Modeling Ultrafiltration of Interacting Brownian Particles

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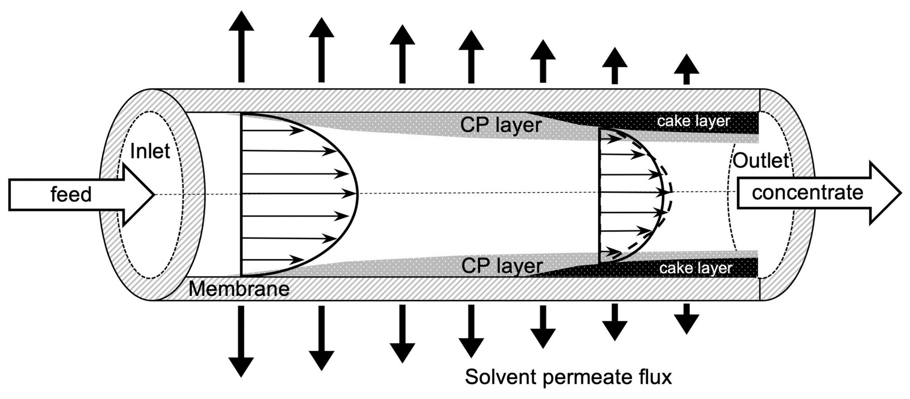
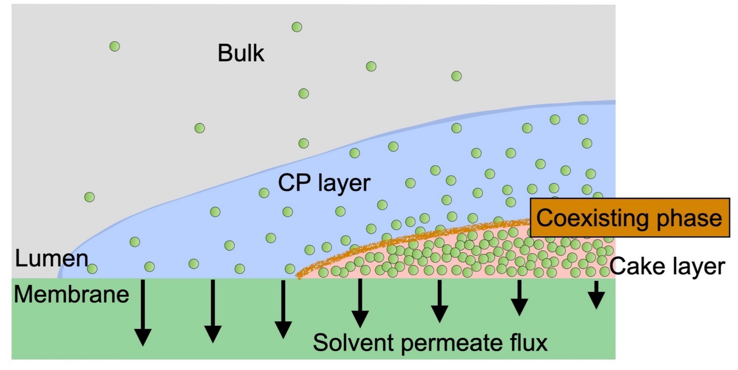
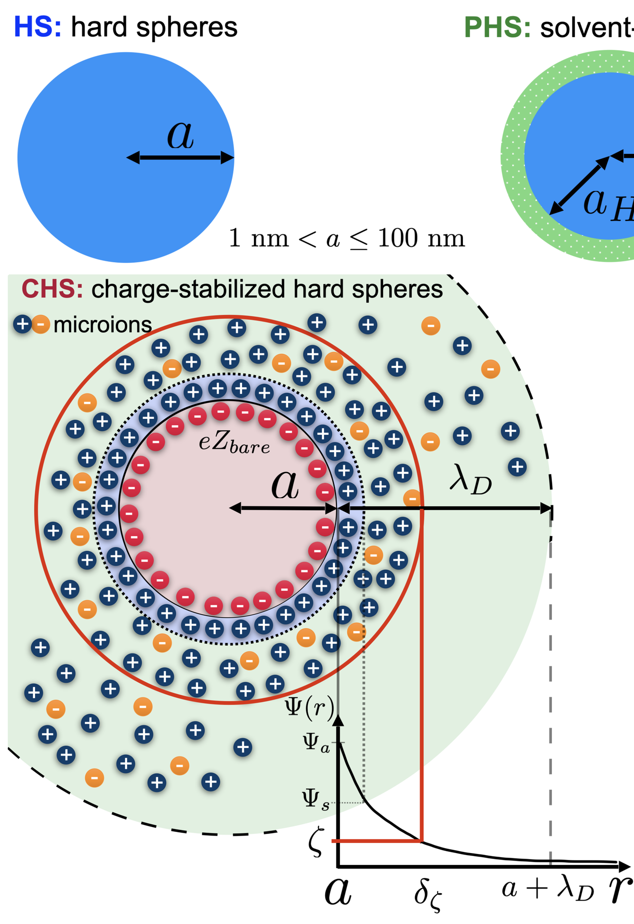
Abstract

Crossflow ultrafiltration (UF) is a pressure-driven separation and enrichment process for colloidal dispersions. The processing operates a continuous feed dispersion through a long and thin hollow membrane channels with non-zero transmembrane pressure (TMP). The TMP causes solvent to permeate through the solvent-permeable membrane, while the colloidal particles are retained inside the pipe forming concentration-polarization (CP) and fouling layers near the membrane surface. The filtration efficiency strongly depends on these multi-layers, and the accurate prediction for the flow and concentration profiles is a difficult task due to the intermingled effect of dispersion/membrane properties and operating conditions. In this study, we present theoretical results for the UF concentration and flow profiles using various types and size of dispersions. The results are obtained using an extended version of modified boundary layer approximation (mBLA) method [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 particles.





