow filtration using microfiltration (MF) and ultrafiltration (UF) to remove particulate materials, colloidal back-diffusion plays an important role in mitigating membrane fouling in terms of particle deposition and cake formation [1, 2]. When MF and UF membranes filter particles ranging in size from 10 nm to 10 μm , the particle diffusion is controlled by two distinct, major factors: thermodynamic entropy and hydrodynamic stress for smaller and larger particles, respectively. Experimental observation of critical fluxes indicates that the borderline between small and large particles is on the order of 0.1 – 1.0 μm . While the significance of each diffusion mechanism was individually studied [4, 5], Sethi and Wiesner proposed 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 neutrally buoyant particles, and therefore was not researched in conjunction with diffusive transport mechanisms.

After being first noted as the “threshold flux” by Cohen and Probstein [9], the concept of critical flux, defined as “a flux below which a decline of flux with time does not occur; above it fouling is observed” was proposed by Field et al. [10]. Subsequently, the critical flux concept was widely adopted in membrane research and development communities. In general the critical flux is dichotomized into two forms: strong and weak. The strong form indicates the first flux for which irreversible fouling appears on the membrane surface, and/or the flux at which the transmembrane pressure starts deviating from the pure water line of Darcy’s law. The weak form assumes rapid initial fouling, which brings forth the flux versus transmembrane pressure (TMP) relationship located below the pure water line with a lesser inclination.

A rigorous analysis of the critical flux concept can be found in Bacchin et al.'s recent review [3].

Brownian diffusion dominates over shear-induced diffusion when particles are below submicron-sized and/or strongly repulsive so that the average inter-particle distance between nearest neighbors is much greater than an order of particle diameter. The absolute shear rate (rather than the crossflow Reynolds number [9]) is an important primary factor that can efficiently control fouling behavior, and the shear-induced diffusivity is an increasing function of the volume fraction of particles [14]. In this light, an analytical expression of effective force acting on a hard sphere undergoing both Brownian and shear-induced diffusion in a concentrated system is of great necessity, hence the introduction of an irreversible chemical potential as a non-equilibrium molar Gibb's free energy.

The current literature lacks fundamental studies on microscopic investigations of the critical flux during colloidal filtration, especially as simultaneously influenced by Brownian and shear-induced diffusion in a unified way. We chose a model filtration system consisting of non-interacting hard spheres in a fast crossflow and performed the HFBMC simulations using the effective drag force to identify the critical flux in terms of particle size and shear rate. Our Monte Carlo simulations showed good agreement with reported experimental observations.

2 Brownian and Shear-Induced Diffusion

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 Gibb's free energy

$G(T, P, n)$ with respect to the mole number of particles n :

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

where T is the absolute temperature, and P is the pressure. For convenience, this study considers Gibb's free energy per particle $\hat{\mu}$ defined as

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

where N_A is Avogadro's number. Incorporating nonequilibrium thermodynamics [18], it is proposed that $\hat{\mu}$ consists of equilibrium ($\hat{\mu}_{eq}$) and irreversible ($\hat{\mu}_{ir}$) terms:

$$\hat{\mu} = \hat{\mu}_{eq} + \hat{\mu}_{ir} \quad (3)$$

Following Førland et al.'s and Hiemenz's approaches [19, 20], the gradient of the generalized chemical potential is assumed to be equal to the phenomenological diffusion force:

$$\nabla \hat{\mu} = \mathbf{F}_{diff} \quad (4)$$

with

$$\mathbf{F}_{diff} = \mathbf{F}_{eq} + \mathbf{F}_{ir} \quad (5)$$

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

$$\nabla \hat{\mu}_{eq} = \mathbf{F}_{eq} \quad (6a)$$

$$\nabla \hat{\mu}_{ir} = \mathbf{F}_{ir} \quad (6b)$$

2.2 Diffusivity Representations

Due to the two origins of diffusion phenomena, an effective diffusivity is treated as a superposition of equilibrium and irreversible terms. The equilibrium part, D_{eq} is the generalized Stokes-Einstein diffusivity [21, 22, 23, 24]:

