

## Double-layer capacitance on a rough metal surface

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An expression for the double layer capacitance of *rough* metal-electrolyte, metal-semiconductor, or semiconductor-electrolyte interfaces is derived which shows the interplay between the Debye length and the lengths characterizing roughness. Different dependencies of the capacitance, as compared to the flat interface, on the concentration of charge carriers in electrolyte or semiconductor are predicted. Examples of the typical roughness spectra are considered. The cases of Euclidean roughness show weak dependence on the particular form of the roughness spectrum, being sensitive only to its main parameters: the random mean square height of roughness and correlation length. A method is proposed for the *in situ* characterization of surface roughness: *the measurement of surface roughness with a "Debye ruler,"* based on the conventional measurements of the double layer capacitance. [S1063-651X(96)05305-3]

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### I. INTRODUCTION

The Gouy-Chapman theory of electrolyte plasma near a flat charged wall [1,2], which appeared a decade earlier than the Debye theory of bulk electrolytes [3], is the basis of many successful constructions in electrochemistry [4], colloid science [5], biophysics [6], and semiconductor science and technology [7]. In the low voltage limit, the Gouy-Chapman theory gives a transparent result for the space charge capacitance

$$C = C_{GC} \equiv \varepsilon \kappa S / 4\pi, \quad (1)$$

where  $\kappa^{-1}$  is the Gouy (=Debye) length,  $\varepsilon$  the dielectric constant of the solvent, and  $S$  the area of the flat interface. As it should be, the capacitance is inversely proportional to the separation between the charge and counter charge, in plasma provided by the Debye length.

A long period in electrochemistry was associated with the studies performed on the liquid mercury drop electrode, and later on Ga, InGa, and GaTl alloys [8]. Providing an ideally smooth interface between the metal and electrolyte, liquid electrodes allowed a set of classical results in electrocapillary phenomena, adsorption and electrochemical kinetics. Studies on solid electrodes (Cd, Pb, Bi, Sn, Cu) faced problems associated with a nonsmooth character of the interface [9]. The concept of the *geometrical roughness factor*  $R = S_{\text{real}}/S$ , i.e., the ratio of the true surface to the apparent surface (flat cross-section area) became common [9]. However, in many cases, experimental data cannot be rationalized in terms of this parameter only. The latter is not surprising. Roughness may be responsible for additional characteristic lengths, which may compete with other typical lengths in the

problem, giving rise to different functional dependencies on electrolyte concentration and potential.

In this article we show how the competition between the Debye length and the correlation length of roughness modifies the Gouy-Chapman result. It is obvious, *a priori*, that the limiting value of capacitance at short Debye lengths should follow Eq. (1) but with  $S$  replaced by  $S_{\text{real}} = RS$ . In the limit of long Debye lengths the roughness would not be manifested in the capacitance which would obey the native Eq. (1). How does the crossover between these two limits occur? One may expect to recover the whole curve, modifying Eq. (1),

$$C = \tilde{R}(\kappa) C_{GC}, \quad (1')$$

where the *roughness function*  $\tilde{R}(\kappa)$  varies between  $\tilde{R}(0) = 1$  and  $\tilde{R}(\infty) = R > 1$ . The problem for the theory is, then, to find this function. For the case of a weak roughness, we derive the general expression for the roughness function, establish its limiting behavior, and study the cases of different surface morphologies (sinusoidal corrugation, random Gaussian roughness, and self-affine fractal structures).

In electrolyte solutions the Debye length can easily be varied by changing the electrolyte concentration with no effect on surface roughness. Experimental data on  $\tilde{R}(\kappa) = C/C_{GC}$  may then be used for probing the roughness of the metal surface in contact with electrolytes. The same idea can be put into the basis of an evaluation of the roughness of metal-semiconductor or semiconductor-electrolyte interfaces. Debye length in semiconductors can be varied by radiation or temperature-induced excitation of charge carriers into the conduction band [10] (doping will require a creation of a new junction with an uncontrollable effect on the structure of the contact).

The idea of a competition between the characteristic scales of roughness and the optical and acoustic wavelengths was explored in the classical works of Rayleigh [11] and Fano [12], and in the subsequent studies in interfacial optics

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[13–15]. Similar methods were used in the theory of friction [16] and quartz microbalance [17]. The interplay between the roughness spectra and diffusion lengths was intensively investigated in the context of the anomalous frequency dependence of the electrochemical impedance [18–21] and diffusion to the surface [22,23]. The competition between the roughness scale and the Debye length has been explored [24–28] in the context of the surface stability and surface forces. However, the features of the space charge (double layer) capacitance, the key quantity in electrochemistry, were not considered.

We address mainly solid metal-liquid electrolyte systems, but the basic results can be extended on other electrified interfaces, such as metal-semiconductor, semiconductor-electrolyte, chargeable biological interfaces, and metal-solid electrolyte contacts [29].

