University of Groningen

Self-affine roughness effects on the double-layer charge density and capacitance in the nonlinear regime

Palasantzas, G.; Backx, G. M. E. A.

Published in:
Journal of Chemical Physics

DOI:
[10.1063/1.1545092](https://doi.org/10.1063/1.1545092)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

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

Publication date:
2003

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

Citation for published version (APA):

Palasantzas, G., & Backx, G. M. E. A. (2003). Self-affine roughness effects on the double-layer charge density and capacitance in the nonlinear regime. *Journal of Chemical Physics*, 118(10), 4631-4635.
<https://doi.org/10.1063/1.1545092>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Self-affine roughness effects on the double-layer charge density and capacitance in the nonlinear regime

G. Palasantzas^{a)}

Department of Applied Physics, Materials Science Center, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

G. M. E. A. Backx

Computational Physics Centre, Briljantstraat 341, 9743 NM Groningen, The Netherlands

(Received 19 September 2002; accepted 16 December 2002)

In this paper we investigate the influence of self-affine roughness on the charge density and capacitance of electrical double layers within the nonlinear regime. The roughness influence is significant for small roughness exponents ($H < 0.5$) and/or large long wavelength roughness ratios w/ξ , as well as small Debye lengths λ_D ($< \xi$). With increasing electrode voltage, the apparent charge density increases fast in an exponential manner for relatively high voltages. On the other hand, the charge capacitance increases up to a maximum after which it approaches an asymptotic value, which is determined by the roughness ratio of the actual to apparent flat interface area. The roughness influence is amplified within the nonlinear regime if the interface becomes rougher at any lateral roughness wavelength (smaller exponent H and/or larger ratio w/ξ). Finally, the total charge capacitance, which is obtained by considering the contribution from the thin Helmholtz layer, is also shown to be highly sensitive to interface roughness details within the nonlinear regime. © 2003 American Institute of Physics. [DOI: 10.1063/1.1545092]

I. INTRODUCTION

A diverse variety of important applications in electrochemistry,¹ colloid science,² biophysics,³ semiconductor technology,⁴ etc., are based on the Gouy–Chapman (GC)^{5,6} theory of electrolyte plasma near a flat charged wall. For a long period electrochemical studies were performed with liquid mercury drop electrode, and later with GaTi, Ga, InGa, etc., electrodes.⁷ Studies with solid electrodes (i.e., Cd, Bi, Cu, Pb) revealed problems that were associated with metal/electrolyte interface roughness.⁸

For low electrode voltages, with flat metal/electrolyte interfaces, the GC theory yields a space charge capacitance^{5,6} $C_{GC} = \epsilon S_{\text{flat}} / 4\pi\lambda_D$, where ϵ is the solvent dielectric constant, S_{flat} is the flat interface area, and λ_D is the Debye length⁶ that measures the separation of charge and counter charge in electrolyte plasma. On the other hand, in order to account for rough metal/electrolyte interfaces, one cannot simply consider the contribution of interface roughness by replacing the flat surface area S_{flat} by RS_{flat} in the equation for C_{GC} , where R is the ratio of the true surface to the apparently flat cross-section area S_{flat} . This is because the characteristic lateral roughness length scale L can compete with system characteristic length scales such as the Debye length λ_D , leading to different functional dependence on electrode potential and electrolyte concentration as was shown by Daikhin *et al.*⁹

The theory of Daikhin *et al.*⁹ was applied for electric double layers with Bi, Sb, and Cd electrodes.¹⁰ The deviations between experimental and theoretical roughness func-

tion curves versus inverse Debye length λ_D were explained by the influence of energetic inhomogeneity of polycrystalline surfaces.¹⁰ Furthermore, extension of the linear theory to the case of the nonlinear Poisson–Boltzmann theory was performed by Daikhin *et al.*¹¹ and Lust *et al.*,¹² who explained successfully data from rough Cd electrodes. In the original work by Daikhin *et al.*¹¹ within the nonlinear Poisson–Boltzmann theory, the case of weak roughness for sinusoidal and Gaussian roughness was explored.

In this work we will present an extension of the nonlinear theory to the case self-affine roughness. This is a more general type of random roughness, which is observed in a wide variety of physical systems (i.e., thin films grown under nonequilibrium conditions).^{13,14} The extension for this type of rough morphology will be accomplished by setting properly the limits of the perturbative approach for weak electrode roughness, where analytic calculations of the average local interface further facilitate analytic results for double-layer properties.

