Electronic Supplementary Material (ESI) for Soft Matter
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Supplementary Material

S2 Calculation of Disjoining Pressure

Several assumptions and simplifications were considered, which are listed below:

- *For the sake of simplicity, the charged particles deposited over the liquid film interface are assumed to establish a static charge layer rather than many discrete point charges. This assumption is particularly realistic when the population of particle is large enough. We also neglect the electrohydrodynamic effect is particulate laden air.*

- *We assumed that the thermodynamic equilibrium with respect to adsorption of potential-determining ions does not attain when the film is thin enough. Therefore, for thin films, the constant surface charge model (instead of the constant surface potential model) was considered. The charge on the interface is dictated by external charging, i.e. charge particle deposition.*
- *We assumed that the volume charge-potential interaction inside the liquid film is governed by linearized Poisson-Boltzmann equation. (valid if the electric potential at interfaces is low.). Since the film is deposited on the grounded surface, the main voltage drop occurs in the air-side. The voltage drop in the dielectric film layer is in the order of hundreds of millivolts, while the voltage drop in the air is in the order of tens of kilovolts. Since the voltage drop is small in the dielectric film, it was reasonable to use the linear model for rough approximation.*
- *For the sake of simplicity, we assumed the charged particles are deposited on the air/oil interface. We did not comment on whether the particles are wetted by ultra-thin spreading silicone oil or not as it cannot be confirmed experimentally. However, since the precursor film is thin, the time for particles to be wetted was assumed to be rather long. This is particularly true when the absolute film thicknesses are small. If the silicone oil wets the particles, a change in curvature should be created, based on mass conservation law, and this needs significant energy to overcome such a large disjoining pressures in the film. Considering this simplification, the mathematical model is expected to be valid since it provides a similarity solution for films confined between layer of particles and substrate. Of course, this assumption should be revisited for more complete models.*
- *The "regulation" of charge and charge exchange with the substrate was assumed to be negligible. This implies that the particles at interface may retain their steady state charge for a long period of time if the corona discharge is continuous. Moreover, this is consistent with the constant surface charge assumption at both interfaces.*
- *The voltage drop across the liquid film was assumed to be related to the charge of particles at the interface.*
- *The short range polarization forces due to steric Born repulsion was neglected.*
- *The thermo-physical and electrical properties were assumed to be not affected by the thickness of the film.*

- *We assumed the effect of charged particles prior to the film expansion is not significant in spreading of the precursor film. This assumption can be easily confirmed by interrupting the corona discharge. By interrupting the exposure, Tthe precursor film spreading is also interrupted. Therefore, charge particle deposited over the substrate and their capillary action may have no relevant contribution in precursor film spreading.*
- *The interaction of particle with each other was assumed to be negligible. We assumed the electric field between particles and solid substrate across the oil film is much more important than the electrostatic interactions of particle-particle at surface. It is particularly true when particles are apart enough otherwise such assumption needs to be revisited.*
- *We assumed the evaporation rate of the liquid is so small that it can be ignored. We performed all the experiments with low volatile silicone oil with vapor pressures less than 4 mmHg in an environmental chamber at atmospheric pressure.*
- *We assumed that the contribution of capillary force in the latest stages of spreading is negligible (see ref. [14] and 16]. The order of magnitude analysis is presented in S4.*