$$D_{\text{eq}} = D_{\text{B}} S(\phi) K(\phi) \quad (7)$$

with the Brownian self-diffusivity

$$D_{\text{B}} = \frac{k_{\text{b}} T}{6\pi\eta a} \quad (8)$$

and

$$S(\phi) = \frac{\partial \phi Z(\phi)}{\partial \phi} \quad (9)$$

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 [25]:

$$Z(\phi) = \frac{1 + \phi + \phi^2 - \phi^3}{(1 - \phi)^3} \quad (10)$$

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

$$S(\phi) = \frac{1 + 4\phi + 4\phi^2 - 4\phi^3 + \phi^4}{(1 - \phi)^4} \quad (11)$$

The friction factor is known as

$$f = 6\pi\eta a K^{-1}(\phi) \quad (12)$$

which represents the amount of drag force per diffusion speed.

We write the irreversible diffusivity, analogous to Eq. (7) as:

$$D_{\text{ir}} = D_{\text{SI}} K(\phi) \quad (13)$$

as a product of the shear-induced diffusivity D_{SI} and the sedimentation coefficient. D_{SI} is represented as

$$D_{\text{SI}} = \dot{\gamma} a^2 \hat{D}(\phi) \quad (14)$$

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 [12, 13, 14]:

$$\hat{D}(\phi) = \frac{1}{3} \phi^2 (1 + 0.5 e^{8.8\phi}) \quad (15)$$

An extensive analysis of $\hat{D}(\phi)$ was conducted by Sierou and Brady for monodispersed identical spheres [26].

The generalized diffusivity is finally expressed as

$$D = D_{\text{eq}} + D_{\text{ir}} = \left[D_{\text{B}} S(\phi) + \dot{\gamma} a^2 \hat{D}(\phi) \right] K(\phi) \quad (16)$$

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]. 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.

3 Critical Flux of Colloidal Crossflow Filtration

3.1 Hydrodynamic Force Bias Monte Carlo

The normal transition probability of a particle during this Monte Carlo simulation is determined as

$$P_z = \min [1, \exp (-\beta \Delta E - \beta \lambda \mathbf{F} \cdot \Delta \mathbf{r})] \quad (17)$$

where $\beta = 1/k_b T$, $\lambda (= 0.5)$ is the well known parameter of the force bias Monte Carlo simulation [28, 29], $\Delta \mathbf{r} (= \mathbf{r}_{new} - \mathbf{r}_{old})$ is the random trial displacement, ΔE is in general the energy difference between the new and old particle positions. \mathbf{F} is the total force acting on each particle, i.e.,

$$\mathbf{F} = \mathbf{F}_g + \mathbf{F}_b + \mathbf{F}_h \quad (18)$$

where \mathbf{F}_g , \mathbf{F}_b , and \mathbf{F}_h are gravitational, buoyant, and (mean-field) hydrodynamic forces, respectively.

Since this study targets hard spheres to investigate effects of Brownian and shear-induced diffusion on the critical flux, ΔE is always set to zero unless particles overlap each other. When the particle moves from \mathbf{r}_{old} to \mathbf{r}_{new} , a random number is generated (using FORTRAN 90 function `rand`), and is compared with the transition probability P_z . If the random number is less than or equal to P_z , then the trial movement is accepted, and the particle moves to the new position \mathbf{r}_{new} ; otherwise, movement is rejected, and the particle stays at the old position \mathbf{r}_{old} . If the particle undergoes any overlap at \mathbf{r}_{new} with another particle, the trial movement is immediately rejected because this situation is equivalent to $\Delta E \rightarrow \infty$, which is thermodynamically forbidden. All the simulations use 2100 particles, and in each MC cycle all the particles attempt to randomly move to new locations via the bias probabilities. The number of MC cycles is 1000, and statistical

data are collected during the second half of the simulation. Due to the absence of strong pair-wise interparticle interactions, the filtration system rapidly converges to a dynamic equilibrium state within the first 500 MC cycles.

