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Published in:
Journal of Applied Physics

DOI:
[10.1063/1.1519952](https://doi.org/10.1063/1.1519952)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2002

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Palasantzas, G., & Backx, G. M. E. A. (2002). Self-affine and mound roughness effects on the double-layer charge capacitance. *Journal of Applied Physics*, 92(12), 7175-7179. <https://doi.org/10.1063/1.1519952>

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Self-affine and mound roughness effects on the double-layer charge capacitance

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(Received 25 March 2002; accepted 13 September 2002)

In this article, we investigate the influence of self-affine and mound roughness on the charge capacitance of double layers. The influence of self-affine roughness is more significant for small roughness exponents ($H < 0.5$) and/or large roughness ratios w/ξ , as well as small charge and counter charge separations in electrolyte plasma as described by the Debye length $\lambda_D (< \xi)$. On the other hand, mound roughness has a more complex influence on the charge capacitance, when the system correlation length ζ is larger than the average mound separation λ . In this case, the charge capacitance oscillates as a function of the parameters λ and ζ before it approaches the Gouy–Chapman [G. Gouy, J. Phys. (Paris) **9**, 457 (1910); D. L. Chapman, Philos. Mag. **25**, 475 (1913)] asymptotic limit for smooth interfaces. Furthermore, the oscillation magnitude is larger for relatively small Debye lengths $\lambda_D (< \zeta, \lambda)$. © 2002 American Institute of Physics.
[DOI: 10.1063/1.1519952]

I. INTRODUCTION

Many important constructions in electrochemistry,¹ colloid science,² biophysics,³ and semiconductor technology,⁴ are based on the Gouy–Chapman (GC)⁵ theory of electrolyte plasma near a flat charged wall. For low voltages, the GC theory yields a space-charge capacitance $C_{GC} = \epsilon S / 4\pi\lambda_D$ with ϵ the solvent dielectric constant, S is the area of the flat interface, and λ_D is the Gouy or Debye length.⁶ The latter is a measure of the separation of charge and counter charge in the electrolyte plasma.

For a long period in electrochemistry, studies were performed on a liquid mercury drop electrode, and later on GaTi, Ga, and InGa electrodes.⁷ Studies on solid electrodes (i.e., Cd, Bi, Cu, and Pb) revealed problems that were associated with metal/electrolyte interface roughness.⁸ We have to stress that one can not consider metal/electrolyte interface roughness by simply replacing surface area S by RS in the equation for C_{GC} , where R is the ratio of the true surface to the apparent flat crosssection area S . This is because the characteristic roughness length scale L can compete with characteristic length scales of the system such as the Debye length λ_D . This competition will lead to a different functional dependence of the charge capacitance on electrode potential and electrolyte concentration.⁹ For short Debye lengths ($\lambda_D \ll L$), the charge capacitance is expected to be given by $C = \epsilon RS / 4\pi\lambda_D$. However, for large Debye lengths ($\lambda_D \gg L$), the charge capacitance C will approach C_{GC} , since the interface roughness does not have any influence on C .⁹

Application of the theory by Daikhin *et al.*⁹ was performed earlier for electric double layers with Bi, Sb, and Cd

electrodes.¹⁰ The deviations between experimental and theoretical curves of the roughness function versus inverse Debye length λ_D were explained in terms of the influence of energetic inhomogeneity of polycrystalline surfaces.¹⁰ Furthermore, extension of the theory to the case of the nonlinear Poisson–Boltzmann theory was performed by Daikhin *et al.*¹¹ and Lust *et al.*¹² who successfully explained data for Cd rough electrodes.

In the original work by Daikhin *et al.*,⁹ which is based on the linear Poisson–Boltzmann theory, the case of intermediate Debye lengths λ_D was explored in the case of weak roughness. The various examples of rough interfaces included sinusoidal corrugation, Gaussian roughness, and some limiting cases of self-affine roughness for significantly large roughness exponents $H (> 0.5)$.⁹ The roughness exponent H characterizes the degree of surface irregularity at short length scales ($< \xi$, where ξ is the lateral roughness correlation length) so as H becomes smaller, the interface becomes more irregular.