1 Interacting Brownian Particles

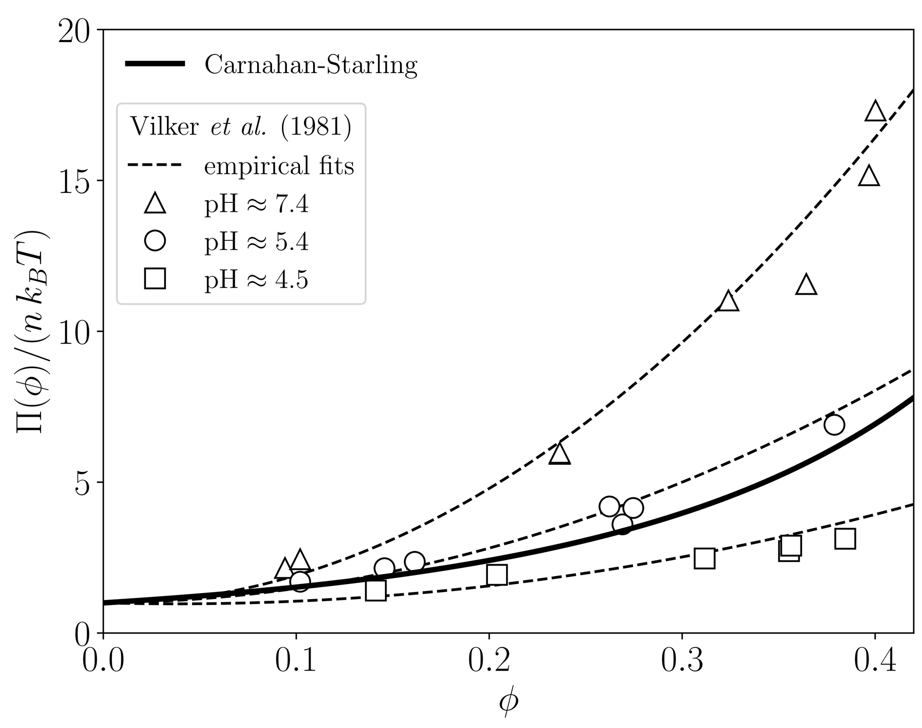


Harmant and Aimar (1998)				
I (M)	10^{-2}			
λ_D (nm)	3			
a (nm)	3.5	6	11	220
κa	1.2	2	3.7	73
ζ (mV)	45-55			55

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

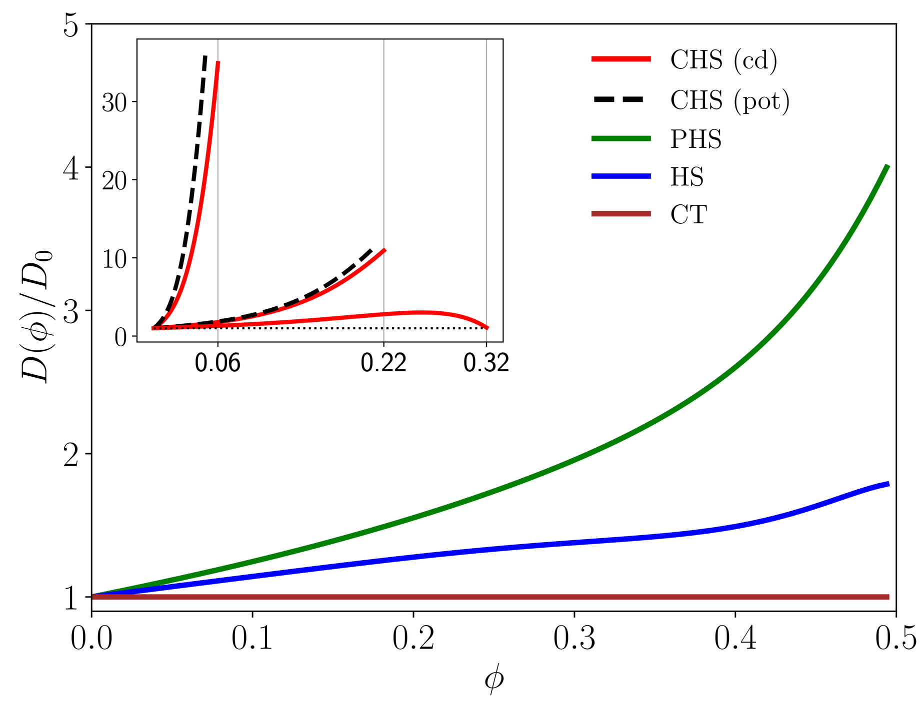
Examples of colloidal dispersions (HS, PHS, and CHS) considered in this study. For CHS, the $a = 220$ nm is selected as the reference case with $Z_{bare} = 5\times10^4$, then Z_{bare} of smaller particles are determined by the same (cd) surface charge density or (pot) surface potential [3].