4 Results and Discussion

4.1 Critical Flux

The critical flux J_{crit} determined using the hydrodynamic Monte Carlo simulations is plotted in Fig. 1 with respect to the particle diameter in comparison to Kwon et al.'s experimental observations [30]. Determination of one value of critical flux as shown in Fig. 1 requires a series of simulations with a fixed value of particle diameter and various permeate fluxes for the phase transition analysis. The total number of simulations performed to obtain the critical fluxes of Fig. 1 is 60 for five different particle diameters with twelve permeate fluxes per particle diameter.

Experimental work performed by Kwon et al. is summarized as follows. Critical fluxes were determined using two different methods: particle mass balance (PMB) and transmembrane pressure (TMP). The PMB method defines the critical flux as the highest flux below which no remarkable particle deposition is observed, and TMP protocol describes the critical flux as the flux below which the TMP does not transiently increase to maintain the permeate flux. It is worth noting that critical fluxes, predicted using our MC simulations and measured by Kwon et al. using the PMB method, show reasonably good agreement for particles greater than $0.3 \mu\text{m}$. In general, our HFBMC predicts slightly lower critical fluxes than their PMB-based flux values, which can be explained in terms of inter-particle interactions. The ionic strength used in their experiments is $10^{-5} M$, where

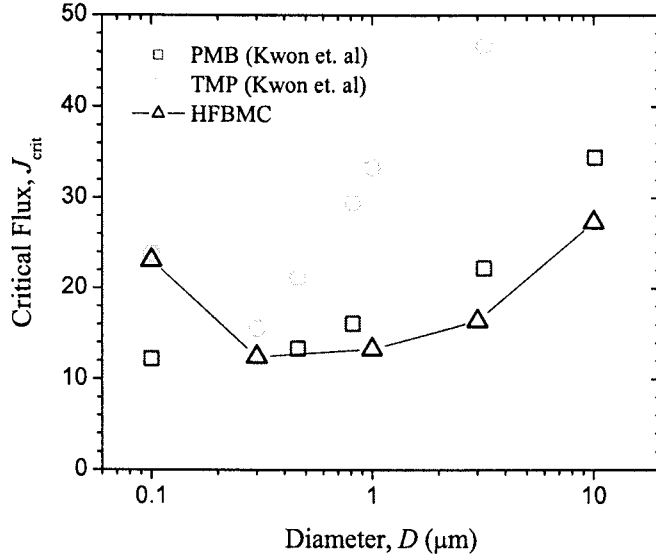


Figure 1: Comparison of critical fluxes of HFBMC simulations and experimental observations by Kwon et al.[30] using particle mass balance (PMB) and transmembrane pressure (TMP) methods. Operational conditions are as follows: crossflow $\bar{u} = 0.2$ m/sec, ionic strength $IS = 10^{-5}$ M, and temperature $T = 25^\circ\text{C}$. The length, width, and height of the membrane channel are 60, 6, and 0.36 mm, respectively. The estimated shear rate is $\gamma_0 = 3.33 \times 10^3 \text{ sec}^{-1}$.

colloidal particles are ususally repulsive if their zeta potential is of an order of $O(10)$ mV in magnitude. Repulsive interparticle interactions may mitigate particle deposition, attenuate structural bisection (i.e., concentration polarization), and so reduce values of the order parameter. In other words, stronger repulsion between particles allows higher critical flux below which no fouling occurs.

