Critical Flux in Particle Ultrafiltration of Variable Sizes: Using Interacting Brownian Dispersions

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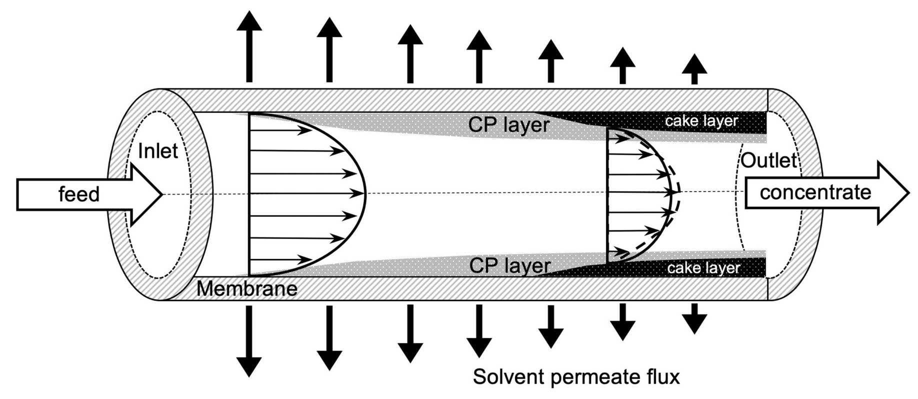
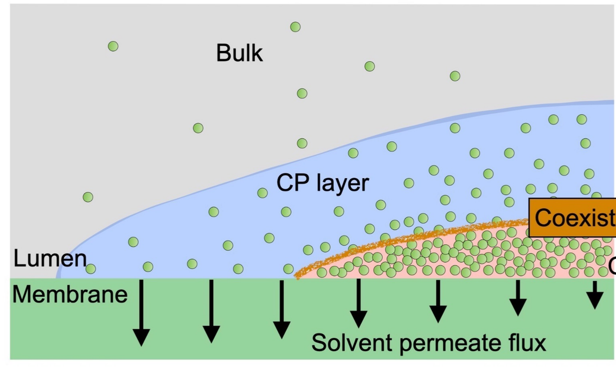
Abstract

Crossflow ultrafiltration (UF) is a pressure-driven separation and enrichment process for colloidal dispersions where the feed dispersion is continuously pumped through a membrane pipe. The transmembrane pressure (TMP) causes solvent to flow out of the membrane, while the colloidal particles are retained inside the pipe. In this study, we present theoretical results for the UF concentration and flow profiles, and the critical flux for dispersions of various sizes of particles. The results are obtained using a recently published modified boundary layer approximation (mBLA) method of crossflow UF [1, 2]. The semi-analytic mBLA method provides an accurate description of UF profiles, on accounting for the concentration dependence of dispersion transport properties and osmotic pressure. The considered model dispersions encompass impermeable and permeable hard spheres and charge-stabilized dispersions.





1 Modeling of Crossflow Ultrafiltration

The present UF model uses the effective Stokes flow and advection-diffusion equation under solvent permeate flux to describe the flow and concentration profiles. The permeate flux is described by Darcy-Starling law at the wall (i.e., surface of the membrane or cake layer)

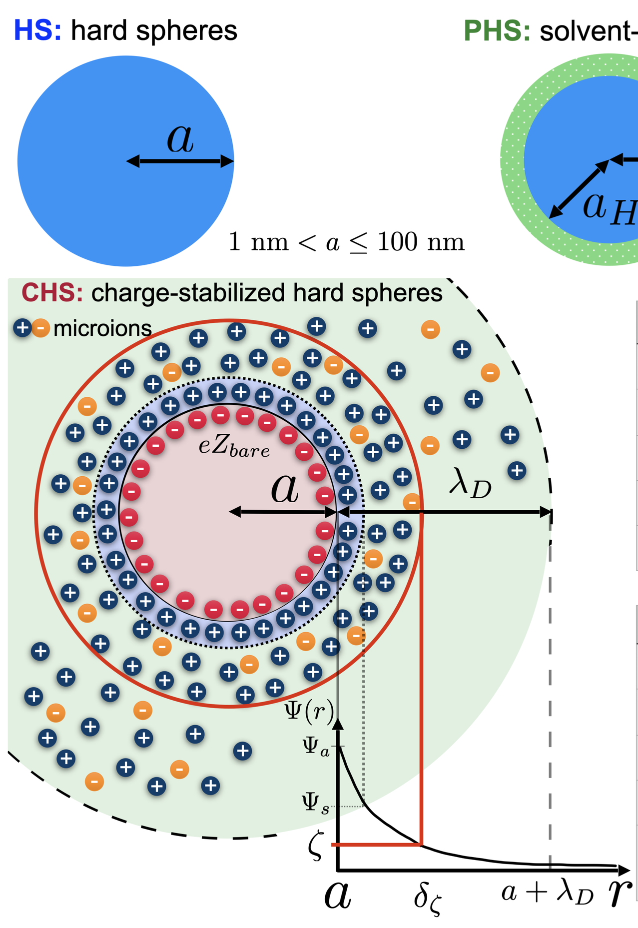
$$v_w(z) = L_p(z)\Big[P(z) - P^{perm} - \Pi(\phi_w(z))\Big]$$