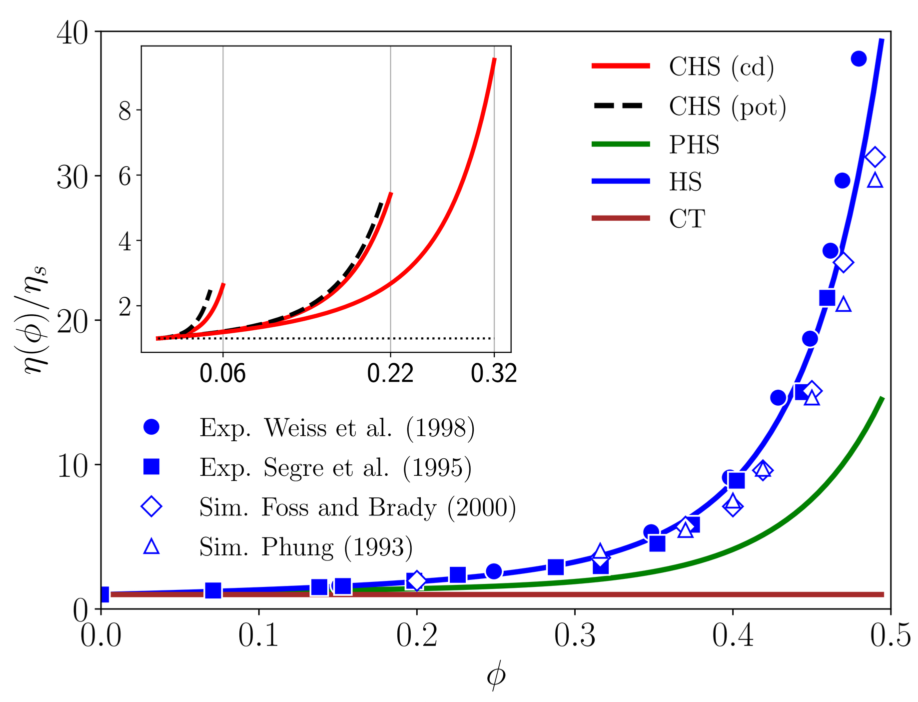
Osmotic pressure



Particle-contributed osmotic pressure, Π, using Carnahan-Starling equation for HS and PHS (solid line). The symbols are the experimental results of BSA proteins at various pH conditions, reproduced from Vilker et al. (1981). The isoelectric pH of BSA solution is 4.72. The osmotic pressure for CHS is not reported here.

Transport properties





Gradient diffusion coefficient, $D(\phi)$, and suspension viscosity, $\eta(\phi)$, for HS, PHS, and CHS as indicated. The CT represents for the constant transport properties with $D = D_0 = k_BT/(6\pi\eta_s a)$, Stokes-Einstein diffusion coefficient, and $\eta = \eta_s$, solvent viscosity.

