Deposition of Colloidal Particles During the Evaporation of Sessile Drops: Dilute Colloidal Dispersions
Supporting Information

1 Boundary Condition Far away from the Drop for the Vapor Domain

Hu and Larson have proved that it is sufficient to use a vapor domain that has a radius of $r_\infty = 20R_c$[1]. Therefore, we also set the boundary of the vapor domain to have a radius of $r_\infty = 20R_c$. When the drop has a contact angle of 90°, the Laplace equation as Equation (1) is solved in the domain with a shape of a fourth of an annulus. The results give Equation (3) at $\sqrt{r^2+z^2} = r_\infty$, so we decided to keep this boundary condition for the whole evaporation process.

The evaporation flux from our model was compared with previous literature for validation. The flux distribution from our FEM simulation is compared to Deegan's[2] and Hu and Larson's[1] evaporation flux expressions as shown in Figure 2. Our simulation results are very close to Hu and Larson's fitting equation to their FEM results at both a small contact angle and a large contact angle. This agreement validates our model for the vapor domain, indicating that the boundary conditions give the right results.

2 Derivation of the Model of Adsorption and Desorption

The adsorption and desorption are both assumed a first-order reaction, with k_1 and k_{-1} as the adsorption and desorption rate constants respectively. Therefore, the dimensional mass flux of particles $\tilde{J_p}$ combining adsorption and desorption is expressed as:

$$\tilde{J_p} = k_1 \cdot \tilde{c_p} - k_{-1}\tilde{\Gamma_s}, \tag{1}$$

where $\tilde{c_p}$ is the dimensional particle bulk concentration and $\tilde{\Gamma_s}$ is the dimensional particle surface concentration. This flux is balanced with diffusion flux:

$$\tilde{J_p} = -D_p \mathbf{n} \cdot \tilde{\nabla} \tilde{c}_p = k_1 \cdot \tilde{c_p} - k_{-1}\tilde{\Gamma_s}. \tag{2}$$

The non-dimensionalization is as follows:

$$-D_p \frac{c_{pc}}{l_c} \mathbf{n} \cdot \nabla c_p = k_1 c_{pc} \cdot c_p - k_{-1}\Gamma_c \cdot \Gamma_s, \tag{3}$$

$$\mathbf{n} \cdot \nabla c_p = \frac{k_1 l_c}{D_p} c_p - \frac{k_{-1}\Gamma_c l_c}{D_p c_{pc}} \Gamma_s, \tag{4}$$

where c_{pc} and Γ_c are defined as the characteristic values of the particle bulk concentration and the surface concentration. $c_{pc} = c_{p,0}$ (the initial particle bulk concentration), and $\Gamma_c = \frac{D_p c_{pc}}{v_c}$. An intrinsic length brought by $\frac{\Gamma_c}{c_{pc}} = \frac{D_p}{v_c} = \frac{R_c}{Pe}$, where Pe is the Peclet number. Substituting Γ_c into Equation 4:

$$\mathbf{n} \cdot \nabla c_p = \frac{k_1 l_c}{D_p} c_p - \frac{k_{-1} l_c}{v_c} \Gamma_s. \tag{5}$$

