Aggregation Kinetics of SERS-active Nanoparticles in Thermally-Stirred Sessile Droplets

* Meysam R. Barmi\textsuperscript{1}, Chrysafis Andreou\textsuperscript{2}, Mehran R. Hoonejani\textsuperscript{1}, Martin Moskovits\textsuperscript{3} and Carl D. Meinhart\textsuperscript{1}\textsuperscript{*}

\textsuperscript{1} Department of Mechanical Engineering, University of California Santa Barbara

\textsuperscript{2} Department of Biomolecular Science and Engineering, University of California Santa Barbara

\textsuperscript{3} Department of Chemistry and Biochemistry, University of California Santa Barbara

* E-mail: meinhart@engineering.ucsb.edu

Supplemental materials

The mixing and aggregation of the nanoparticles and the analyte inside of the droplet are achieved based on the droplet internal flow due to evaporation and Marangoni stress. The governing equations for the fluid flows, heat transfer and mass transport are as follows.

Fluid flow in the droplet is governed by the continuity and the incompressible Navier-Stokes equations as:

\[
\rho \left[ \frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} \right] = -\nabla p + \nabla \cdot (\mu \nabla \mathbf{u}) + \mathbf{F}_B \quad (1)
\]

\[
\nabla \cdot \mathbf{u} = 0
\]
where, $u$ is velocity vector, $p$ is pressure, $\mu$ is dynamic viscosity and $F_B = \rho g \beta (T - T_\infty)$ is the buoyancy force which depends on expansion coefficient of water $\beta = 2.07 \times 10^{-4} \text{ K}^{-1}$ at 20°C. The energy equation, determining heat transport in all domains is:

$$\rho c \left( \frac{\partial T}{\partial t} + u \cdot \nabla T \right) = \nabla \cdot (k \nabla T)$$

(2)

where, $T$ is temperature, $k$ is thermal conductivity, $\rho$ is density, and $c$ is heat capacity of each domain.

Finally, the convection-diffusion equation in air is taken into account to find the distribution of partial pressure of water vapor in air and hence calculate the evaporation rate from the droplet surface:

$$\frac{\partial p_v}{\partial t} + u \cdot \nabla p_v = \nabla \cdot (D \nabla p_v)$$

(3)

where, $p_v$ is the partial pressure of water vapor and $D$ is the diffusivity of water vapor in air. The evaporation flux from the water/air interface can be calculated from $J_e = M_w D \nabla n C = \frac{M_w D}{RT} \nabla n p_v$, where $J_e$ is the evaporation flux from the curved interface, $R$ is gas constant, and $C$ is concentration of water vapor, which is related to the vapor pressure by the equation of state of ideal gases. The subscript ‘$n$’ indicates that the gradients are perpendicular to the curve interface.

For the boundary conditions, we apply ambient conditions far from the surface ($T_\infty$, $p_{v,\infty} = RH \times p_{v,\text{sat}}$ where $RH$ is the specified relative humidity). On the air/water interface, we apply the Marangoni shear stress to find the velocity field inside of the droplet. The saturated water vapor applied on the water/air interface at temperature $T$ is determined by the Antoine equation as $\log_{10}(p_{v,\text{sat}}[\text{Pa}]) = 10.1962 - \frac{1730.63}{T[\text{K}]-39.724}$. Since the radius of curvature of the droplet is large, we neglect the change in vapor pressure due to the curved droplet interface described by the Kelvin equation. To account for the mass loss in the droplet during evaporation, a moving boundary module is added to the numerical model to track the moving water/air interface. The sessile droplet is assumed to have the shape of a spherical cap resting on the surface. The droplet shape is controlled by surface tension and gravity through the Bond number, $Bo = gL^2 (\rho_L - \rho_G)/\sigma$, which accounts for the balance of surface tension and gravitational force on the droplet. For a microscale droplet, the Bond number is in the range of 0.05 ~
0.1. Therefore the droplet remains as a spherical cap during evaporation; hence, in the axisymmetric model the interface follows \( z = (R_c^2 - r^2)^{1/2} - (R_c - h) \). The velocity of the interface, \( u_i \), as shown in Figure S1, is vertical due to the pinned contact-line and can be calculated as,

\[
 u_i = -\frac{dz}{dt} = -\frac{dz}{dR_c} \frac{dR_c}{dt} - \frac{dz}{dh} \frac{dh}{dt} \tag{4}
\]

Figure S1: The velocity of the interface in an axisymmetric spherical droplet with pinned contact-line.

The droplet volume, \( V = \frac{\pi h}{6}(3a^2 + h^2) \), and radius of curvature, \( R_c = \frac{h}{2} + \frac{a^2}{2h} \) of the spherical droplet depend on the droplet height, \( h \), and the constant contact-line radius, \( a \). Therefore,

\[
 \frac{dh}{dt} = \frac{2}{\pi(a^2+h^2)} \frac{dV}{dt} \quad , \quad \frac{dR_c}{dt} = \frac{1}{2} \left( 1 - \frac{a^2}{h^2} \right) \frac{2}{\pi(a^2+h^2)} \frac{dV}{dt} \tag{5}
\]

From the analytical expression for the interface,

\[
 \frac{dz}{dR_c} = R_c(R_c^2 - r^2)^{-1/2} - 1 \quad , \quad \frac{dz}{dh} = 1 \tag{6}
\]

The average evaporation rate can be calculated by integration of the evaporation flux along the interface \( S(t) \),

\[
 \frac{dV}{dt} = -\frac{J_e}{\rho} = -\int_{S(t)} 2\pi r \frac{M_w D}{\rho RT} \nabla_n p_v \, dl \tag{7}
\]
Experimental Determination of Aggregation Constants

To determine the parameters in the reaction rate equation, we measure the aggregation kinetics for 1,4-BDT using the method described by Moskovits and Vlčková. The rate of aggregation is determined by measuring the decrease in the absorbance peak of silver monomers (402 nm) for different concentrations of the analyte. The time evolution of absorbance of colloid and analyte mixture is measured using a plate reader (Tecan Infinite M200 Pro) at room temperature. Different concentrations of 1,4-BDT in water from 700 nM to 300 mM are placed in a 96 well plate. Then the silver sol is injected into each well and the absorbance is measured at one second intervals. The rate constant can be calculated from the initial rate of change of the absorbance as,

\[ k = -\frac{1}{c_{NP}} \frac{dA}{dt} \bigg|_{t=0} \]  \hspace{1cm} (8)

where \( c_{NP} \) is the concentration of silver colloid and \( A \) is the absorbance at silver monomer resonance peak. The results for initial rate of change of the absorbance are illustrated in Figure S2. The parameters of the reaction rate equation are calculated to fit the measured values. These parameters are estimated as: \( V_0 \approx 3.21 \, k_B T \approx 0.08 \, eV \) and \( \beta \approx 2.82 \times 10^4 \, M^{-1} \) at \( T = 23^\circ C \).

Figure S2: The normalized rate constant of Ag nanoparticle dimerization as a function of concentration of 1,4-BDT determined experimentally by measuring the peak absorbance of the monomers. The fitted curve is:

\[ \frac{k}{k_0} = \exp \left( -\frac{V_0}{k_B T (1+\beta c_a)^{12/5}} \right) \]  \hspace{1cm} where \( V_0 \approx 3.21 \, k_B T \approx 0.08 \, eV \) and \( \beta \approx 2.82 \times 10^4 \, M^{-1} \).