II. DOUBLE-LAYER THEORY AND INTERFACE ROUGHNESS MODELS

In this paper we will assume that the rough metal/electrolyte interface can be described by a single valued random function $z = h(R_{in})$ of the in-plane position vector $R_{in} = (x, y)$ with the average flat interface area at $z = 0$ ($\langle h(R_{in}) \rangle = 0$). The rough interface is assumed to be held at potential Φ_0 . For any electrostatic potential $\Phi(r)$, one has to solve the Poisson–Boltzmann equation $\nabla^2 \Phi - (k_D^2/e\beta) \sinh(e\beta\Phi) = 0$ ($\lambda_D = k_D^{-1}$ and $\beta = 1/k_B T$) with boundary conditions $\Phi(x, y, z = h(r)) = \Phi_0$ and $\Phi(x, y, z \rightarrow +\infty) = 0$ (assuming that the electrolyte occupies the half

^{a)} Author to whom correspondence should be addressed; electronic mail: G.Palasantzas@phys.rug.nl

space $z > 0$).¹¹ In the weak roughness limit ($|\nabla h| \ll 1$ and $h \ll \lambda_D$), the apparent charge density σ_{ap} on the metal electrode is given by¹¹

$$\sigma_{ap} = \frac{e}{2\pi\lambda_D L_B} \sinh(e\beta\Phi_0) R_1(\Phi_0),$$

$$R_1(\Phi_0) = 1 + \frac{1}{2} \int_{0 < q < Q_c} F(q, e\beta\Phi_0) \langle |h(q)|^2 \rangle \frac{d^2 q}{(2\pi)^2}, \quad (1)$$

with $L_B = e^2\beta/\varepsilon$ the Bjerrum length and ε the dielectric constant of the electrolyte solvent. Moreover, we have $F(q, e\beta\Phi_0) = q^2 \{1 - q^2/(K_{\text{eff}} + M(q))^2\}$, $M(q) = \sqrt{\lambda_D^{-2} + q^2}$, and $K_{\text{eff}} = \lambda_D^{-1} \cosh(e\beta\Phi_0)$. Furthermore, for the diffuse charge capacitance C we have¹¹

$$C = \tilde{R}(\Phi_0) C_{\text{GO}},$$

$$\tilde{R}(\Phi_0) = 1 + \frac{1}{2} \int_{0 < q < Q_c} F_1(q, e\beta\Phi_0) \langle |h(q)|^2 \rangle \frac{d^2 q}{(2\pi)^2}, \quad (2)$$

$$F_1(q, e\beta\Phi_0) = q^2 \{1 - q^2 [M(q) - K_{\text{eff}} + 2(\lambda_D^{-2}/K_{\text{eff}})] \times [K_{\text{eff}} + M(q)]^{-3}\},$$

where $\langle |h(q)|^2 \rangle$ is the metal/electrolyte interface roughness spectrum. Moreover, the requirement of weak roughness ($|\nabla h| \ll 1$ and $h \ll \lambda_D$) for the validity of Eqs. (1) and (2) can be reformulated more precisely by the requirement that the average local interface slope be small or $\rho_{\text{rms}} = \sqrt{\langle |\nabla h|^2 \rangle} \ll 1$ and $w/\lambda_D \ll 1$ with $w = \sqrt{\langle h^2 \rangle}$ the saturated 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

$$\rho_{\text{rms}} = \left\{ \int_{0 < q < Q_c} q^2 \langle |h(q)|^2 \rangle \frac{d^2 q}{(2\pi)^2} \right\}^{1/2}, \quad (3)$$

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

In the following we will consider a model for the roughness spectrum $\langle |h(q)|^2 \rangle$, which is necessary for the calculation of the charge density and capacitance in terms of Eqs. (1)–(2). Any physical self-affine morphology is characterized by a finite correlation length ξ , an rms roughness amplitude w , and a roughness exponent H ($0 < H < 1$) that is a measure of the degree of surface irregularity.^{13,14} 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, namely, $\langle |h(q)|^2 \rangle \propto q^{-2-2H}$ if $q\xi \gg 1$ and $\langle |h(q)|^2 \rangle \propto \text{const}$ if $q\xi \ll 1$.¹⁵ This scaling behavior is satisfied by the simple Lorentzian model for $\langle |h(q)|^2 \rangle$ (Ref. 14)

$$\langle |h(q)|^2 \rangle = \frac{2\pi w^2 \xi^2}{(1 + a q^2 \xi^2)^{1+H}} \quad (4)$$

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

FIG. 1. Local slope vs the roughness ratio w/ξ for various roughness exponents H .