where z is longitudinal distance from inlet, $L_p(z)$ is hydraulic permeability of membrane plus cake layer, $P(z) - P^{perm}$ is the local TMP, and Π is the osmotic pressure as function of particle wall volume fraction ϕ_w. The associated boundary conditions are provided by the operating conditions: TMP, constant pressure at permeate side P^{perm}, mean-inlet velocity $\overline{u}^0$, and feed concentration ϕ_b. The required dispersion properties are osmotic pressure $\Pi(\phi)$, gradient diffusion coefficient $D(\phi)$, and viscosity $\eta(\phi)$.

The mBLA method is based on matched asymptotic expansion and fixed-point calculation:

1. Outer solution
   - $\phi^{out} \approx \phi_b \ll 1$
   - Semi-analytic flow profile
2. Boundary layer (inner) solution
   - $\phi_b \ll \phi^{in} \leq \phi_f$ (≈ 0.494 for HS)
   - Strong influence of $D(\phi)$ and $\eta(\phi)$
3. Cross-sectional particle flux $\Phi(z)$ conservation
   - $\Phi(z) = \Phi(0)$ in steady-state
   - Fixed-point iteration (FPI) to calculate $\phi_w(z)$ and $L_p(z)$

2 Interacting Brownian Particles

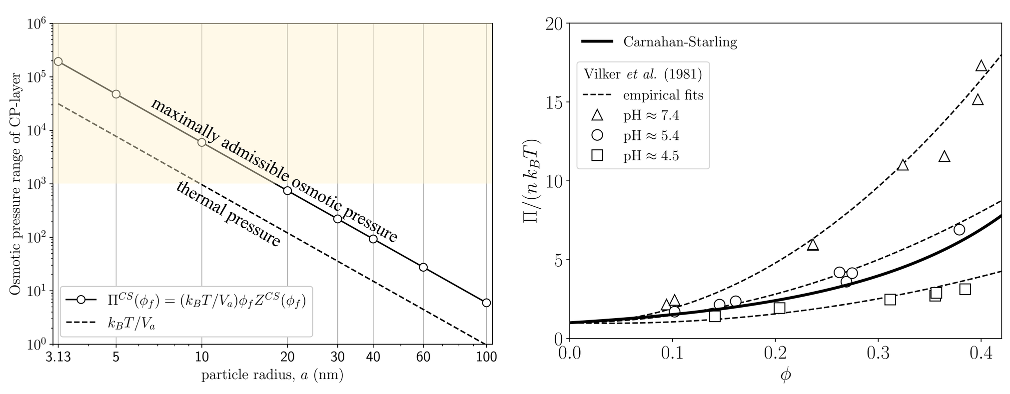


Harmant and Aimar (1998)				
I (M)	10^{-2}			
λ_D (nm)	3			
a (nm)	3.5	6	11	220
κa	1.2	2	3.7	73
ζ (mV)	45-55			55

This study			
I (M)	5×10^{-4}		
λ_D (nm)	14		
a (nm)	23.82	100	220
κa	1.7	7.3	16
$\frac{Z_{bare}}{5\times10^4}$	0.012	0.21	1
	0.11	0.45	1

