

Supporting Information

Gold Substrates of Controlled Roughness and Electrokinetic Properties Formed by Nanoparticle Deposition

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1. The General Random Sequential Adsorption (RSA) Model

The constitutive equation describing the kinetics of particle transport through an adsorption layer at planar interfaces has the following form:¹

$$j_a = \frac{1}{S_g} \frac{d\Theta}{dt} = k_a n(\delta_a) \overset{\circ}{B}(\Theta) - \frac{k_d}{S_g} \Theta \quad (S1)$$

where j_a is the net adsorption/desorption flux, S_g is the particle characteristic cross-section area, Θ is the particle dimensionless coverage, t is the adsorption time, $\overset{\circ}{B}(\Theta)$ is the generalized available surface function (called often less precisely surface blocking function), k_a , k_d are the adsorption and desorption constants, $n(\delta_a)$ is the concentration of particles at the adsorption boundary layer of the thickness δ_a .

For spherical particle deposition, the general blocking function $\overset{\circ}{B}(\Theta)$ can be approximated by the blocking function derived from the random sequential adsorption (RSA) model, which assumes the following form for spherical particles:

$$B(\Theta) = \left[1 + 0.812\bar{\Theta} + 0.4258(\bar{\Theta})^2 + 0.0716(\bar{\Theta})^3 \right] (1 - \bar{\Theta})^3 \quad (S2)$$

where $\bar{\Theta} = \frac{\Theta}{\Theta_\infty}$ and Θ_∞ is the maximum coverage of particles that can be calculated using the effective hard particle approach derived in Ref.¹

It should be mentioned that the kinetic adsorption and desorption constants occurring in eqn (S1) can be expressed in terms of physical parameters characterizing the transport conditions such as the particle diffusion coefficient D and the specific energy distribution governed by the depth of the primary minimum ϕ_m , and the energy barrier height ϕ_b .

In the case of the diffusion-controlled transport of particles, the constitutive expression for the flux, eqn (S1) cannot be directly integrated because the concentration $n(\delta_a)$ remains non-stationary for all times. In this case, in order to explicitly evaluate particle adsorption kinetics, one has to solve the non-stationary bulk diffusion equation with eqn (S1) serving as the boundary condition. For sake of convenience it is transformed to a dimensionless form involving the adsorption and desorption constants given by:

$$\bar{k}_a = k_a t_{ch} / L = \frac{1}{D S_g n_b} k_a \quad (S3A)$$

$$\bar{k}_d = k_d / t_{ch} = \frac{1}{D (S_g n_b)^2} k_d \quad (S3B)$$

where t_{ch} is the characteristic time and the L is length scale given by:

$$t_{ch} = L^2 / D = \frac{1}{D (S_g n_b)^2} \quad (S4A)$$

$$L = \frac{1}{S_g n_b} \quad (\text{S4B})$$

As can be noticed, the characteristic monolayer formation time rapidly increases for dilute suspensions, proportionally to n_b^{-2} analogously as the dimensionless desorption constant \bar{k}_d . On the other hand, the dimensionless adsorption constant \bar{k}_a increases proportionally to n_b^{-1} . As a result, these two parameters become much larger than unity for dilute particle suspensions, often met under experimental conditions. In this work, the bulk transport diffusion equation with the boundary condition eqn (S1) was numerically solved using the efficient finite-difference method.

2. Basic parameters characterizing rough surface topology

Basic parameters characterising rough surfaces (see Fig. S1) are as follows:²

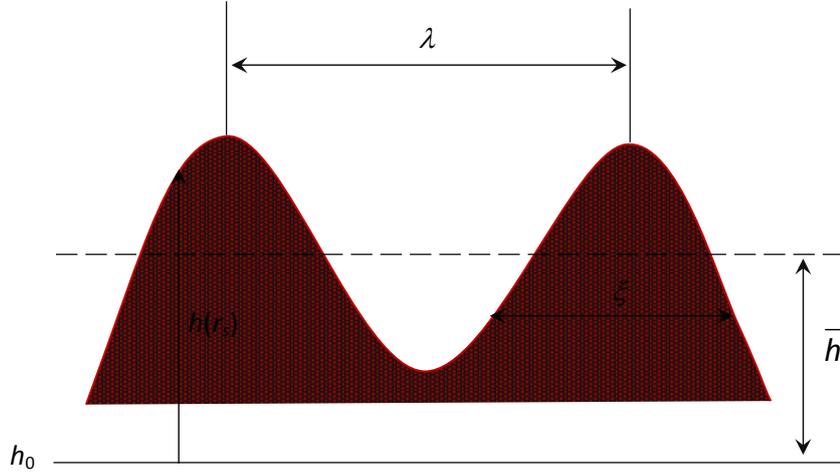


Fig. S1 Definition of basic parameters for rough surfaces.