As noted above, the goal of the current study is to delineate in a consistent way a base line of the critical flux using the non-interacting hard spheres undergoing Brownian and shear-induced diffusion only, i.e., pure equilibrium thermodynamic and non-equilibrium hydrodynamic origins, respectively. Without enough shear rate (subject to the particle size), the critical flux must decrease with respect to increasing particle size since larger particles will undergo stronger hydrodynamic drag forces toward the membrane surface. Stronger shear enhances back-diffusion of larger particles from the membrane surface to the bulk phase even though their Brownina diffusion is negligible. The HFBMC results shown in Fig. 1 indicate that the critical flux of repulsive particles is higher than that of hard spheres larger than an order of $O(10^{-1})$ μm with shear rate of an order of $O(10^3)$ sec^{-1} .

The PMB result is close to the current HFBMC simulation because both deal with concentration polarization (i.e., spatial deviation of particle distribution away from the uniform configuration) as a main criteria to determine the critical flux. The PMB and HFBMC both represent the first steady state near which the initial, noticeable concentration polarization occurs with abrupt spatial bias of particle distribution. Therefore, the hydrodynamics (i.e., convective drag force) and thermodynamics (i.e., Brownian and shear-induced diffusion) are appropriately balanced in the steady state. Larger-scale simulations with accurate hydrodynamics (such as Stokesian dynamics) are of great necessary for further investigation dealing with particle motions near membrane pores [32, 33] as indicated by Kwon et al [30].

5 Conclusions

The HFBMC was developed to investigate the crossflow filtration of colloidal hard spheres undergoing both Brownian and shear-induced diffusion simultaneously. An effective hydrodynamic drag force acting on a hard sphere in a concentrated shear flow within a membrane channel is incorporated into the HFBMC simulations. Results of critical flux from the HFBMC using non-interacting hard spheres follow the same experimental propensity of those estimated using the PMB method [30]. This is because the experimental and simulation approaches are based on formation of the concentration polarization, causing the initial deposition of particles as characterized by the biased distribution.

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References

- [1] American Water Works Association Research Foundation, Water Treatment Membrane Processes, McGraw-Hill, New York, 1996.
- [2] M. Mulder, Basic Principles of Membrane Technology, Kluwer Academic Publishers, Boston, MA, 1996.

- [3] P. Bacchin, P. Aimar, R. Field, Critical and sustainable fluxes: Theory, experiments and applications, *Journal of Membrane Science* 281 (1-2) (2006) 42–69.
- [4] C. A. Romero, R. H. Davis, Transient model of crossflow micro-filtration, *Chemical Engineering Science* 45 (1990) 13–25.
- [5] L. F. Song, M. Elimelech, Theory of concentration polarization crossflow filtration, *Journal of Chemical Society Faraday Transactions* 91 (1995) 3389–3398.
- [6] S. Sethi, M. R. Wiesner, Modeling of transient permeate flux in cross-flow membrane filtration incorporating multiple particle transport mechanisms, *Journal of Membrane Science* 136 (1997) 191–205.
- [7] G. Segre, A. Silberberg, Radial particle displacements in poiseuille flow of suspensions, *Nature* 189 (21) (1961) 209 – 210.
- [8] S. Chellam, M. R. Wiesner, Particle transport in clean membrane filters in laminar flow, *Environmental Science and Technology* 26 (8) (1992) 1611–1621.
- [9] R. D. Cohen, R. F. Probstein, Colloidal fouling of reverse osmosis membranes, *Journal of Colloid and Interface Science* 114 (1) (1986) 194–207.
- [10] R. W. Field, D. Wu, J. A. Howell, B. B. Gupta, Critical flux concept for microfiltration fouling, *Journal of Membrane Science* 100 (3) (1995) 259–272.
- [11] A. Einstein, *Investigation on the Theory of the Brownian Movement*, Dover Publications, Inc., New York, 1956.