III. RESULTS: DISCUSSION

During the calculations we considered the dielectric constant $\varepsilon = 80$ and room system temperature $T = 300$ K. These parameters yield a Bjerrum length $L_B = 8.7$ nm. Moreover, the calculations were performed for roughness amplitudes $w = 1$ nm, Debye lengths $\lambda_D > w$, and small local interface slopes ($\rho_{\text{rms}} = \sqrt{\langle |\nabla h|^2 \rangle} < 1$) as can be seen in Fig. 1. Substitution of Eq. (4) to Eq. (3) yields for the average local slope the simple analytic result¹⁵

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

We should also note that for the lower roughness cut-off we have considered the value $c = 0.3$ nm, which corresponds to a typical lattice constant for metals. However, a lower value might be necessary for a particular physical system (depending on the material) because the actual smallest step height might be smaller than the lattice constant.

FIG. 2. Apparent charge density vs field strength $e\beta\Phi_0$ for various roughness exponents H , $w = 1$ nm, $\xi = 50$ nm, and $\lambda_D = 10$ nm. The inset shows similar plots for various values of the correlation length $\xi = 10$, and 50 nm, as well as $H = 0.7$.

FIG. 3. (a) Apparent charge density vs field strength $e\beta\Phi_0$ for various Debye lengths λ_D for $H=0.7$, $w=1$ nm, $\xi=50$ nm. (b) Apparent (solid line) and true (dotted line) charge density vs $e\beta\Phi_0$ for $H=0.3$, $\lambda_D=10$ nm, $w=1$ nm, and $\xi=50$ nm.

In general, the charge density and capacitance will have a simple dependence on the roughness amplitude w since $\langle |h(q)|^2 \rangle \propto w^2$, while any complex dependence will arise from the roughness parameters H and ξ . Figure 2 shows the dependence of the apparent charge density for increasing applied voltage magnitude. Clearly the effect of the roughness exponent H and the roughness ratio w/ξ (or correlation length ξ for fixed roughness amplitude w) becomes more pronounced for large voltages ($\Phi_0 \gg 1/e\beta$) within the nonlinear regime. This also further enhanced for smaller Debye lengths λ_D ($< \xi$) or higher electrolyte concentrations “ n ” since $\lambda_D = (\epsilon\beta/8\pi e^2 n)^{1/2}$ [Fig. 3(a)].

We should note that for the calculation of the true rather than the apparent charge density of the metal electrode, the knowledge of the actual rough interface area is necessary. Under the restriction of Gaussian height–height distribution, the ratio of the actual to the apparent flat surface area is given as a function of the average local slope ρ_{rms} by¹⁶

$$R = S_{true}/S_{flat} = \int_0^{+\infty} e^{-u} \sqrt{1 + \rho_{rms}^2 u} du. \quad (6)$$

Equations (1), (4), and (6) yield for the true charge density the simpler expression $\sigma_{true} = \sigma_{ap}/R$. In Eq. (6) “ u ” is an

FIG. 4. Capacitance ratio C/C_{GC} vs field strength $e\beta\Phi_0$ for $\lambda_D=10$ nm: (a) for $\xi=50$ nm and various roughness exponents H , and (b) for $H=0.5$ and various correlation lengths ξ .

integration variable from 0 to $+\infty$. Figure 3(b) shows both the apparent and true charge density for various electrode voltages $e\beta\Phi_0$. Clearly, significant differences occur for large electrode voltages with the nonlinear regime.

Furthermore, the diffuse charge capacitance C for rougher interfaces (smaller exponent H and/or larger ratio w/ξ) increases faster with electrode voltage, having a more pronounced maximum about the value $e\beta\Phi_{0,max} \approx 10$. The maximum position shifts to larger values for rougher interfaces that correspond to smaller roughness exponents H and/or larger roughness ratios w/ξ (Fig. 4). The effect of the roughness exponent H on the capacitance also becomes more distinguishable for larger roughness exponents within the nonlinear regime ($e\beta\Phi_0 \gg 1$, Fig. 4). In addition, with decreasing Debye length λ_D the observed maximum shifts to lower field strengths $e\beta\Phi_0$ (Fig. 5).

