SUPPLEMENTAL INFORMATION for A Predictive Model of Super High Resolution Separations in Dead-End Filtration through Ultrathin Membranes

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1. Derivation of The Sieving Coefficient

K^{-1} and G are interpolated from Paine and Scherr's [1] numerical simulations using a polynomial fit of their data of order 40. It's important to note that Paine and Scheer assume that there is no electrostatic repulsion ($E(\beta) = 0$) within the pore for the calculation of these values. Dechadilok and Deen examine electrostatic effects on both G [2] and K^{-1} [3]; they found that accounting for electrostatics did marginally change both values, but the greater impact of charge-based repulsion came from whether or not the particles made it into the pore in the first place. Since we are accounting for electrostatics elsewhere, Paine and Sheer is a reasonable approximation. Note also that extensive experimental evidence indicates that the viscosity of water in pores down to a size of $30\mathring{A}$ does not deviate significantly from its bulk value [4], and we can thus treat viscosity as uniform everywhere in our system.

The final component we need to create a mathematical model of gold transport through the membrane is a formulation of $E(\beta)$. This is considerably more complicated than dealing with the neutral pore/neutral particle case. We intend to use the Smith and Deen model of solute partitioning within a charged pore, which uses the linearized Poisson-Boltzman equation in both spherical and

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cylindrical coordinates to find an expression for the change in free energy between a charged particle in the bulk ionic solution and a charged particle within the confines of a charged pore [5] In Electrostatic Effects on the Partitioning of Spherical Colloids between Dilute Bulk Solution and Cylindrical Pores, Smith et. al. find

$$E(\beta) = R_0\epsilon(RT/F)^2\Delta G \tag{1}$$

where $R_0, \epsilon, R, F, \Delta G$ are the Cylinder radius, the solvent dielectric permittivity, the gas constant, the faraday constant, and the Gibbs free energy, respectively. ΔG at constant surface charge represents the change in free energy between a charged particle in solution and the charged particle within a charged pore, and is given as the following equation:

$$\Delta G = \frac{\frac{8\pi\tau\alpha^4 e^{\tau\alpha}}{1+\tau\alpha^2}\Lambda\sigma_s^2 + \frac{4\pi^2\alpha^2 I_0(\tau\beta)}{(1+\tau\alpha)I_1(\tau)}\sigma_s\sigma_c + \left(\frac{\pi I_0(\tau\beta)}{\tau I_1(\tau)}\right)^2 \frac{(e^{\tau\alpha}-e^{-\tau\alpha})\tau\alpha L(\tau\alpha))}{1+\tau\alpha}\sigma_c^2}{\pi\tau e^{-\tau\alpha} - \frac{2(e^{\tau\alpha}-e^{-\tau\alpha})\tau\alpha L(\tau\alpha)\Lambda))}{1+\tau\alpha}} \tag{2}$$

where τ is the ratio of pore radius to debye length (equation **??**), $L(\tau\alpha) = \coth(\tau\alpha) - \frac{1}{\tau\alpha}$, I is the modified bessel function of the first kind, σ_s and σ_c are the surface charge of the sphere and the cylinder, respectively, and when the dielectric constant of the metal is much higher than that of the solvent, Λ can be approximated:

$$\Lambda \approx \frac{\pi}{2} I_0(\tau\beta) \sum_{t=0}^{\infty} \frac{\beta^t (2t)!}{2^3 (t!)^2} I_t(\tau\beta) \times \left[\tau K_{t+1}(2\tau) + \frac{3}{4} K_t(2\tau)\right] \tag{3}$$

where K is the modified bessel function of the second kind [5]. Note that σ_s and σ_c are both exclusively in the numerator of equation 2, meaning as either surface's charge increase the associated change in free energy likewise increases. Further note that because the surface charges are additive, even if one of the surfaces charges were zero there would still be an electrostatic component to the difference in free energy. Only if both of the particles had zero surface charge would this expression go to zero. This expression is derived by describing a charged sphere and a charged cylinder using the linearized Poisson-Boltzman equation in both spherical and cylindrical coordinates (respectively), identifying

the boundary conditions of the two systems of equations, and then performing a coordinate transformation to apply one set of boundary conditions to the next.