$h(\mathbf{r}_s)$ is the local height of the surface profile measured relatively to the reference value h_0 , \mathbf{r}_s is the surface position vector, \bar{h} is the height averaged over the entire surface area S , defined as:

$$\bar{h} = \frac{1}{S} \int_S h(\mathbf{r}_s) d\mathbf{r}_s \quad (\text{S5})$$

ξ is the lateral correlation range (characteristic size of the surface roughness) and λ is the wavelength of the surface (characteristic distance between roughness maxima).

The root mean square roughness (the interface width) rms is defined as:

$$rms^2 = \frac{1}{S} \int_S (h(\mathbf{r}_s) - \bar{h})^2 d\mathbf{r}_s = \frac{1}{S} \int_S h^2(\mathbf{r}_s) - \bar{h}^2 \quad (\text{S6})$$

3. Roughness Parameters for Surfaces Covered by Features of Regular Shape

Let us first consider a single feature of a regular shape (see Fig. S2) having a flat basis of the surface area equal to S_1 . Exploiting the definitions, eqns (S5)–(S6), the expressions for the

average height \bar{h}_1 (measured relative to the basal plane of the feature) and the rms_1 are given by:

$$\bar{h}_1 = \frac{1}{S_1} \int_{s_1} h(\mathbf{r}_s) d\mathbf{r}_s = v_1 / S_1 \quad (S7)$$

$$rms_1^2 = \frac{1}{S_1} \int_{s_1} h^2(\mathbf{r}_s) - \bar{h}_1^2 = \bar{f}_1^2 - \bar{h}_1^2 \quad (S8)$$

where v_1 is the volume of the feature and $\bar{f}_1^2 = \frac{1}{S_1} \int_{s_1} h^2(\mathbf{r}_s) ds$ is the mean square height of the feature.

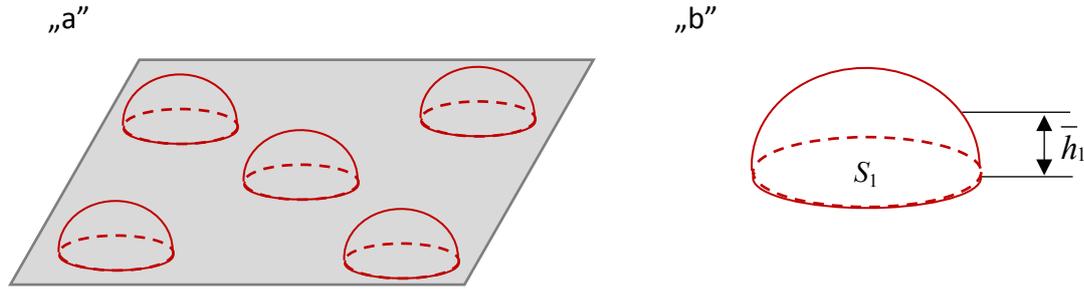


Fig. S2 Schematic view of flat interface covered by features.

If there are N_f features on the surface (of equal size and shape) the average height and the rms factor are given by:

$$\bar{h} = \frac{S_1}{S} N_f \bar{h}_1 = \Theta_f \bar{h}_1 \quad (S9)$$

$$rms^2 = \frac{S_1}{S} N_f \bar{f}_1^2 - \bar{h}^2 = \Theta_f (\bar{f}_1^2 - \bar{h}_1^2 \Theta_f) \quad (S10)$$

where

$$\Theta_f = \frac{S_1}{S} N_f \quad (S11)$$

is the feature coverage.

In the case where $\Theta_f \ll \bar{f}_1^2 / \bar{h}^2$ the expression for rms simplifies to:

$$rms = \bar{f}_1 \Theta_f^{1/2} \quad (S12)$$

Thus, in this case, the feature coverage is given by a simple expression

$$\Theta_f = \left(\frac{rms}{\bar{f}_1} \right)^2 \quad (S13)$$

Hence, measuring the rms factor, one can determine the unknown coverage of features.

In the general case, the inversion of eqn (S10) gives the following expression for the feature coverage:

$$\Theta_f = \frac{\bar{f}_1^2}{2} \left\{ 1 \pm \left[1 - \left(\frac{2\bar{h} \text{ rms}}{\bar{f}_1^2} \right)^2 \right]^{1/2} \right\} \quad (\text{S14})$$

where the minus sign denotes the lower value of the coverage (below the minimum).