Indeed, for high electrode potentials $e\beta\Phi_0 \gg 1$, we have $K_{eff} \approx (\lambda_D^{-1}/2) \exp(e\beta\Phi_0/2)$, which upon substitution in Eq. (2) yields for the diffuse capacitance C the simpler expression

$$\begin{aligned} \frac{C}{C_{GC}} \approx & 1 + \frac{1}{2} \int_{0 < q < Q_c} q^2 \langle |h(q)|^2 \rangle \frac{d^2 q}{(2\pi)^2} \\ & + 4\lambda_D^2 D_D^2 e^{-e\beta\Phi_0} \int_{0 < q < Q_c} q^4 \langle |h(q)|^2 \rangle \frac{d^2 q}{(2\pi)^2}. \end{aligned} \quad (7)$$

FIG. 5. Capacitance ratio C/C_{GC} vs roughness exponent H for various field strengths $e\beta\Phi_0$, $\lambda_D = 10$ nm, $w = 1$ nm, $\xi = 50$ nm.

If we consider Eqs. (3)–(5), substitution to Eq. (7) yields the analytic result

$$\begin{aligned} \frac{C}{C_{GC}} \approx & 1 + \frac{w^2}{4a\xi^2} \left\{ \frac{1}{1-H} [X_C^{1-H} - 1] - 2a \right\} \\ & + 2\lambda_D^2 e^{-e\beta\Phi_0} \frac{w^2}{a^3\xi^4} \left\{ \frac{1}{2-H} [X_C^{2-H} - 1] \right. \\ & \left. + \frac{2}{1-H} [1 - X_C^{1-H}] - \frac{1}{H} [X_C^{-H} - 1] \right\}, \end{aligned} \quad (8)$$

with $X_C = 1 + aQ_c^2\xi^2$. As Eq. (8) indicates, the capacitance C converges to the geometrical value $C \approx RC_{GC}$ for $e\beta\Phi_0 \gg 1$. This is the saturated value for the capacitance that appears in Figs. 3 and 4 beyond the observed maximum. Note that for weak roughness ($\rho_{rms} < 1$) the roughness ratio R is given by the asymptotic expansion, $R \approx 1 + \rho_{rms}^2/2 + \sum_{n=2}^{\infty} R(n)\rho_{rms}^{2n}$ with $R(n) = \{1 \cdot 3 \cdot 5 \cdots (2n-3)\}(-1)^{n-1}/2^n$.

On the other hand, the apparent surface charge density is a monotonically increasing function of the applied voltage as is shown in Figs. 2 and 3. Indeed, in this case for $e\beta\Phi_0 \gg 1$ we have $\sinh(e\beta\Phi_0) \approx e^{e\beta\Phi_0/2}/2$, $\cosh(e\beta\Phi_0) \approx e^{e\beta\Phi_0/2}/2$, $R_1(\Phi_0) \approx R - (2\lambda_D^2) \int_0 < q < Q_c q^4 \langle |h(q)|^2 \rangle d^2q / [(2\pi)^2] e^{-e\beta\Phi_0}$ which yields

$$\begin{aligned} \sigma_{ap} \approx & \frac{e}{4\pi\lambda_D L_B} e^{e\beta\Phi_0/2} R - e \frac{\lambda_D}{L_B} \frac{w^2}{\pi a^3 \xi^4} \left\{ \frac{1}{2-H} [X_C^{2-H} - 1] \right. \\ & \left. + \frac{2}{1-H} [1 - X_C^{1-H}] - \frac{1}{H} [X_C^{-H} - 1] \right\} e^{-e\beta\Phi_0} \end{aligned} \quad (9)$$

with $R \approx 1 + (1/2) \int_0 < q < Q_c q^2 \langle |h(q)|^2 \rangle d^2q / [(2\pi)^2]$. The first term in Eq. (9) dominates exponentially for large $e\beta\Phi_0$. If we also consider the true charge density from the relation $\sigma_{true} = \sigma_{ap}/R$, then Eq. (9) yields as a dominant term (which is independent of interface roughness) $\sigma_{true} \approx (e/4\pi\lambda_D L_B) e^{e\beta\Phi_0/2}$.