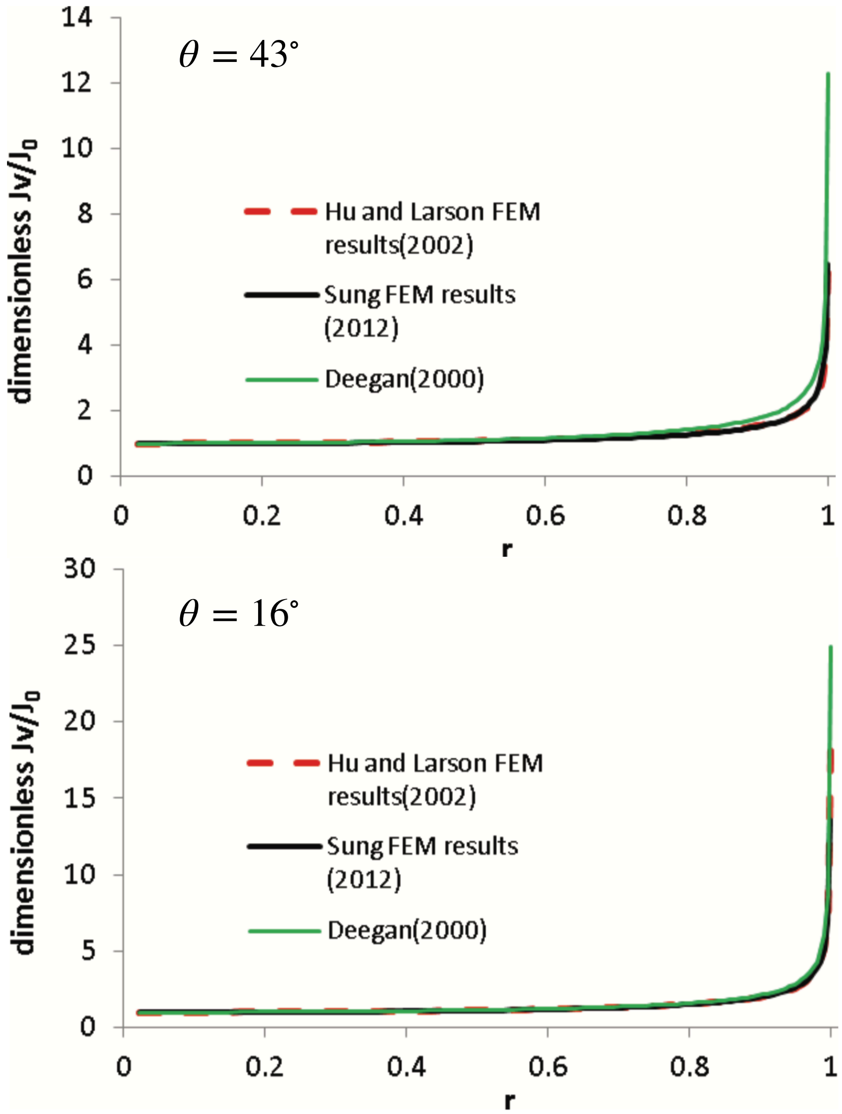

Figure 1: The comparison of evaporation flux distribution between our FEM results, Deegan(2000)'s and Hu(2002)'s results.

Further, Damkholer number $Da = \frac{k_1 l_c}{D_p}$ and desorption Damkholer number $Da_{-1} = \frac{k_{-1} l_c}{v_c}$ are defined. $Da = \frac{k_1 l_c}{D_p}$ gives the ratio of particle adsorption to particle diffusion. $Da_{-1} = \frac{k_{-1} l_c}{v_c}$ gives the ratio of particle desorption to particle convection.

3 A Sketch of the "Solid" Region

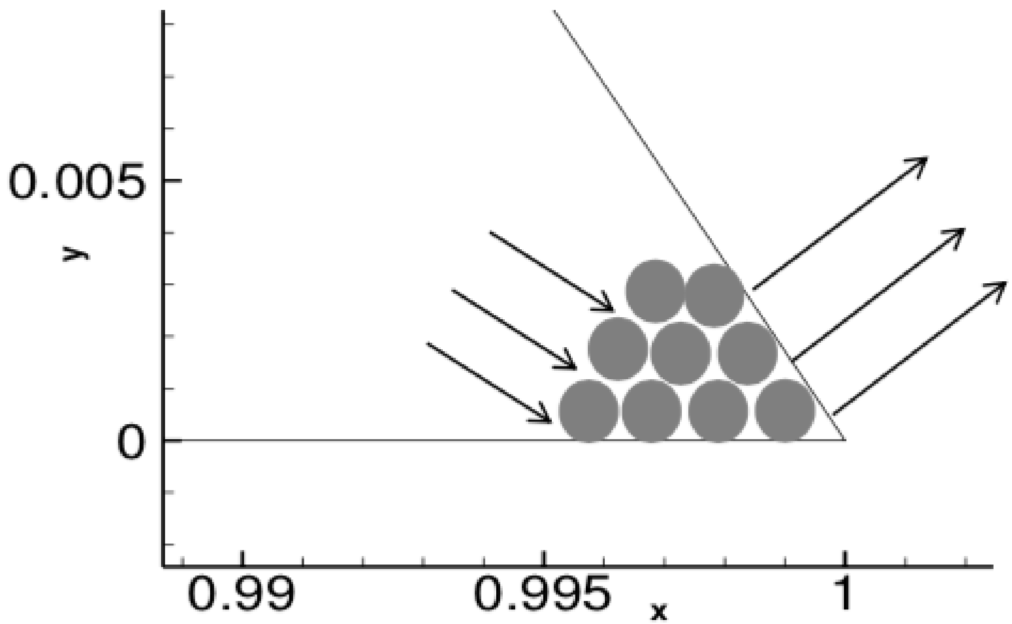

Figure 2: Evaporation is still considered on the surface of the solid phase and drives the liquid in the drop phase to flow toward the contact line.

References

[1] Hua Hu and Ronald G Larson. Evaporation of a sessile droplet on a substrate. *The Journal of Physical Chemistry B*, 106(6):1334–1344, 2002.

[2] Robert D. Deegan, Olgica Bakajin, Todd F. Dupont, Greg Huber, Sidney R. Nagel, and Thomas A. Witten. Contact line deposits in an evaporating drop. *Physical Review E - Statistical Physics, Plasmas, Fluids, and Related Interdisciplinary Topics*, 62(1 B):756–765, 2000.