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

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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 $w/\xi$, as well as small charge and counter charge separations in electrolyte plasma as described by the Debye length $\lambda_D(\ll \xi)$. On the other hand, mound roughness has a more complex influence on the charge capacitance, when the system correlation length $\xi$ is larger than the average mound separation $\lambda$. In this case, the charge capacitance oscillates as a function of the parameters $\lambda$ and $\xi$ 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 $\lambda_D(\ll \xi, \lambda)$. © 2002 American Institute of Physics.

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I. INTRODUCTION

Many important constructions in electrochemistry, colloid science, biophysics, and semiconductor technology, are based on the Gouy–Chapman (GC) theory of electrolyte plasma near a flat charged wall. For low voltages, the GC theory yields a space-charge capacitance $C_{GC}=\varepsilon S/4\pi\lambda_D$ with $\varepsilon$ the solvent dielectric constant, $S$ the area of the flat interface, and $\lambda_D$ is the Gouy or Debye length. $L$ 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. Studies on solid electrodes (i.e., Cd, Bi, Cu, and Pb) revealed problems that were associated with metal/electrolyte interface roughness. 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 $\lambda_D$. This competition will lead to a different functional dependence of the charge capacitance on electrode potential and electrolyte concentration. For short Debye lengths ($\lambda_D \ll L$), the charge capacitance is expected to be given by $C = \varepsilon RS/4\pi\lambda_D$. 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 $C$. The application of the theory by Daikhin et al., was performed earlier for electric double layers with Bi, Sb, and Cd electrodes. The deviations between experimental and theoretical curves of the roughness function versus inverse Debye length $\lambda_D$ were explained in terms of the influence of energetic inhomogeneity of polycrystalline surfaces. Furthermore, extension of the theory to the case of nonlinear Poisson–Boltzmann theory was performed by Daikhin et al. and Lust et al., who successfully explained data for Cd rough electrodes.

In the original work by Daikhin et al., which is based on the linear Poisson–Boltzmann theory, the case of intermediate Debye lengths $\lambda_D$ 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 $H (>0.5)$. The roughness exponent $H$ characterizes the degree of surface irregularity at short length scales ($<\xi$, where $\xi$ 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. Moreover, we will extend these studies to the case of mound roughness, which is observed during unstable film growth. In many cases, the film growth front is rough because multilayer step structures are formed during growth, or alternatively noise induced roughening can lead to the formation of self-affine rough morphologies. 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.
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 \( \Phi_0 \). For low electrostatic potential \( \Phi(r) \) \((k_B T/e)\), 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 \( \Phi(x, y, z \to \pm \infty) = 0 \). 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 expression \(^9\)

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

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 \( \rho_{rms} = \sqrt{\langle \nabla h \rangle} \ll 1 \) and \( w/\lambda_D \ll 1 \) with \( w = \sqrt{h^2} \) the saturated root-mean-square (rms) roughness amplitude. The average local slope \( \rho_{rms} \) is given in terms of the roughness spectrum \( \langle |h(q)|^2 \rangle \) by the expression

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

where \( Q_c = \pi/\epsilon \) with \( \epsilon \) 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 \( \xi \), 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 \( H \) \((\sim 0)\) characterize extremely jagged or irregular surfaces, while large values \( H(\sim 1)\) 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 \( \langle |h(q)|^2 \rangle \propto \xi^2 \) constant if \( q \xi \ll 1 \). \(^15\) This scaling behavior is satisfied by the simple Lorentzian model \(^16\)

\[
\langle |h(q)|^2 \rangle = \frac{2 \pi w^2 \xi^2}{(1 + a q^2 \xi^2)^{1+\eta}}
\]