It is useful to derive explicit expressions for some model features of a regular shape. For example, in the case of cylindrical features having the length (height) L and the basal radius R_c (see Fig. 3, part a) one has:

$$\bar{h}_1 = L \quad (\text{S15A})$$

$$\bar{f}_1^2 = L^2 \quad (\text{S15B})$$

$$\text{rms} = [\Theta_f (1 - \Theta_f)]^{1/2} L \quad (\text{S15C})$$

$$\Theta_f = \frac{1}{2} \left\{ 1 \pm \left[1 - \left(\frac{2\text{rms}}{L} \right)^2 \right]^{1/2} \right\} \quad (\text{S15D})$$

“a”

“b”

“c”

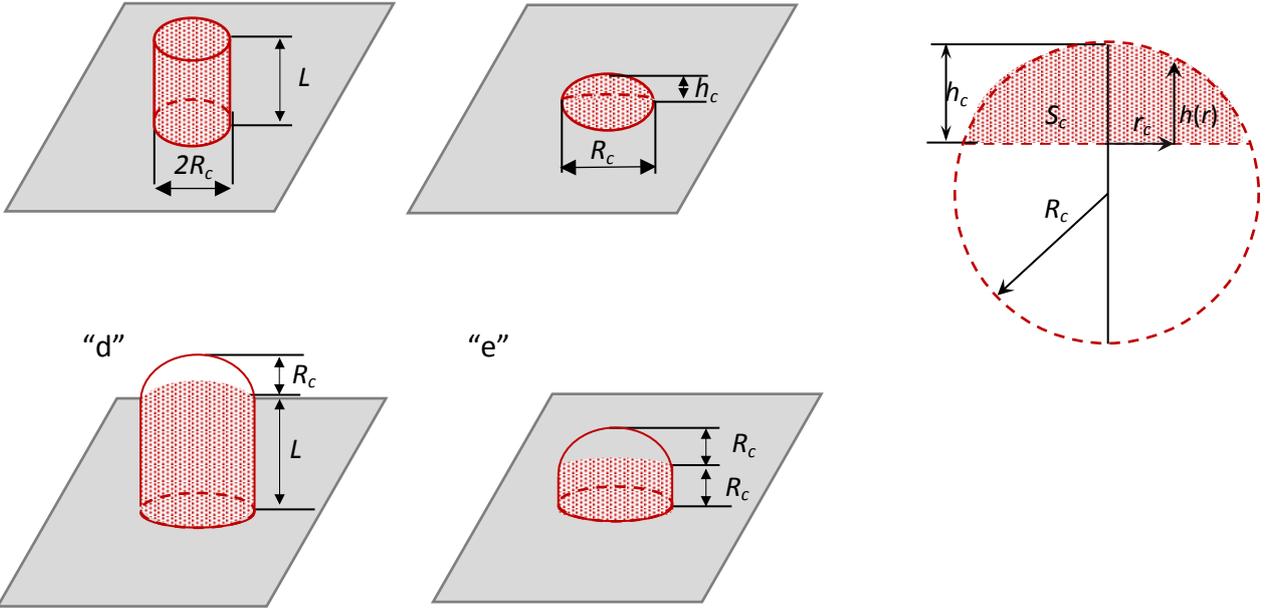


Fig. S3 Schematic view of features in the form of cylinders (pillars) part a, caps, part b-c and semi-spherocylinders, parts d-e.

For features in the form of spherical caps (see Fig. S3, part b) one has:

$$\bar{h}_1 = \frac{1}{S_1} \int_0^{r_c} 2\pi h(r) r dr = \frac{2}{3} \frac{R_c^3 - (R_c^2 - r_c^2)^{3/2}}{r_c^2} - (R_c - h_c) \quad (\text{S16A})$$

$$\bar{f}_1^2 = \frac{1}{2} \left[\frac{R_c^4 - (R_c^2 - r_c^2)^2}{r_c^2} \right] - \frac{4}{3} \frac{(R_c - h_c) [R_c^3 - (R_c^2 - r_c^2)^{3/2}]}{r_c^2} + (R_c - h_c)^2 \quad (\text{S16B})$$

where:

$$\begin{aligned}
r_c^2 &= h_c(2R_c - h_c) \\
h_c &= R_c - (R_c^2 - r^2)^{1/2} \\
h(r) &= (R_c^2 - r^2)^{1/2} - R_c + h_c \\
S_1 &= 2\pi R_c h_c = \pi(r_c^2 + h_c^2) \quad (\text{cap surface area}) \\
S_2 &= \pi r_c^2 \quad (\text{cap cross - section area at the interface}) \\
v_c &= \frac{1}{3}\pi h_c^2(3R_c - h_c) \quad (\text{cap volume})
\end{aligned} \tag{S17}$$

and the r_c, h_c, R_c parameters are defined in Fig. S3 part c.