In this work, we present an extension of the former studies to the case of self-affine roughness with roughness exponents $H < 0.5$, by properly setting the limits of the perturbative approach for weak electrode roughness.⁹ Moreover, we will extend these studies to the case of mound roughness, which is observed during unstable film growth.^{13,14} In many cases, the film growth front is rough because multilayer step structures are formed during growth,^{13,14} or alternatively noise induced roughening can lead to the formation of self-affine rough morphologies.^{15,16} In the first case, the existence of an asymmetric step-edge diffusion barrier or Schwoebel barrier inhibits the downhill diffusion of incoming atoms, leading to the creation of large structures in the form of mounds.^{13,14}

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II. CHARGE CAPACITANCE THEORY

In this article, we will assume that the rough metal/electrolyte interface can be described by a single valued random function of the in-plane position vector $r=(x,y)$ $z=h(r)$ with the average flat interface area at $z=0$ ($\langle h(r) \rangle = 0$). The rough interface is assumed to be held at potential Φ_0 . For low electrostatic potential $\Phi(r)$ ($\langle k_B T/e \rangle$), the problem simplifies to the solution of the linear Poisson–Boltzmann equation $\nabla^2 \Phi - \lambda_D^{-2} \Phi = 0$ with boundary conditions $\Phi[x,y,z=h(x,y)] = \Phi_0$ and $\Phi(x,y,z \rightarrow +\infty) = 0$.⁹ Furthermore, it is assumed that the electrolyte occupies the half-space $z > 0$. In the limit of weak roughness ($|\nabla h| \ll 1$ and $h \ll \lambda_D$), the charge capacitance C is given by the expression⁹

$$\frac{C}{C_{GC}} = 1 + \frac{1}{\lambda_D} \int_{0 < q < Q_c} [\sqrt{(\lambda_D^{-2} + q^2)} - \lambda_D^{-1}] \times \langle |h(q)|^2 \rangle \frac{d^2 q}{(2\pi)^2}, \quad (1)$$

where $\langle |h(q)|^2 \rangle$ is the metal/electrolyte interface roughness spectrum.

The requirement of weak roughness ($|\nabla h| \ll 1$ and $h \ll \lambda_D$) for the validity of Eq. (1) can be reformulated more precisely by the requirement that the average local interface slope to be small or $\rho_{rms} = \sqrt{\langle |\nabla h|^2 \rangle} \ll 1$, and $w/\lambda_D \ll 1$ with $w = \sqrt{\langle h^2 \rangle}$ the saturated root-mean-square (rms) roughness amplitude. The average local slope ρ_{rms} is given in terms of the roughness spectrum $\langle |h(q)|^2 \rangle$ by the expression

$$\rho_{rms} = \left\{ \int_{0 < q < Q_c} q^2 \langle |h(q)|^2 \rangle \frac{d^2 q}{(2\pi)^2} \right\}^{1/2}, \quad (2)$$

where $Q_c = \pi/c$ with c a lower roughness cutoff of the order of atomic dimensions.

III. ROUGHNESS MODELS

In this section, we will consider models for the roughness spectrum $\langle |h(q)|^2 \rangle$ which are necessary for the calculation of the charge capacitance in terms of Eq. (1).

A. Self-affine roughness

Any physical self-affine morphology is characterized by the finite correlation length ξ , the rms roughness amplitude w , and the roughness exponent H ($0 < H < 1$) which is a measure of the degree of surface irregularity.¹⁵ Small values of H (~ 0) characterize extremely jagged or irregular surfaces, while large values H (~ 1) characterize surfaces with smooth hills and valleys.¹⁵ For self-affine fractals, the roughness spectrum $\langle |h(q)|^2 \rangle$ is characterized by the power-law scaling behavior $\langle |h(q)|^2 \rangle \propto q^{-2-2H}$ if $q\xi \gg 1$, and $\langle |h(q)|^2 \rangle \propto \text{constant}$ if $q\xi \ll 1$.¹⁵ This scaling behavior is satisfied by the simple Lorentzian model¹⁶

$$\langle |h(q)|^2 \rangle = \frac{2\pi w^2 \xi^2}{(1 + a q^2 \xi^2)^{1+H}} \quad (3)$$

with $a = (1/2H)[1 - (1 + a Q_c^2 \xi^2)^{-H}]$ if $0 < H < 1$, and $a = 1/2 \ln(1 + a Q_c^2 \xi^2)$ if $H = 0$.