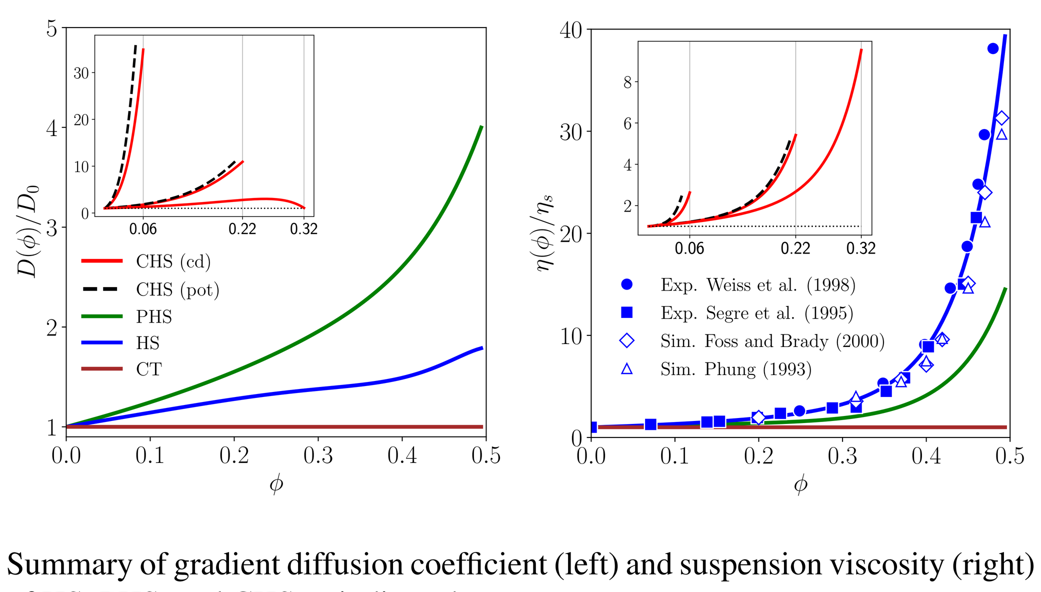
Examples of interacting Brownian particles of HS, PHS, and CHS. For CHS, the reference parameters are provided with $a = 220$ nm case, then Z_{bare} of smaller particles are determined either by the same (cd) surface charge density or (pot) surface potential [3].

2.1 Osmotic pressure



Maximally admissible osmotic pressure, Π, using Carnahan-Starling (CS) equation (left), and its comparison with the experimentally measured osmotic pressure of BSA proteins at various pH (right) with isoelectric pH is about 4.72.

2.2 Transport properties

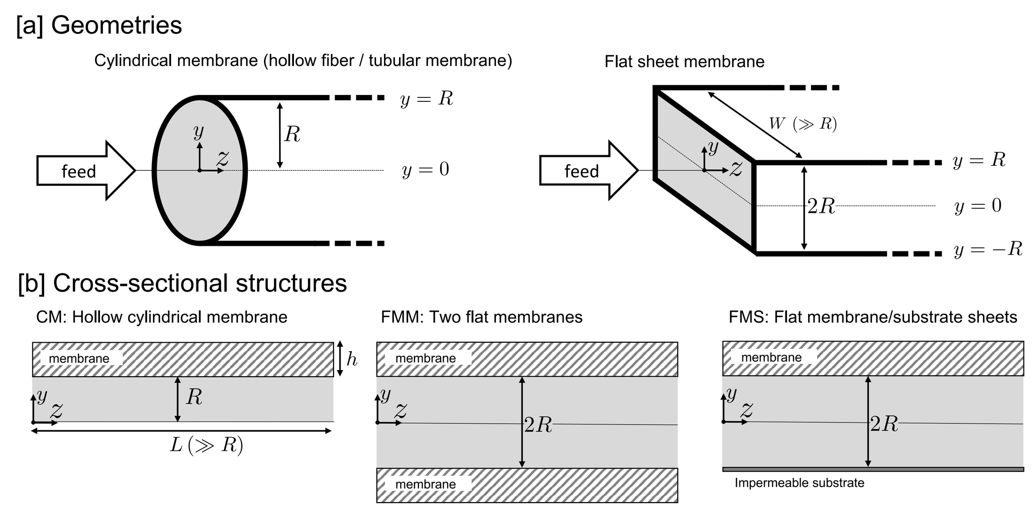


Summary of gradient diffusion coefficient (left) and suspension viscosity (right) of HS, PHS, and CHS as indicated.