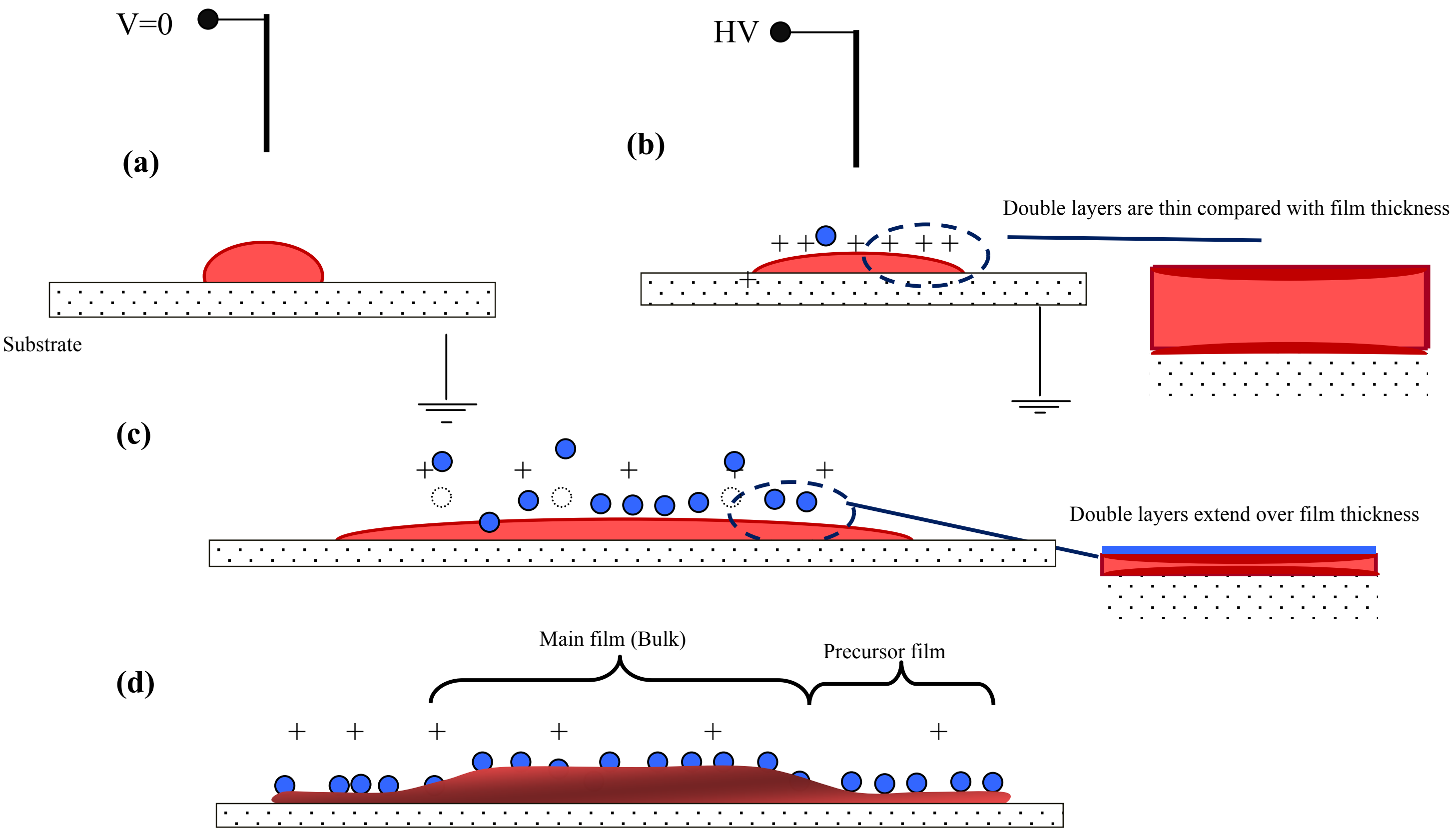

Fig. S2-1 hypothetical model for spreading of precursor based on the simplification assumptions

Starting with linearized Poisson-Boltzmann equation in the liquid film with the following boundary conditions

$$\frac{d^2\varphi}{dx^2} = \kappa^2\varphi \qquad \text{(S2-1)}$$

$$\left.\frac{d\varphi}{dx}\right|_{x=0^+} = -\frac{\sigma_1}{\varepsilon_r\varepsilon_o} \qquad \text{(S2-2)}$$

$$\left.\frac{d\varphi}{dx}\right|_{x=h^-} = +\frac{\sigma_2}{\varepsilon_r\varepsilon_o} \qquad \text{(S2-3)}$$

where φ, *h*, κ and ε are the electric potential, thickness of the film, Debye-Hückel parameter and permittivity of the oil film. For dielectric liquids with low concentration of ion pairs, Debye-Hückel parameter can be estimated as $\kappa \approx 1/\sqrt{D\tau}$, where

$D = bkT/e$ is diffusion coefficient and b, k, T, e and τ are ion mobility, Boltzmann constant, absolute temperature, electron charge, and charge relaxation time (the ratio of oil permittivity to electrical conductivity of the bulk $\varepsilon_o\varepsilon_r/\sigma$).