2 Modeling Crossflow Ultrafiltration

The present UF model describes the dispersion-averaged flow using the effective Stokes and advection-diffusion equations. The operating conditions are specified by TMP, constant pressure at permeate side P^{perm}, mean-inlet velocity $\overline{u}^0$, and feed concentration ϕ_b. The solvent permeate flux through the membrane is modelled by Darcy-Starling law

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

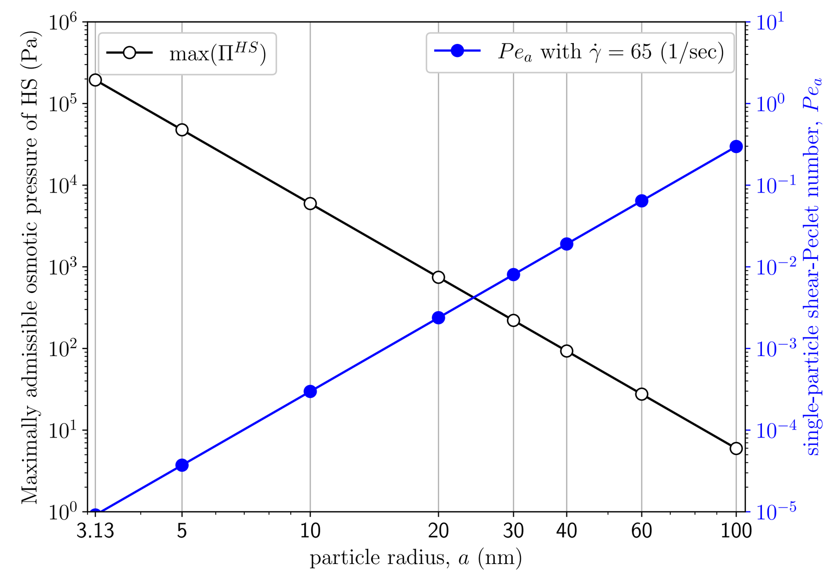
where z is longitudinal distance from inlet, $L_P(z)$ is the hydraulic permeability of membrane and cake layer, and $P(z) - P^{perm}$ is the local TMP. The mBLA method [1, 2] is extended with the cake layer using hydraulic resistance model for $L_P(z)$.

The CP-layer profile is related to the balance between particle advection toward the membrane and particle diffusion away from the membrane. The characteristic thickness of the CP-layer is often small compared to the channel radius R, which is estimated by the inverse of transversal Péclet number,

$$\frac{\delta_{CP}}{R} = \frac{1}{Pe_R} = \frac{D_0}{v_w^* R},$$

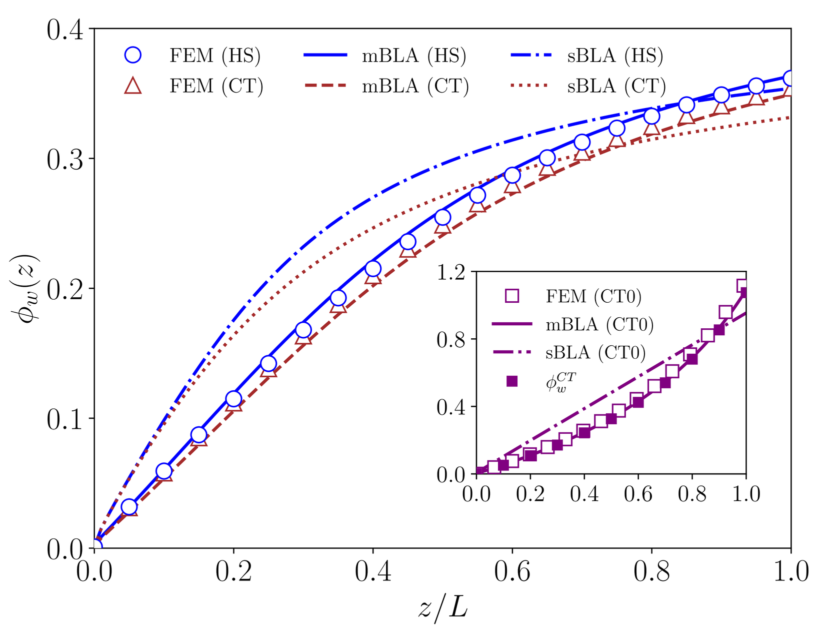
where v_w^* is a characteristic permeate flux. The smallness dimensionless value, δ_{CP}/R, is used for the asymptotic expansion in mBLA method.