B. Mound roughness

Mound rough surfaces have been described in the past by the interface width w , the system correlation length ξ which determines how randomly the mounds are distributed on the surface, and the average mound separation λ .¹⁴ This rough morphology (which effectively corresponds to roughness exponent $H=1$) can be described in Fourier space by the model¹⁴

$$\langle |h(q)|^2 \rangle = \pi w^2 \xi^2 e^{-(4\pi^2 + q^2 \lambda^2)(\xi^2/4\lambda^2)} I_0(\pi q \xi^2/\lambda), \quad (4)$$

with $I_0(x)$ as the modified Bessel function of first kind and zero order. Note that for $\xi \gg \lambda$ (strong Schwoebel barrier effect during roughness growth), a characteristic satellite ring at $q = 2\pi/\lambda$ of the power spectrum $\langle |h(q)|^2 \rangle$ occurs.¹⁴

IV. RESULTS AND DISCUSSION

In general, the charge capacitance will have a simple dependence on the roughness amplitude w , since $\langle |h(q)|^2 \rangle \propto w^2$, while a more complex dependence will arise from the roughness parameters H and ξ for self-affine roughness, or from the roughness parameters λ and ξ for mound roughness. Our calculations were performed for roughness amplitude $w = 1$ nm and Debye lengths λ_D such that $w/\lambda_D \leq 0.1$, a lower roughness cutoff $c = 0.3$ nm, and local interface slopes $\rho_{rms} = \sqrt{\langle |\nabla h|^2 \rangle} < 1$. We have to point out that the lower roughness cutoff ($c = 0.3$ nm in present calculations) corresponds to a typical lattice constant for metals. However, a lower value might be necessary for real physical systems (depending on the material), since the actual smallest step height might be smaller than the lattice constant.

From the self-affine roughness model given by Eq. (3), we obtain the following analytic expression for the average local slope

$$\rho_{rms}^{\text{self-affine}} = \frac{w}{\sqrt{2}a\xi} \left\{ \frac{1}{1-H} [(1 + a Q_c^2 \xi^2)^{1-H} - 1] - 2a \right\}^{1/2}. \quad (5)$$

For mound roughness, if we extend the integration in Eq. (2) to infinity, we obtain for the average local slope the approximate result

$$\rho_{rms}^{\text{mound}} \approx \frac{w}{\sqrt{2}} \left[\frac{1}{\xi^2} + \frac{\pi^2}{\lambda^2} \right]^{1/2} \quad (6)$$

Figure 1(a) shows the dependence of the local slope versus the roughness ratio w/ξ for the case of self-affine roughness. Clearly, the roughness exponent H strongly influences the local slope. This result implies that Eq. (1) for the charge capacitance will be valid if H decreases below 0.5 for lower ratio w/ξ . For logarithmic roughness ($H=0$), Eq. (1) is only valid for ratios $w/\xi \ll 1$. On the other hand for mound roughness (corresponding to $H=1$), the validity of Eq. (1) is less restricted for the roughness parameters used in Fig. 1(b).

Figure 2 indicates that the charge capacitance C increases with decreasing Debye length λ_D which is consistent for small roughness exponents $H < 0.3$ as well as large ones $H > 0.5$, based on the simple model for the roughness spectrum given by Eq. (3). One should note that with decreasing

FIG. 1. (a) Local slope for self-affine roughness vs the roughness ratio w/ξ and various roughness exponents H as indicated. (b) Local slope for mound roughness vs roughness ratio w/λ for various system correlation lengths ζ as indicated.

roughness exponent H (increasing roughness irregularity at short lateral wavelengths $< \xi$), the charge capacitance strongly increases even for very small long wavelength roughness ratios w/ξ (≤ 0.01). Figure 3 shows the dependence of the charge capacitance on the length scale ratio λ_D/ξ for various roughness exponents H . Clearly, the effect of the roughness exponent H on the charge capacitance is significant for relatively short Debye lengths $\lambda_D < \xi$, when the roughness exponent H remains significantly small ($H < 0.5$).