The solution of the above equation can be obtained as [14]

$$\phi(x) = \frac{\phi_{01}\cosh\left[\kappa\left(h-x\right)\right] + \phi_{02}\cosh(\kappa x)}{\sinh(\kappa h)} \qquad 0 \le x \le h \qquad \text{(S2-4)}$$

The disjoining pressure due to the double layer interactions can be estimated as

$$\Pi_{el}(h) = \left\{\Pi_{os,1} + \Pi_{Max,1}\right\} - \left\{\Pi_{os,2} + \Pi_{Max,2}\right\} \qquad \text{(S2-5)}$$

$$\Pi_{el}(h) = -\frac{1}{2}\varepsilon_r\varepsilon_o\left(\left(\frac{d\varphi}{dx}\right)_{x=h^+}\right)^2 + 2nkT\left\{\cosh\left(\frac{ze\varphi(h^+)}{kT}\right) - 1\right\} \qquad \text{(S2-6)}$$

The first component, Π_{os}, corresponds to disjoining pressure, which arises from electrostatic attraction between the particulate interface and solid substrate. While the second component, $\Pi_{Max,1}$, represents the steric repulsion due to the overlapping double layers. Since the repulsion has entropic origins the temperature T may appear in Eq.(S2-6).

Assuming low potentials over the boundaries, the expression above would be simplified to

$$\Pi_{el}(h) = \frac{1}{2}\varepsilon_r\varepsilon_o\left[\kappa^2\varphi^2(h) - \left(\left(\frac{d\varphi}{dx}\right)_{x=h^+}\right)^2\right] \qquad \text{(S2-7)}$$

Therefore, substituting electric potential distribution in the overlapping double layers presented in Eq.(4) to Eq.(6), one may obtain disjoining pressure due to the double layer interactions as:

$$\begin{aligned}\Pi_{el}(h) &= \frac{1}{2}\varepsilon_r\varepsilon_o\kappa^2\left[\left(\frac{\varphi_{01}+\varphi_{02}}{2}\right)^2\frac{1}{\sinh^2(\kappa h/2)} - \left(\frac{\varphi_{01}-\varphi_{02}}{2}\right)^2\frac{1}{\cosh^2(\kappa h/2)}\right] \\ &= \frac{1}{2}\varepsilon_r\varepsilon_o\kappa^2\left[\frac{2\varphi_{01}\varphi_{02}\cosh(\kappa h) + \left(\varphi_{01}^{\ 2} + \varphi_{02}^{\ 2}\right)}{\sinh^2(\kappa h)}\right] \qquad (S2-8)\end{aligned}$$

where φ_{01} and φ_{02}, are the electric potentials of two sides of film calculated as:

$$\phi_{01} = \frac{\sigma_1}{\varepsilon_r\varepsilon_o\kappa}; \phi_{02} = \frac{\sigma_2}{\varepsilon_r\varepsilon_o\kappa} \qquad \text{(S2-9)}$$

In the precursor region, the change in surface potential can be assumed to be negligible and the liquid interface tends to get the electric potential values between zero at the solid substrate and the finite surface potential at slightly above the solid interface. This situation is consistent with intuition since the jump from finite voltage to absolute zero is not realistic. Similar situation exists for conventional precursor film in which the chemical potential in the precursor region may find some intermediate values rather that a sudden jump. This can be also concluded from the theoretical model when the film thickness is small enough. Therefore, it would be reasonable to simplify the disjoining pressure as following

$$\Pi_{el}(h) = \frac{1}{2}\varepsilon_r\varepsilon_o\kappa^2\left[\frac{2\varphi_{01}\varphi_{02}\cosh(\kappa h) + \left(\varphi_{01}{}^2 + \varphi_{02}{}^2\right)}{\sinh^2(\kappa h)}\right] \sim \varepsilon_r\varepsilon_o\left(\frac{+V^{*2}}{h^2}\right) \qquad for \quad \kappa h < 1 \qquad (S2-10)$$

For thin films of dielectric liquids, one may find more simplified expression for the disjoining pressure as

$$\Pi_{el}(h) = +2\varepsilon_f\frac{V_f^{*2}}{h^2} \qquad where \;\; V_f^{*} \sim (\phi_{01} + \phi_{02})/2 \, when \qquad \kappa h << 1 \qquad (S2-11)$$

The total disjoining pressure can be obtained by including the dispersive component of disjoining pressure due to the van der Waals interactions as

$$\Pi(\mathrm{h}) = \Pi_{\mathrm{el}}(\mathrm{h}) + \Pi_{\mathrm{vvw}}(\mathrm{h}) \qquad \text{(S2-12)}$$

Typical comparison of disjoining pressures of van der Waals and double layer interactions shows that the van der Waals is considerably smaller that that of double layer interactions for $\kappa h \sim O(10^{-2} - 10^{-1})$ (see Fig. 5). This may further confirm that the double layer disjoining pressure in the precursor region is the most important driving force.

The total disjoining pressure of films exposed to corona discharge can be therefore simplified as

$$\Pi(h) \sim \Pi_{el}(h) \qquad (S2-13)$$