If $h_c = R_c$ one obtains the following simple expressions:

$$\bar{h}_1 = \frac{2}{3}h_c \Theta_f; \bar{f}_1^2 = \frac{1}{2}R_c^2 \tag{S18A}$$

$$rms = \left[\frac{1}{2}\Theta_f \left(1 - \frac{8}{9}\Theta_f \right) \right]^{1/2} R_c \tag{S18B}$$

$$\Theta_f = \frac{9}{16} \left\{ 1 \pm \left[1 - \frac{64}{9} \left(\frac{rms}{R_c} \right)^2 \right]^{1/2} \right\} \tag{S18C}$$

In the case of semi-spherocylinders (see Fig. S3, parts d-e) one obtains the following expressions:

$$\bar{h}_1 = \frac{2}{3}R_c + L \tag{S19A}$$

$$\bar{f}_1^2 = \frac{1}{2}R_c^2 + L \left(L + \frac{4}{3}R_c \right) \tag{S19B}$$

$$rms^2 = \Theta_f \left[\frac{1}{2}R_c^2 + L \left(L + \frac{4}{3}R_c \right) - \Theta_f \left(\frac{2}{3}R_c + L \right)^2 \right] \tag{S19C}$$

If $L = R_c$ that well approximates the situation of a nanoparticle monolayers at a flat interface, eqns (S19A)–(S19C) simplifies to the form:

$$\bar{h}_1 = \frac{5}{3}R_c \tag{S20A}$$

$$\bar{f}_1^2 = \frac{17}{6}R_c^2 \tag{S20B}$$

$$rms = \left[\frac{17}{24}\Theta_f \left(1 - \frac{50}{51}\Theta_f \right) \right]^{1/2} d_p \tag{S20C}$$

where $d_p = 2R_c$ is the particle diameter.

The particle coverage is given by:

$$\Theta_f = 0.51 \left\{ 1 \pm \left[1 - \frac{50 \times 24}{51 \times 17} \left(\frac{2rms}{d_p} \right)^2 \right]^{1/2} \right\} \quad (S21)$$

where the minus sign denotes the lower value of the coverage (before the minimum).
For $\Theta_f \ll 1$ one obtains the simple expression:

$$\Theta_f = \frac{24}{17} \left(\frac{rms}{d_p} \right)^2 \quad (S22)$$

4. Correction for Finite Tip Dimensions

It should be mentioned that the above values of the *rms* parameter are the maximum ones pertinent to the situation where the entire interface area of a substrate covered by particles is accessible. For any real experimental system, the *rms* of a surface is smaller than this limiting value because of finite tip dimension, which is typically equal to ca. 10 nm for an AFM tip. The correction induced by finite tip dimensions can be efficiently analyzed introducing the available surface function, denoted by *ASF*, which characterizes the fraction of the bare substrate surface area accessible to the tip of a defined size and shape (see Fig. S4). In the general case, the ASF function depends on the ratio of the tip to particle size λ_f , particle coverage and the structure of the monolayer characterized in terms of the general correlation function (the simplest one being the pair correlation function).