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

B. Mound roughness

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

\[
\langle |h(q)|^2 \rangle = \pi w^2 \xi^2 \frac{1}{\xi^2 + q^2} I_0(\pi q \xi^2/\lambda),
\]

where \( I_0(x) \) is the modified Bessel function of first kind and zero order. Note that for \( \zeta = \lambda \) (strong Schwoebel barrier effect during roughness growth), a characteristic satellite ring at \( q = 2/\xi \) in 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 \( \xi \) for self-affine roughness, or from the roughness parameters \( \lambda \) and \( \zeta \) for mound roughness. Our calculations were performed for roughness amplitude \( w = 1 \) nm and Debye lengths \( \lambda_D \) such that \( w/\lambda_D \leq 0.1 \), a lower roughness cutoff \( \epsilon = 0.3 \) nm, and local interface slopes \( \rho_{rms} = \sqrt{\langle \nabla h \rangle} \ll 1 \). We have to point out that the lower roughness cutoff \( \epsilon = 0.3 \) 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

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

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

\[
\rho_{rms}^{mound} = \frac{w}{\sqrt{2} \xi^3} \left[ \frac{\pi^2}{\lambda^2} \right]^{1/2}
\]

Figure 1(a) shows the dependence of the local slope versus the roughness ratio \( w/\xi \) 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 \( w/\xi \). For logarithmic roughness \((H = 0)\), Eq. (1) is only valid for ratios \( w/\xi \leq 1 \). 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 \( \lambda_D \) 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

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roughness exponent \( H \) (increasing roughness irregularity at short lateral wavelengths \(< \xi\)), the charge capacitance strongly increases even for very small long wavelength roughness ratios \( w/\xi \) \((\approx 0.01)\). Figure 3 shows the dependence of the charge capacitance on the length scale ratio \( \lambda_D/\xi \) 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 \( \lambda_D \), the capacitance magnitude decreases towards the GC prediction for flat interfaces. The capacitance decrement takes place in a oscillating manner with increasing average mound separation \( \lambda \). The oscillations are higher in magnitude if the average mound separation \( \lambda \) is smaller than the system correlation length \( \zeta \). 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 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 \( \zeta \). Due to the exponential dependence on \( \zeta \) of Eq. (4), the charge capacitance will decrease with increasing \( \zeta \) due to interface smoothing. However, at intermediate values which are comparable to the average mound separation \( \lambda \) and for relatively small \( \lambda \), an oscillatory behavior develops as Fig. 5(a) indicates. These oscillations fade away with increasing Debye length \( \lambda_D \), 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 \( \langle h(q) \rangle^2 \).\(^{14}\) The latter yields upon integration the height–height correlation function \( C(r) \).
\[ \times \left[ \frac{1}{\sqrt{2\pi \sigma^2 \rho_0^2}} e^{-\frac{(q - q_0)^2}{2\sigma^2}} \right] = \frac{1}{\sqrt{2\pi \sigma^2 \rho_0^2}} e^{-\frac{(q - q_0)^2}{2\sigma^2}} \] which exhibits similar oscillation behavior in real space due to 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 \( \rho_0 \) 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 \( w/\xi \), as well as small Debye lengths \( \lambda_D (< \xi) \). On the other hand, mound roughness has a more complex influence on the charge capacitance if the system correlation length \( \zeta \) is larger than the average mound separation \( \lambda \). In this case, the charge capacitance oscillates as a function of the parameters \( \lambda \) and \( \zeta \) before it approaches the GC asymptotic limit for smooth interfaces \( (w/\xi = 1) \). Moreover, the oscillation magnitude is larger for smaller Debye lengths \( \lambda_D \).

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6. P. Debye and W. Huckel, Phys. Z. 24, 185 (1924); ibid. 24, 305 (1924); P. Debye, ibid. 25, 97 (1924).
Besides the simplicity of 

\[ \langle bh(q) \rangle^2 \]

it yields the analytic correlation function

\[ C(r) = \frac{w^2}{a} r^{-1} \Gamma(1 + H) \frac{K_0(r/2a^{1/2})}{r/2a^{1/2}} \]

with \( K_0(x) \) the second kind Bessel function of order \( H \).