3 Effect of CP Layer (HS)

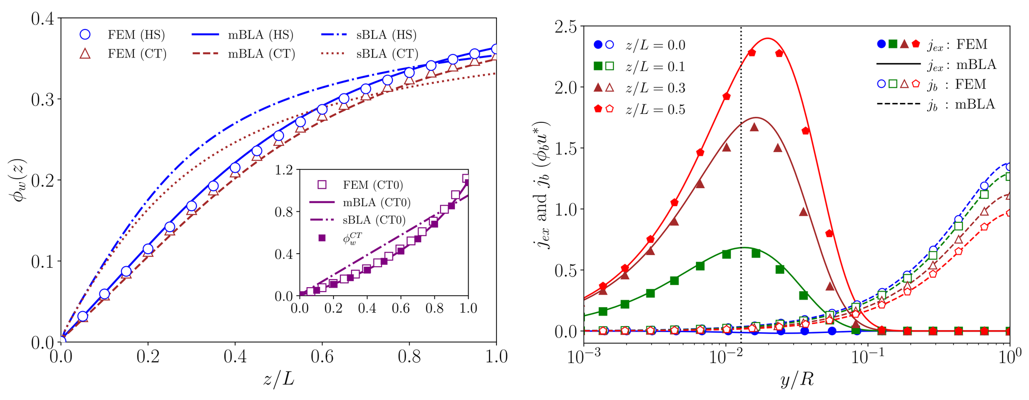
With a fully particle-retentive membrane, the permeate flux induces the particle advection toward the membrane surface, which is counter-balanced by the particle diffusion away from the membrane. To this end, the so-called concentration-polarization (CP) layer is formed near the inner membrane surface, which increases the particle-contributed osmotic pressure, Π. The actual contribution of Π on the permeate flux depends on the concentration and properties of particles with size dependence of $\Pi \propto 1/a^3$.

3.1 Membrane geometries



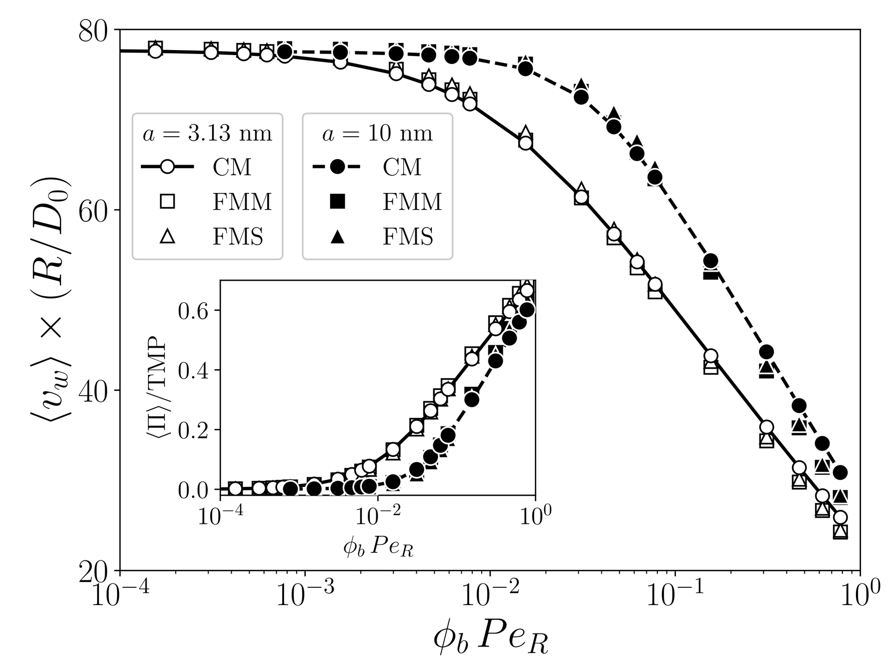
Membrane geometries of CM, FMM, and FMS as indicated. The flat–sheet membrane geometries (FMM and FMS) are commonly used in mass filtration processing in industry. The FMS geometry has demanding from laboratory for monitoring purpose with optically transparent glass substrate.