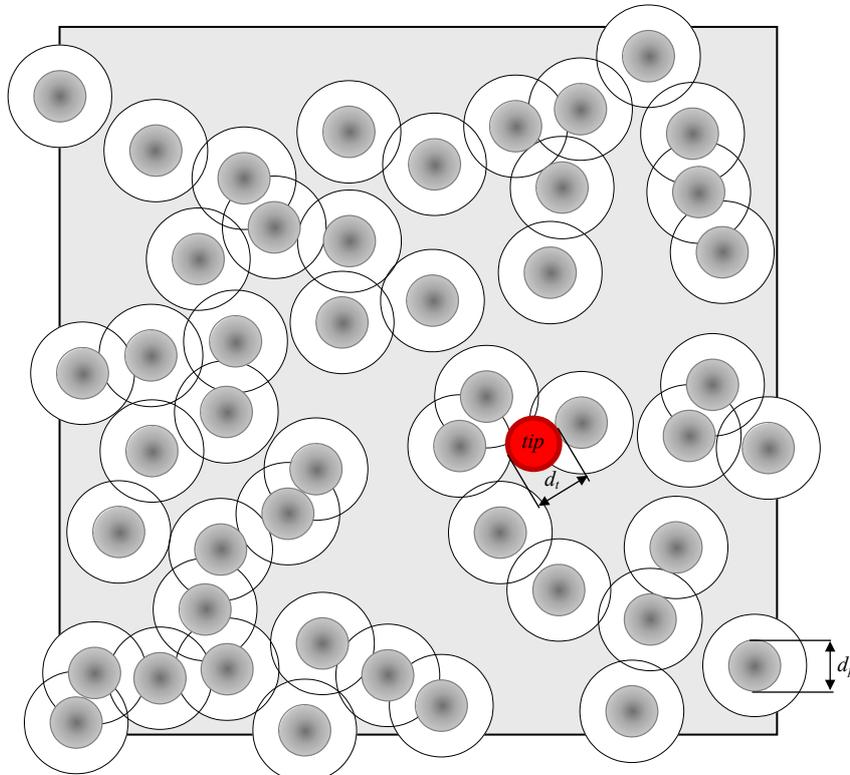


Fig. S4 Schematic view of the surface covered by spherical features of the size d_p . The white disks show the exclusion areas inaccessible to the tip (shown as the red ring) whereas the shadowed area is accessible to the tip.

Since the *rms* for the accessible surface areas is by definition zero (for smooth substrates), the net *rms* for the surface is governed by the inaccessible area (shadowed part in Fig. S4) equal to $1-ASF(\Theta_f, \lambda_f, \mathbf{g})$, where \mathbf{g} is the correlation function characterizing the structure of the feature monolayer. Considering this, the correction to the *rms* due to the finite size of a tip can be calculated from eqns (S20A)–(S20C) if the *ASF* function is known for a given tip to feature size ratio. In Ref.¹ an appropriate equation for surfaces covered by bimodal mixture of circular features was derived using the scaled particle theory formulated in Ref.³ In the case of spherical features and axis-symmetrical tips this equation assumes the following form:

$$ASF = (1 - \Theta_f) e^{-\frac{\lambda_f(\lambda_f+2)\Theta_f}{1-\Theta_f} - \frac{(\lambda_f\Theta_f)^2}{(1-\Theta_f)^2}} \quad (S23)$$

Eqn (S23) is valid for an arbitrary tip to particle size ratio λ_f , feature coverage Θ_f and for an equilibrium distribution of features. It is interesting to mention that for Θ_f approaching zero the *ASF* approaches $1 - (1+\lambda_f)^2\Theta_f$. Knowing the *ASF* one can express the rms_t parameter for finite tip dimensions from the formula:

$$rms_t = C_1 \left\{ (1 - ASF) \left[1 - \frac{50}{51} (1 - ASF) \right] \right\}^{1/2} d_p \quad (S24)$$

The constant in eqn (S24) can be calculated by matching the value of rms_t in the limit of for Θ_f approaching zero with that derived from eqns (S20A)–(S20C). In this way one obtains:

$$C_1 = \left(\frac{17}{24} \right)^{1/2} \frac{1}{1 + \lambda_f} \quad (S25)$$

5. Correction for Particle Dispersity

It is also interesting to calculate the correction for the feature dispersity. If the size distribution is described by the normalized Gauss distribution, i.e.:

$$\delta_p(z) = \frac{1}{(2\pi)^{1/2} \sigma} e^{-z^2} \quad (S26)$$

where σ is the standard deviation of the size distribution, $z = (d_p - \bar{d}_p) / 2^{1/2} \sigma$, \bar{d}_p is the average particle size one can show⁴ [4] that the correction to any continuous function of d_p is given by the general expression:

$$\bar{f}_e = f + \frac{1}{2} f'' \sigma^2 + \frac{1}{4} f'''' \sigma^4 + \dots \quad (S27)$$

where \bar{f}_e is the experimentally determined function for disperse systems, f is the corrected value of the function for monodisperse systems, f'' is the second derivative of the function and f'''' is the fourth derivative of the function.

If $\sigma \ll \bar{d}_p$, eqn (S27) can be inverted yielding the useful first order correction formula:

$$f = \bar{f}_e - \frac{1}{2} f_0'' \sigma^2 + \dots \quad (\text{S28})$$

where f_0'' is the value of the second derivative evaluated at $d_p = \bar{d}_p$.

References

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