Furthermore, we will examine the diffuse capacitance C as a function of the Debye length within the nonlinear regime. Indeed, the capacitance C has a value close to the geometric result RC_{GC} for small Debye lengths λ_D ($\ll \xi$), and a value close to C_{GC} for large λ_D and low voltages $e\beta\Phi_0$

FIG. 6. Capacitance ratio C/C_{GC} vs Debye length λ_D for roughness exponent $H=0.3$, various field strengths $e\beta\Phi_0$, $w = 1$ nm, and $\xi = 50$ nm.

(~ 1) as Fig. 6 indicates. However, for significant electrode voltages $e\beta\Phi_0$ (with C close to its maximum value, Fig. 4), the capacitance decreases at a lower rate with increasing λ_D even for Debye lengths $\lambda_D > \xi$ (Fig. 6). For further increment of the voltage (within the saturation regime in Fig. 4), the effect of the Debye length is rather negligible, even for $\lambda_D > \xi$.

Finally, some consideration will be given to the case of the total capacitance C_T which is obtained by the diffuse capacitance C and the Helmholtz capacitance C_H assuming a series connection or $1/C_T = 1/C + 1/C_H$.^{9,11,17} The capacitance C_H is due to a thin layer of several angstroms thick (say of thickness L_H) of solvent molecules at the metal/solvent interface with dielectric constant ϵ_* different from that of the bulk electrolyte where the GC theory is applicable. For a flat interface we have $C_{H,flat} = \epsilon_*/4\pi L_H$,¹⁷ while for a rough interface we have $C_H = RC_{H,flat}$ under the assumption that the layer thickness L_H is smaller than all characteristic roughness length scales, namely, $L_H < w, \xi$.¹¹ The total capacitance C_T is given by

$$C_T = C_{GC} \frac{R\tilde{R}(\Phi_0)}{R + \tilde{R}(\Phi_0)(L_H/\lambda_D)(\epsilon/\epsilon_*)}. \quad (10)$$

We should point out that for sufficiently rough metal surfaces ($H \ll 1$ and $w/\xi \sim 1$ which implies strong roughness or $\rho_{rms} \gg 1$) the diffuse layer/Helmholtz layer interface will not have the same roughness parameters even for thin Helmholtz layers. Although this case falls out of the regime that the present theory applies ($\rho_{rms} < 1$ or weak roughness), it should be taken carefully into account in future studies with rough metal electrodes within the strong roughness limit ($\rho_{rms} > 1$).

Calculations of the total capacitance C_T are given in Fig. 7 for $L_H = 0.4$ nm where we considered for simplicity the case $\epsilon_* = \epsilon$. Similarly with the diffuse capacitance C , the total capacitance C_T is also strongly influenced by the metal/solvent interface roughness [Fig. 7(a)]. Moreover, the maximum of C_T as a function of electrode voltage $e\beta\Phi_0$ shifts to larger values with increasing Debye length λ_D . In comparison with the diffuse capacitance C shown in Fig. 5

FIG. 7. (a) Total capacitance ratio C_T/C_{GC} vs field strength $e\beta\Phi_0$ for $\lambda_D = 10$ nm, $w = 1$ nm, $\xi = 50$ nm, and various roughness exponents H . (b) Total capacitance ratio C_T/C_{GC} vs field strength $e\beta\Phi_0$ for various Debye lengths λ_D , $H = 0.3$, $w = 1$ nm, and $\xi = 50$ nm.

for various Debye lengths λ_D , the total capacitance C_T is less sensitive to changes of λ_D for $e\beta\Phi_0 < 10$, while the saturation regime ($e\beta\Phi_0 > 10$) is more influenced by changes of λ_D .