- [12] D. Leighton, A. Acrivos, Measurement of the shear induced coefficient of self-diffusion in concentration suspensions of spheres, *Journal of Fluid Mechanics* 177 (1987) 109–131.
- [13] D. Leighton, A. Acrivos, The shear-induced migration of particles in concentrated suspensions, *Journal of Fluid Mechanics* 181 (1987) 415–439.
- [14] D. Leighton, A. Acrivos, Viscous resuspension, *Chemical Engineering Science* 41 (6) (1986) 1377–1384.
- [15] D. A. Drew, J. A. Schonberg, G. Belfort, Lateral inertial migration of a small sphere in fast laminar flow through a membrane duct, *Chemical Engineering Science* 46 (12) (1991) 3219–3224.
- [16] F. W. Altena, R. J. Weigand, G. Belfort, Lateral migration of spherical particles in laminar porous tube flow: application to membrane filtration, *PhysicoChemical Hydrodynamics* 6 (1985) 393–413.
- [17] F. W. Altena, G. Belfort, Lateral migration of spherical particles in porous channels: application to membrane filtration, *Chemical Engineering Science* 39 (1985) 343–355.
- [18] B. C. Eu, *Generalized Thermodynamics: Thermodynamics of Irreversible Processes and Generalized Hydrodynamics (Fundamental Theories of Physics)*, Kluwer Academic Publishers, New York, 2002.
- [19] K. S. Førland, T. Førland, S. K. Ratkje, *Irreversible Thermodynamics: Theory and Applications*, John Wiley and Sons, New York, 1988.
- [20] P. C. Hiemenz, *Principles of Colloid and Surface Chemistry*, Marcel Dekker, New York, 1986.

- [21] G. K. Batchelor, Brownian diffusion of particles with hydrodynamic interaction, *Journal of Fluid Mechanics* 74 (1976) 1–29.
- [22] J. P. Hansen, I. R. McDonald, *Theory of simple liquids*, Academic Press, London, 1976.
- [23] R. J. Hunter, *Foundations of Colloid Science*, Oxford Univ. Press, New York, 1986.
- [24] W. B. Russel, D. A. Saville, W. R. Schowalter, *Colloidal Dispersions*, Cambridge Univ. Press, New York, 1989.
- [25] N. F. Carnahan, K. E. Starling, Equation of state for nonattracting rigid spheres, *The Journal of Chemical Physics* 51 (2) (1969) 635–636.
- [26] A. Sierou, J. F. Brady, Shear-induced self-diffusion in non-colloidal suspensions, *Journal of Fluid Mechanics* 506 (2004) 285–314.
- [27] D. J. Pine, J. P. Gollub, J. F. Brady, A. M. Leshansky, Chaos and threshold for irreversibility in sheared suspensions, *Nature* 438 (15) (2005) 997.
- [28] M. Rao, B. J. Berne, On the force-bias monte carlo simulation of simple liquid, *Journal of Chemical Physics* 71 (1979) 129–132.
- [29] M. P. D’evelyn, S. A. Rice, Comment on the configuration space diffusion criterion for optimization of the force bias monte carlo method, *Chemical Physics Letters* 77 (3) (1981) 630–633.
- [30] S. Kwon, D. Y. and Vigneswaran, A. G. Fane, R. B. Aim, Experimental determination of critical flux in cross-flow microfiltration, *Separation and Purification Technology* 19 (3) (2000) 169–181.

- [31] J. C. Chen, M. Elimelech, A. S. Kim, Monte carlo simulation of colloidal membrane filtration: Model development with application to characterization of colloid phase transition, *Journal of Membrane Science* 255 (2005) 291–305.
- [32] M. M. Kim, A. L. Zydney, Particle-particle interactions during normal flow filtration: Model simulations, *Chemical Engineering Science* 60 (15) (2005) 4073–4082.
- [33] M. M. Kim, A. L. Zydney, Theoretical analysis of particle trajectories and sieving in a two-dimensional cross-flow filtration system, *Journal of Membrane Science* 281 (1-2) (2006) 666–675.