Effect of particle size



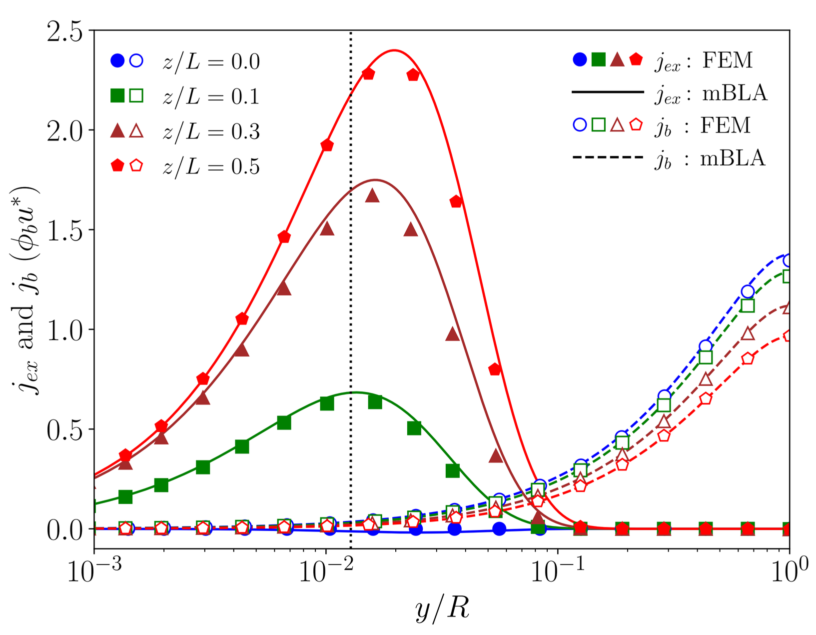
Maximally admissible osmotic pressure, Π, of hard spheres using Carnahan-Starling equation (left axis), and single-particle shear-Péclet number, Pe_a (right axis). Within the UF operating condition where $Pe_a = \dot{\gamma}a^2/D_0 \ll 1$ with a characteristic shear-rate $\dot{\gamma}$.

Concentration profile



Longitudinal variation of particle wall concentration, $\phi_w(z)$, of HS and CT dispersions calculated by mBLA, similarity solution, and finite-element method (FEM). The inset (CT0) represents a fictitious condition for CT without osmotic pressure contribution (i.e., $\Pi = 0$) and no-upper-limit of particle concentration.

Axial particle transport

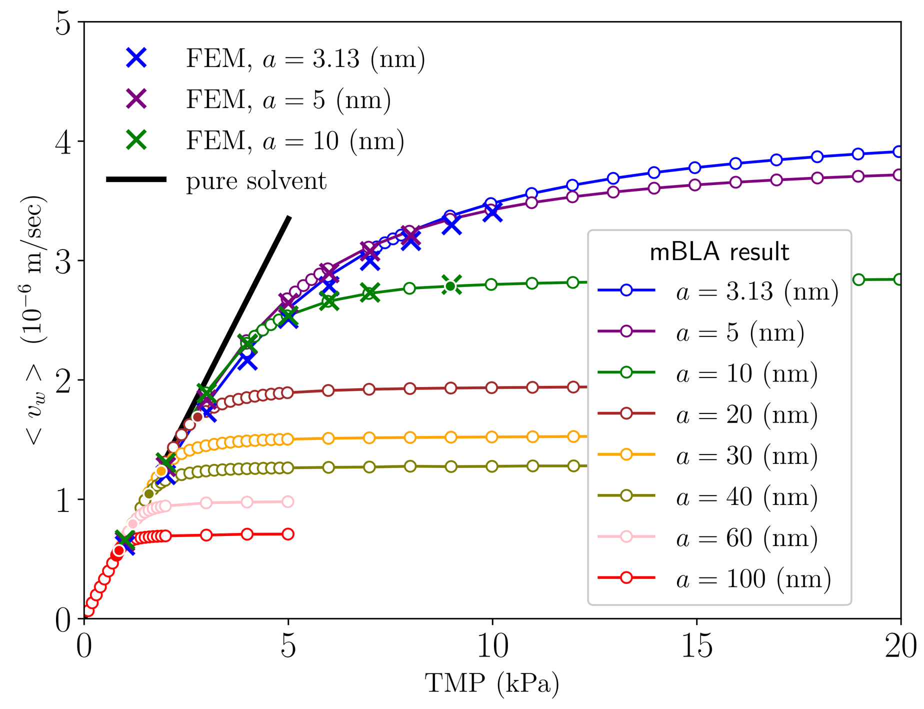


Transversal dependence of the excess, j_{ex}, and bulk axial particle fluxes, j_b, of hard-sphere dispersion. The lines are calculated by mBLA method and symbols are FEM result. The coordinate y is the transversal distance from membrane surface. The vertical-dotted line represents the characteristic thickness of the CP-layer with $y = \delta_{CP}$.