IV. CONCLUSIONS

In summary, we investigated the influence of self-affine roughness on the charge density and diffuse capacitance in electrical double layers within the nonlinear regime. Analytic calculations of the average interface slope ρ_{rms} further facilitate analytic calculation of double layer properties for various asymptotic limits. Furthermore, in agreement with the linear case,⁹ the roughness influence is significant for small roughness exponents ($H < 0.5$) and/or large long wavelength roughness ratios w/ξ , as well as small Debye lengths ($\lambda_D < \xi$). With increasing applied voltage the apparent charge density increases exponentially, while the charge capacitance

increases up to a maximum after which it approaches an asymptotic value that is determined by the ratio of the actual to average flat electrode area. In addition, the roughness influence is amplified within the nonlinear regime when the interface becomes rougher at short and/or long roughness wave lengths as quantified respectively by the roughness exponent H and the ratio w/ξ . Finally, the total capacitance (which is obtained by considering the contribution of the Helmholtz layer) is also shown to be highly sensitive to interface roughness details and the value of the Debye length within the nonlinear regime ($e\beta\Phi_0 \gg 1$).

ACKNOWLEDGMENT

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

- ¹P. Delahay, *Double Layer and Electrode Kinetics* (Wiley, New York, 1965); E. Gileadi, E. Kirowa-Eisner, and J. Penciner, *Interfacial Electrochemistry* (Addison-Wesley, Reading, MA, 1975); B. B. Damaskin and O. A. Petrii, *Introduction to Electrochemical Kinetics* (Vyshaya Shkola, Moscow, 1975).
- ²J. N. Israelachvili, *Intermolecular and Surface Forces* (Academic, London, 1990).
- ³D. Andelman, in *Handbook of Physics of Biological Systems*, edited by R. Lipowsky (Elsevier, New York, 1994), p. 577.
- ⁴S. Liu, in *Condensed Matter Physics Aspects of Electrochemistry*, edited by M. P. Tosi and A. A. Kornyshev (World Scientific, Singapore, 1991), p. 329.
- ⁵G. Gouy, *J. Phys. (Paris)* **9**, 457 (1910); D. L. Chapman, *Philos. Mag.* **25**, 475 (1913).
- ⁶P. Debye and W. Huckel, *Phys. Z.* **24**, 185 (1924); **24**, 305 (1924); P. Debye, *ibid.* **25**, 97 (1924).
- ⁷A. N. Frumkin, *Potentials of Zero Charge* (Moscow, Nauka, 1979); R. Parsons, *Electrochim. Acta* **21**, 681 (1976); B. B. Damaskin and R. V. Ivanova, *Usp. Khim.* **48**, 1747 (1979); I. A. Bagotskaya and L. I. Shlepkov, *Elektrokhimiya* **16**, 565 (1980).
- ⁸M. A. Vorotyntsev, in *Modern Aspects of Electrochemistry*, edited by J. O'M. Bockris, B. E. Conway, and R. E. White (Plenum, New York, 1986), Vol. 17, p. 131.
- ⁹L. I. Daikhin, A. A. Kornyshev, and M. Urbakh, *Phys. Rev. E* **53**, 6192 (1996).
- ¹⁰E. Lust, A. Janes, V. Sammelselg, P. Miidla, and K. Lust, *Electrochim. Acta* **44**, 373 (1998).
- ¹¹L. I. Daikhin, A. A. Kornyshev, and M. Urbakh, *J. Chem. Phys.* **108**, 1715 (1998).
- ¹²E. Lust, A. Janes, V. Sammelselg, and P. Miidla, *Electrochim. Acta* **46**, 185 (2000).
- ¹³P. Meakin, *Phys. Rep.* **235**, 1991 (1994); J. Krim and G. Palasantzas, *Int. J. Mod. Phys. B* **9**, 599 (1995); F. Family and T. Viscek, *Dynamics of Fractal Surfaces* (World Scientific, Singapore, 1991).
- ¹⁴G. Palasantzas, *Phys. Rev. B* **48**, 14472 (1993); **49**, 5785(E) (1994). Besides the simplicity of $\langle |h(q)|^2 \rangle$, it yields the analytic correlation function $C(r) = [w^2/a\Gamma(1+H)](r/2a^{1/2}\xi)^H K_H(r/2a^{1/2}\xi)$ with $K_H(x)$ the second kind Bessel function of order H .
- ¹⁵G. Palasantzas, *Phys. Rev. E* **56**, 1254 (1997).
- ¹⁶B. N. J. Persson and E. Tosatti, *J. Chem. Phys.* **115**, 3840 (2001).
- ¹⁷A. A. Kornyshev, W. Schmickler, and M. A. Vorotyntsev, *Phys. Rev. B* **25**, 5244 (1982).