Although the situation for self-affine roughness is rather straightforward, the influence of mound roughness appears to be more complex. Figure 4(a) indicates that by increasing Debye length λ_D , the capacitance magnitude decreases towards the GC prediction for flat interfaces. The capacitance decrement takes place in an oscillating manner with increasing average mound separation λ . The oscillations are higher in magnitude if the average mound separation λ is smaller than the system correlation length ζ . Indeed, $\lambda < \zeta$ represents the case of significant Schowebel barriers during roughness growth.¹¹ The latter is also clearly observed in Fig. 4(b) where the charge capacitance strongly fluctuates from the GC prediction when $\lambda < \zeta$.

Figure 5 shows the direct dependence of the charge capacitance on the system correlation length ζ . Due to the exponential dependence on ζ of Eq. (4), the charge capacitance

FIG. 2. Capacitance ratio C/C_{GC} vs roughness ratio w/ξ for various Debye lengths and (a) $H=0.8$ and (b) $H=0.3$.

will decrease with increasing ζ due to interface smoothing. However, at intermediate values which are comparable to the average mound separation λ (and for relatively small λ), an oscillatory behavior develops as Fig. 5(a) indicates. These oscillations fade away with increasing Debye length λ_D , as is clearly shown in Fig. 5(b). The oscillations of the local slope (Fig. 1) and of the charge capacitance in Figs. 4 and 5 are related with the characteristic satellite ring at $q = 2\pi/\lambda$ of the power spectrum $\langle |h(q)|^2 \rangle$.¹⁴ The latter yields upon integration the height–height correlation function $C(r)$

FIG. 3. Capacitance ratio C/C_{GC} vs λ_D/ξ for $\xi=100$ nm ($w/\xi \leq 1$), and various roughness exponents H .

FIG. 4. (a) Capacitance ratio C/C_{GC} vs average mound separation λ for $\zeta = 40$ nm, and various Debye lengths λ_D . (b) Capacitance ratio C/C_{GC} vs average mound separation λ for a small Debye length $\lambda_D = 10$ nm, and various system correlation lengths ζ .

$\times [\propto \int \langle |h(q)|^2 \rangle e^{-iqr} d^2r] = w^2 e^{-(n/\zeta)^2} J_0(2\pi r/\lambda)$ which exhibits similar oscillation behavior in real space due the presence of the zero-order Bessel function $J_0(x)$. For the local slope and thus for the charge capacitance, the oscillatory behavior is preserved if we keep the upper limit of integration Q_c finite, due to the presence of the modified Bessel function $I_0(x)$ in Eq. (4).

V. CONCLUSIONS

In summary, we have investigated the influence of self-affine and mound roughness on the charge capacitance of double layers. The criterion of the average local interface slope $\rho_{rms} = \sqrt{\langle |\nabla h|^2 \rangle}$ (besides the requirement of low rms roughness amplitude $w < \lambda_D$) provides the necessary tool for the correct application of the perturbative approach in the limit of weak roughness. The influence of self-affine roughness is more significant for small roughness exponents ($H < 0.5$) and/or large roughness ratios w/ξ , as well as small Debye lengths λ_D ($< \xi$). On the other hand, mound roughness has a more complex influence on the charge capacitance if the system correlation length ζ is larger than the average mound separation λ . In this case, the charge capacitance oscillates as a function of the parameters λ and ζ before it approaches the GC asymptotic limit for smooth interfaces (w/ζ and $w/\lambda \ll 1$). Moreover, the oscillation magnitude is larger for smaller Debye lengths λ_D .

FIG. 5. (a) Capacitance ratio C/C_{GC} vs system correlation length ζ for various average mound separation λ and Debye lengths $\lambda_D = 10$ nm. (b) Capacitance ratio C/C_{GC} vs system correlation length ζ for average mound separation $\lambda = 60$ nm and various Debye lengths λ_D .

ACKNOWLEDGMENT

The authors would like to acknowledge support from the “Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO).”

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