2. TEM-derived Gold Nanoparticle Size Distributions

Table 1: Gold Nanoparticle Size Distributions

Manufacturer Reported Size (nm)	Actual Size (nm)	Std. Dev. (nm)
5	6.2	±1.4
10	9.3	±1.1
15	17.4	±1.2
20	20.7	±2.0
30	31.6	±2.8
40	37.8	±2.4
50	50.3	±3.6
60	59.4	±6.0
80	85.8	±7.4

3. Measuring the Zetapotential of NPN and Alumina-Coated NPN Membranes

We used a custom streaming potential rig (pictured in Figure 4) to measure the zetapotential of three bare NPN and three alumina-coated NPN membranes. 10 mM KCl (1 mM phosphate buffered, pH 7.4, conductivity 1.405 mS/cm, filtered through a 0.2 micron Pall Aerodisc syringe filter to remove salt aggregates) was forced through the NPN or alumina-coated NPN chip using several different pressures as provided by a nitrogen tank (pressure monitored with a VWR manometer, #8215). Transmembrane voltage at these various pressures was measured with handmade electrodes (silver wire wrapped around a small nail to form a coil, then dipped into Ag/AgCl ink - product #AGCL-675, purchased from www.conductivecompounds.com) connected to an Agilent 34401A $6\frac{1}{2}$ Digit

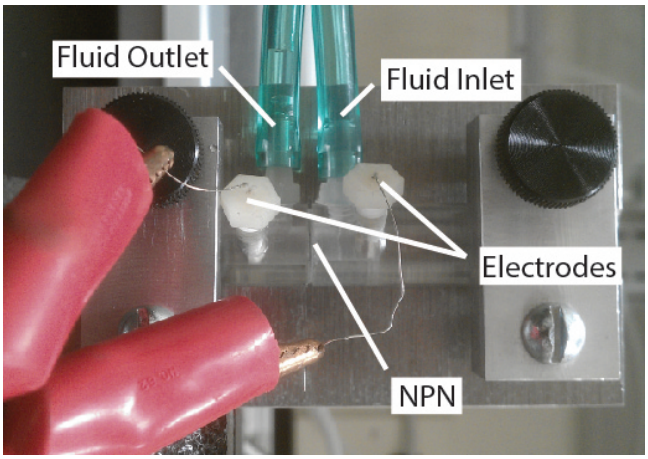

Figure 1: Pressure is applied to the fluid via a nitrogen tank while the transmembrane pressure is monitored through two Ag/AgCl electrodes hooked up to a voltmeter. The NPN or alumina-coated NPN chip is sandwiched between two o-rings. The chamber is machined out of polycarbonate and held in place with an aluminum housing. We based our streaming potential device on Burns et Al.'s device[6]

Multimeter. We then made a pressure vs. transmembrane voltage plot. The Helmholtz-Smoluchowski equation:

$$\zeta = \frac{dE_z}{d\Delta P} \cdot \frac{\eta \Lambda_0}{\epsilon_0 \epsilon_r} \tag{4}$$

The Debye length (the distance over which charge-charge interactions are important in an electrolyte) is given as $K^{-1} = \frac{0.304}{\sqrt{I(M)}}$, where K^{-1} is the debye length in nm and $I(M)$ is the molar concentration of a monovalent salt at $25°C$. where ζ is the apparent zeta potential, E_z is the streaming potential, ΔP is the applied pressure, η is the solution viscosity, Λ is the solution conductivity, ε_0 is the permittivity of free space, and ε_r is the dielectric constant of the solution [7] to determine the zetapotential of the membranes. Alumina-coated NPN had an Average Zetapotential of -20.6 +/- 1.4 mV, while bare SiN has a zetapotential of -18.8 +/- 1.0 mV.