3.2 Concentration profile and particle flux



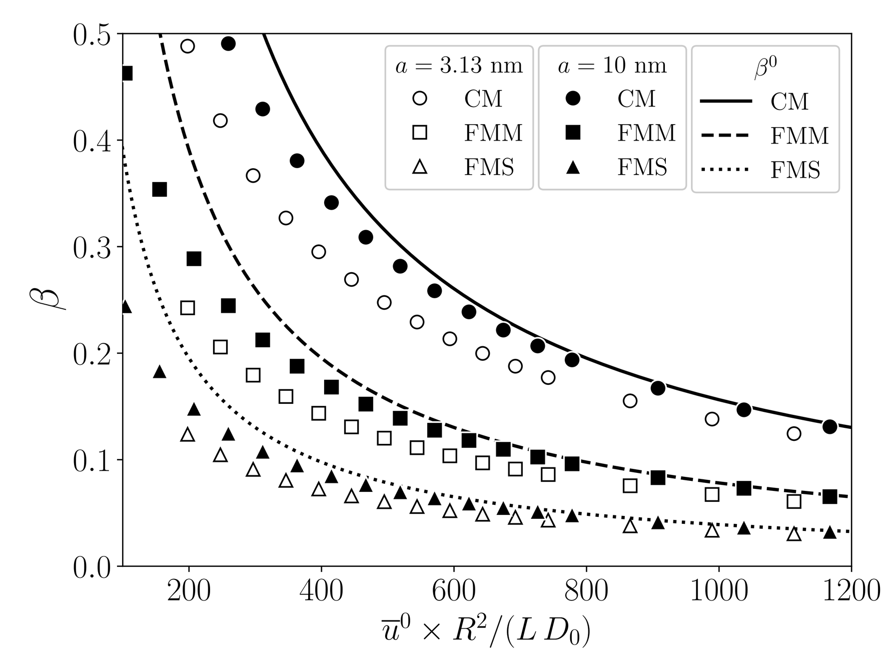
Left: Longitudinal variation of particle wall concentration, $\phi_w(z)$, for HS dispersions of CM geometry using mBLA, similarity solution, and FEM calculations. CT indicates constant-transport properties with $D = D_0$ and $\eta = \eta_s$ with $\Pi(\phi)$ of Carnahan-Starling equation. CT0 in the inset present CT with $\Pi = 0$, where the analytic solution is available (black square). Right: Transversal dependence of the excess and bulk axial particle fluxes, j_{ex} and j_b, in comparison with FEM calculations (symbols).

3.3 Effect of feed concentration



Mean permeate flux $\langle v_w \rangle$ vs. feed concentration ϕ_b. Pe_R is the transversal Peclet number, $Pe_R = Rv_w^*/D_0$, where its value is fixed to 78, here.

3.4 Effect of mean-inlet velocity

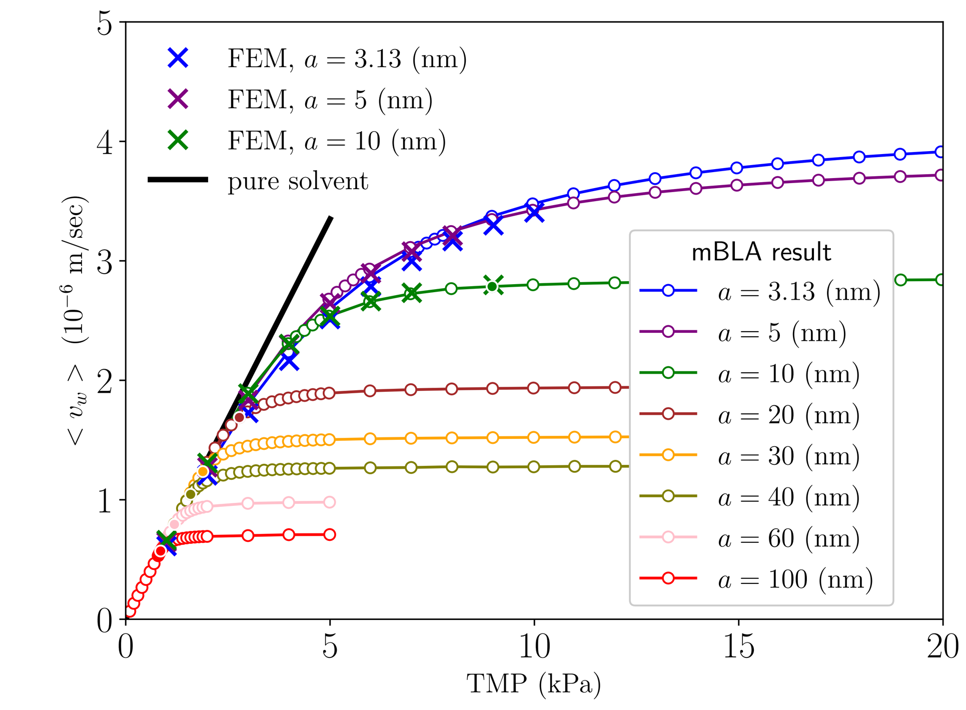


Solvent recovery indicator, β, (total permeate flux / total influx) vs. mean-inlet velocity, $\overline{u}^0$. The corresponding TMP are 16kPa for $a = 3.13$ nm and 5 kPa for $a = 10$ nm. β^0 (lines) represent the pure solvent predictions.