3 Cake Layer and Permeate Flux

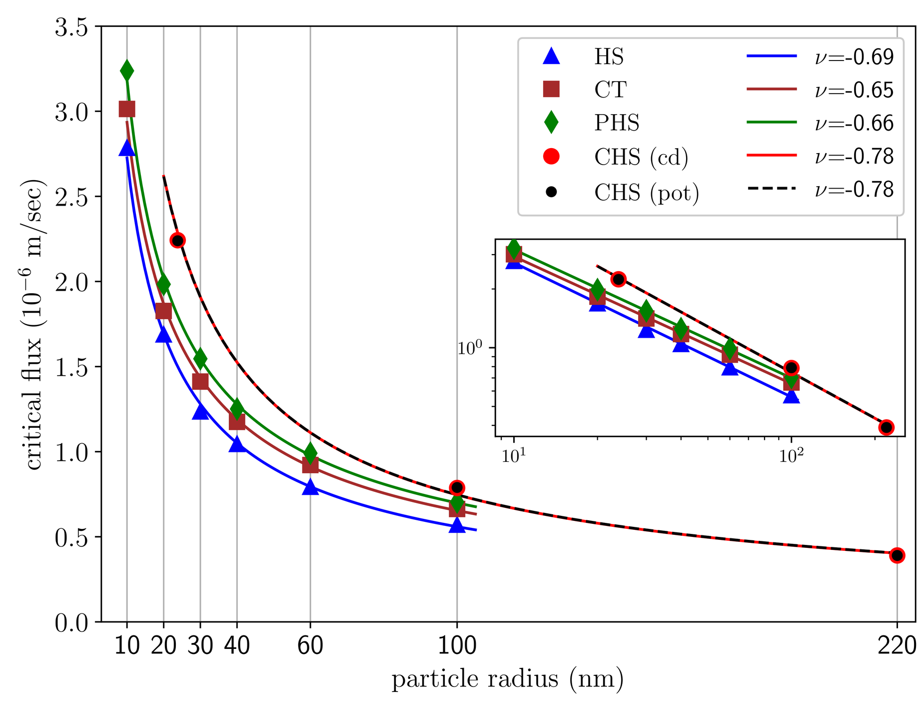
When the particle concentration reaches a solidification limit (due to high TMPs), an immobilized particulate layer, termed *cake layer*, is formed next to the membrane surface. For hard-sphere dispersion, the freezing concentration, $\phi_f = 0.494$, is used to identify the formation of cake layer. For the charge-stabilized dispersion, the freezing concentration is characterized by Hansen-Verlet criterion with a value of 3.1.

Permeate flux vs. TMP (HS)



Mean permeate flux vs. the applied TMP using mBLA method (open circles) and FEM calculation (crosses). For each size of particles, the closed circle indicates the lowest TMP condition of cake formation, and its corresponding mean permeate flux is called *the critical flux*.

Critical flux vs. particle size (HS, PHS, and CHS)



Critical flux for various size of dispersions in the type of HS, CT, PHS, and CHS. Symbols are mBLA calculations and lines are regression fit with exponent ν with the values as indicated. The classical film theory with the mass transfer coefficient predicts $\nu = -2/3$.

Concluding Remarks

- The modified boundary layer approximation (mBLA) method provides an accurate semi-analytic flow and concentration profiles of crossflow ultrafiltration process.
- The considered dispersion systems are hard spheres (HS) [1, 2], solvent-permeable hard spheres (PHS) [1], and charge-stabilized dispersions (CHS) [3].
- The mBLA calculation provides a relation between the critical flux and particle size, which is similar to the classical film theory using the mass transfer coefficient.
- The equilibrium dispersion properties are used within the ultrafiltration operating condition. For the future, the mBLA method will be extended to microfiltration where the shear-induced migration becomes important [4].

Acknowledgments

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