4. Additional Experimental Data and Model Predictions

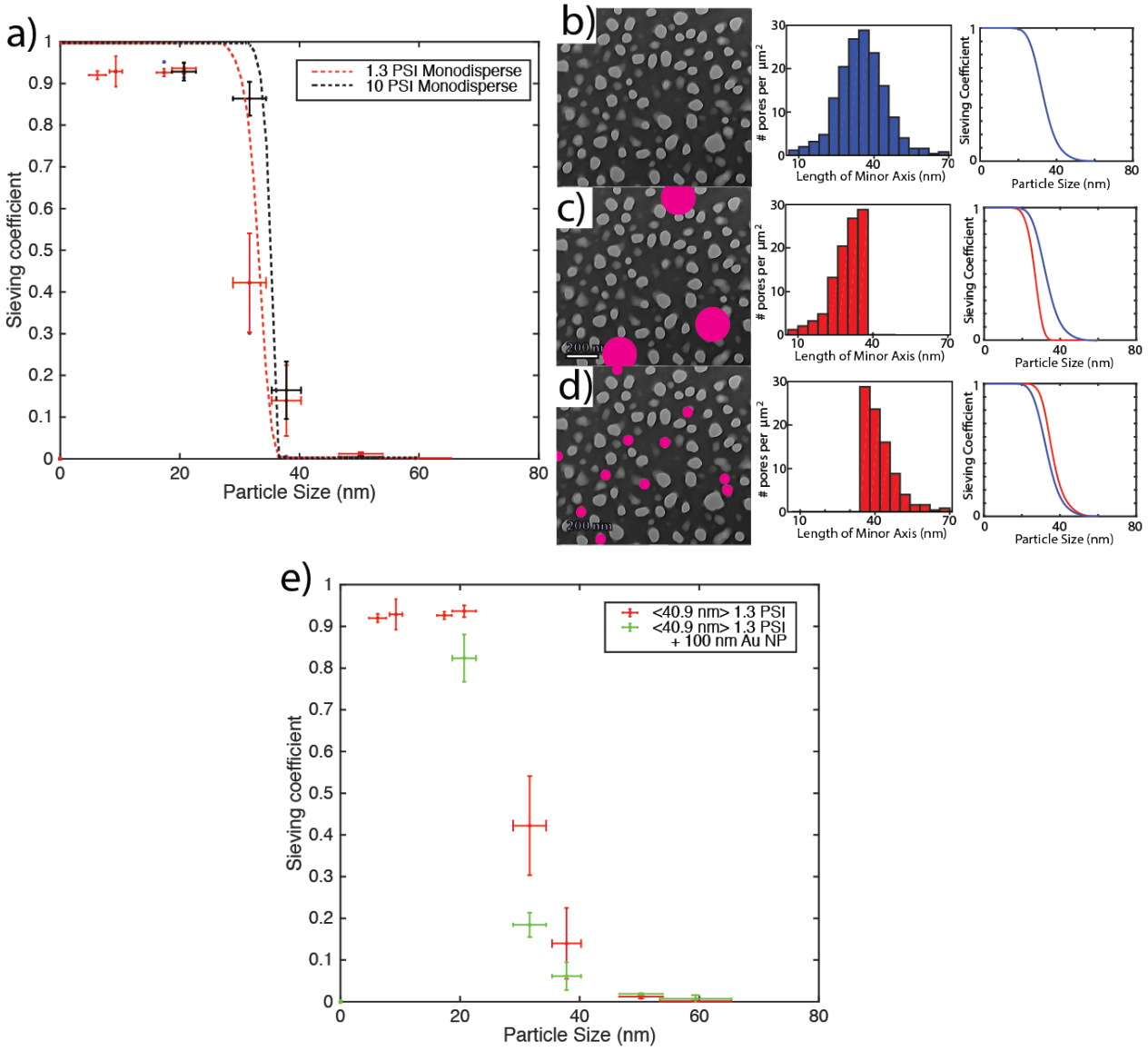

Figure 2: a) A model that assumes uniformly sized pores captures the experimental observation that the sieving curves get sharper at higher pressures better than the model using the size distribution. We hypothesize that during separations, the normal distribution of pores (b) can be "truncated" by selective plugging of the smallest pores, leading to a sieving curve that shifts and more closely resembles the monodisperse model (c). We have seen that adding a small amount of 100 nm gold NPs to a gold size ladder can cause a shift in the sieving characteristics of a membrane (e) which we believe to be due to a similar gold-size-dependent truncation of the pore size distribution (d), albeit from the opposite direction.