4 Effect of Cake Layer (HS, PHS, CHS)

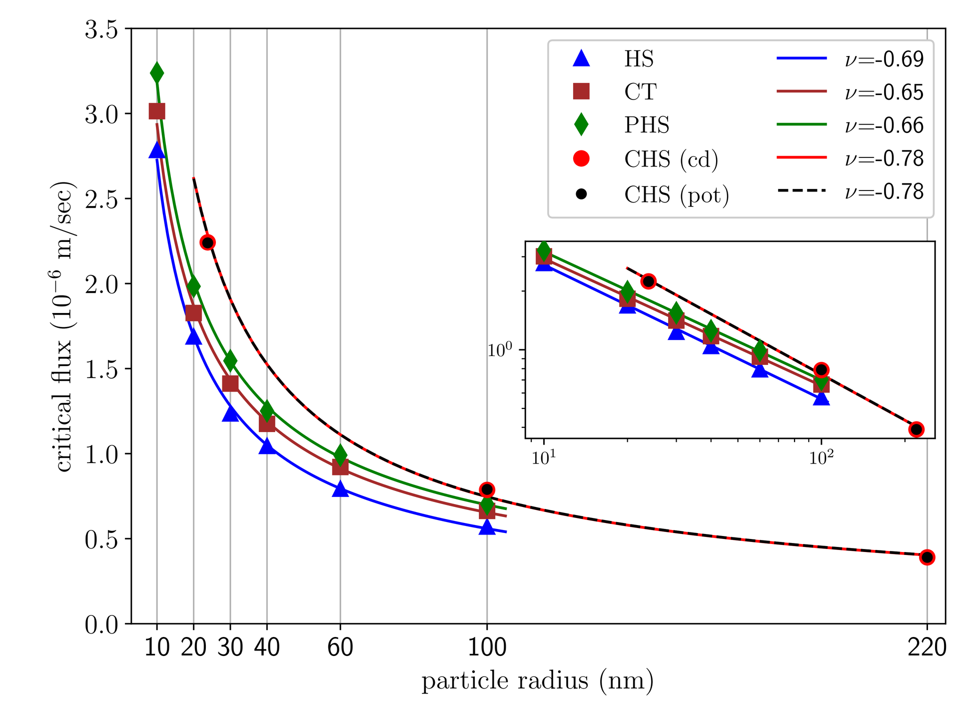
With sufficiently high TMP, the particles near the membrane surface may reach the freezing concentration ϕ_f (0.494 for HS), forming a cake layer. The critical flux is the steady-state mean permeate flux when the cake layer is observed for the first time during TMP-sweep test. Beyond this point, the reduction of permeate flux (compared to pure solvent prediction) significantly depends on the hydraulic resistance of the cake layer. With further increasing TMP, the permeate flux eventually becomes insensitive to the TMP, exhibiting limiting flux behavior. This section shows the relation between permeate flux and TMP with variable particle sizes, and theoretical understanding for the critical flux compared to particle sizes [4].

4.1 Permeate flux with CP and cake layers



Calculated mean permeate flux of the applied TMP for each size of HS particles in CM geometry. Critical flux is represented by closed circles.

4.2 Critical flux vs. particle size



Critical flux of interacting Brownian particles using HS, CT, PHS, and CHS. Symbols are mBLA calculations and lines are regression fit with exponent ν with values as indicated. The classical film theory with mass transfer coefficient predicts $\nu = -2/3$.

Concluding Remarks

- Recent development of calculating semi-analytic flow and concentration profiles is summarized. The considered dispersion systems are hard spheres (HS), solvent-permeable hard spheres (PHS), and charge-stabilized dispersions (CHS).
- Effect of CP and cake layers on permeate flux is provided with remarks on the critical and limiting flux behaviors.
- The mBLA calculation shows exponent to $\nu \approx -2/3$ for critical flux and particle size relation similar to the classical film theory with the mass transfer coefficient.
- Work in progress: the mBLA method is extending with dispersions under the effect of shear-induced migration [4].

Acknowledgments

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[3] G. W. Park, M. Brito, and G. Nägele. "Charge-stabilized dispersions in crossflow ultrafilration" (work in progress).

[4] G. W. Park, J. K. G. Dhont, and G. Nägele. "Critical flux in crossflow ultrafiltration: Interacting Brownian particles and the effect of shear-induced migrations" (manuscript in preparation).