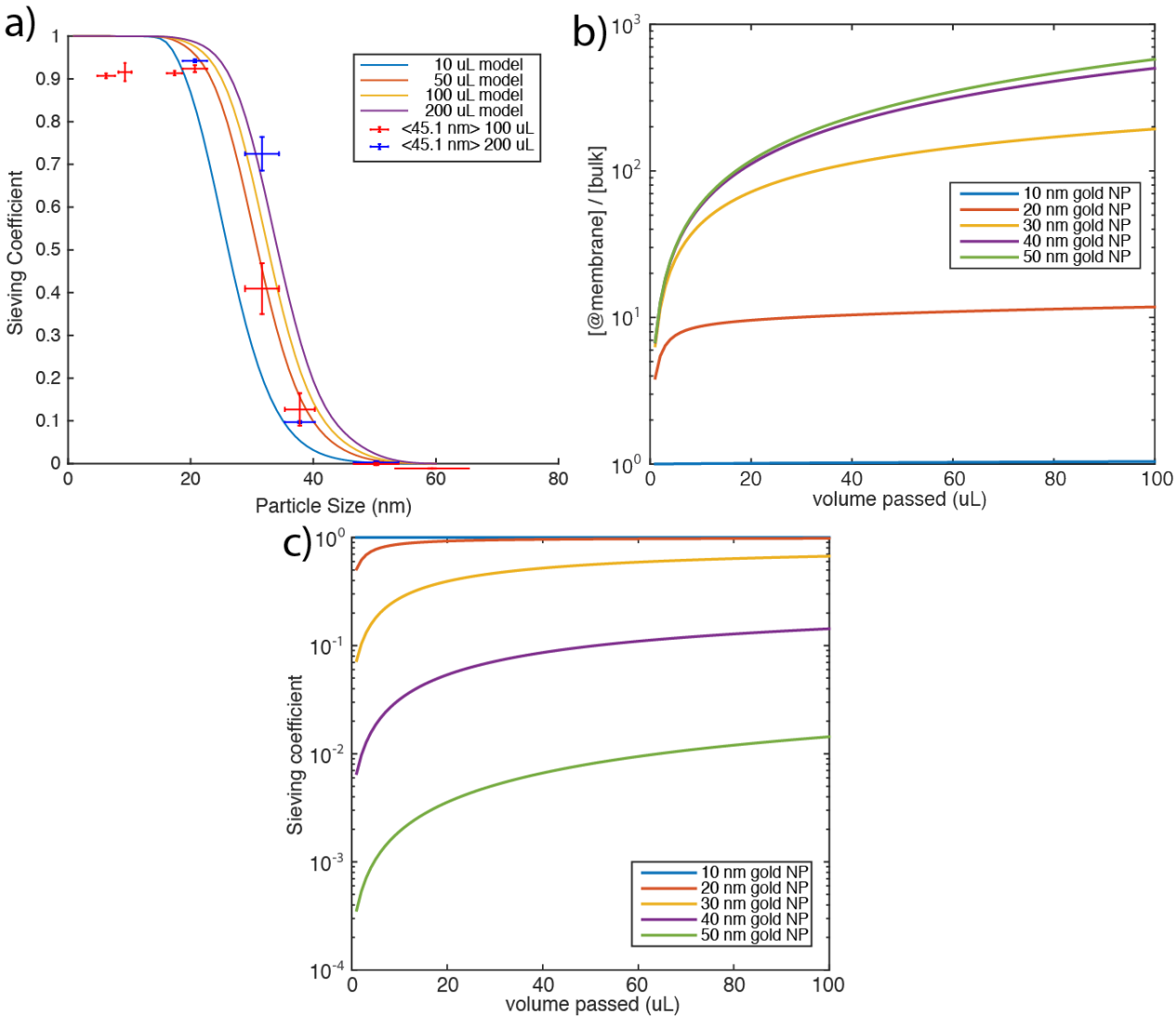

Figure 3: a) The sieving coefficients of gold nanoparticle separations are weakly dependent on the volume passed through the membrane. This is because over time the concentration at the membrane of nanoparticles increase, as shown in b). This results in gold-size-dependent relationship between increased volume passed and sieving coefficient, as shown in c).

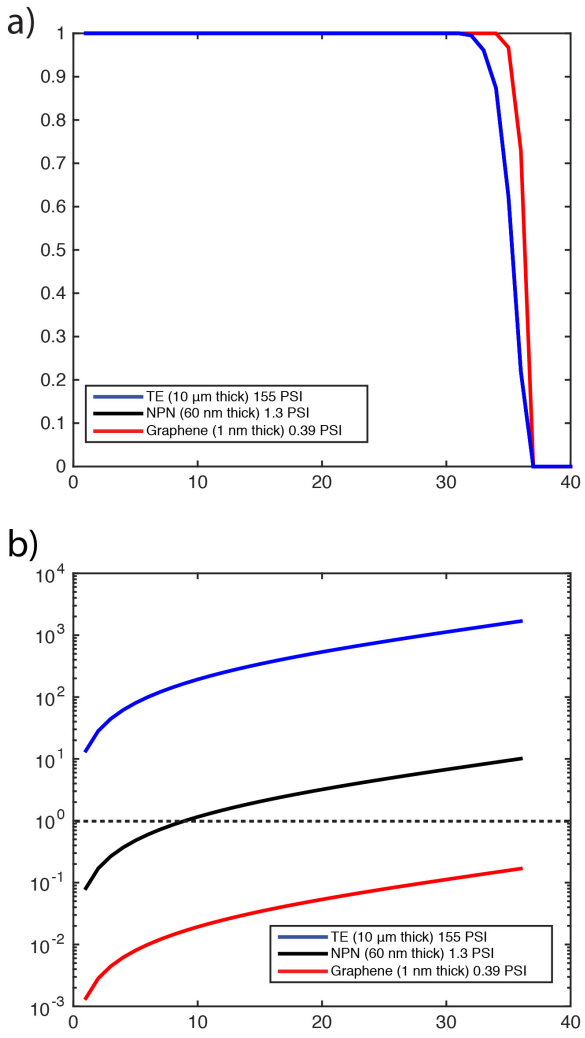

Figure 4: When the membranes are compared during higher pressure but still iso-flux separations, the Péclet number of NPN rises above 1 for small particle sizes (dashed line in Figure 2a), meaning NPN and TE performance, both being dominated by convection, are indistinguishable. Note that in Figure 2a, NPN and TE perfectly overlap. Graphene, with a Péclet number below zero for all sizes of gold nanoparticles modeled, has better performance.

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