## II. BASIC EXPRESSION FOR CAPACITANCE

### A. Boundary problem for potential

Consider a rough metal surface in contact with an electrolyte. We take the  $z$  axis pointing towards the electrolyte and describe the interface by the equation  $z = \xi(x, y)$ . The plane  $z = 0$  is chosen such that the average value of the function  $\xi(x, y)$  over the surface is equal to zero.

In the Gouy-Chapman theory, the distribution of the electrostatic potential  $\phi(\mathbf{r})$  in the electrolyte is described by the nonlinear Poisson-Boltzmann equation. As a first step we restrict our consideration by its linearized version, valid for low electrode potentials  $\phi < k_B T/e$ :

$$(\nabla^2 - \kappa^2) \phi(\mathbf{r}) = 0. \quad (2)$$

For a 1-1 binary electrolyte solution, the Debye length,  $\kappa^{-1} = (\epsilon k_B T / 8 \pi n e^2)^{1/2}$ , where  $n$  is the electrolyte concentration,  $\epsilon$  the dielectric constant of the solvent,  $e$  charge of electron,  $T$  the temperature, and  $k_B$  the Boltzmann constant [for multivalent ions  $n$  must be replaced by the ‘‘ionic strength’’  $I = n(1/2) \sum z_i^2 \nu_i$  where  $z_i$  and  $\nu_i$  are the valence and the stoichiometric coefficients of the ion of sort  $i$ ]. For nondegenerate semiconductors with one sort of charge carriers,  $\kappa^{-1} = (\epsilon k_B T / 4 \pi n e^2)^{1/2}$  where  $n$  is the density of charge carriers and  $\epsilon$  is the high frequency dielectric constant of the semiconductor. An expression for  $\kappa$  exists for solid electrolytes with the same type of dependence on mobile ions concentration and temperature [30].

The solution of Eq. (2) must satisfy the boundary condition which fixes the potential at the metal-electrolyte interface

$$\phi(x, y, z = \xi(x, y)) = \phi_0 \quad (3)$$

relative to the zero level in the bulk of the electrolyte:  $\phi(z \rightarrow \infty) = 0$ .

### B. Perturbation theory

Consider weakly rough surfaces for which  $h$ , the characteristic size of roughness in the  $z$  direction, is less than the tangential one,  $l$ . The height  $h$  denotes the root mean square departure of the surface from flatness, and the correlation length (or a period)  $l$  is a measure of the average distance

between consecutive peaks and valleys on the rough surface. We will also assume that  $h < \kappa^{-1}$ .

Solving Eq. (2), it is convenient to Fourier transform the potential and the surface profile function from tangential coordinates  $\mathbf{R} = (x, y)$  to the corresponding wave vectors  $\mathbf{K} = (K_x, K_y)$  as  $f(\mathbf{K}) = \int d\mathbf{R} f(\mathbf{R}) \exp(-i\mathbf{K} \cdot \mathbf{R})$ . Equation (2) then transforms to

$$\left\{ \frac{d^2}{dz^2} - K^2 - \kappa^2 \right\} \phi(\mathbf{K}, z) = 0. \quad (4)$$

According to the Rayleigh approximation [11] the solution of Eq. (4) in the half space  $z < \xi(x, y)$ , has the form

$$\phi(\mathbf{K}, z) = A(\mathbf{K}) \exp(-q_K z), \quad (5)$$

where  $q_K = (\kappa^2 + K^2)^{1/2}$ . This approximation neglects the terms proportional  $\exp(q_K z)$  which would be important inside deep protrusions and grooves in the metal surface, ignored in our consideration. The boundary condition (3) leads to the integral equation on the prefactor  $A(\mathbf{K})$ ,

$$\int \frac{d\mathbf{K}}{(2\pi)^2} A(\mathbf{K}) \int d\mathbf{R} \exp[-q_K \xi(x, y)] \times \exp[-i(\mathbf{K}' - \mathbf{K}) \cdot \mathbf{R}] = (2\pi)^2 \phi_0 \delta(\mathbf{K}'), \quad (6)$$

where  $\delta(\mathbf{K})$  is the two-dimensional Dirac  $\delta$  function.

Since we are bound to the case of weak roughness,

$$|\nabla \xi(x, y)| \ll 1, \quad h\kappa \ll 1, \quad (7)$$

the standard perturbation technique [11–17, 20, 23, 25] may be applied to find  $A(\mathbf{K})$ . The first exponential in Eq. (6) is expanded into the series,

$$\int d\mathbf{R} \exp[-q_K \xi(x, y)] \exp[-i(\mathbf{K}' - \mathbf{K}) \cdot \mathbf{R}] \simeq (2\pi)^2 \delta(\mathbf{K} - \mathbf{K}') - q_K \xi(\mathbf{K}' - \mathbf{K}) + \frac{1}{2} q_K^2 \int \frac{d\mathbf{K}''}{(2\pi)^2} \xi(\mathbf{K}' - \mathbf{K} - \mathbf{K}'') \xi(\mathbf{K}''), \quad (8)$$

and Eq. (6) may be solved by iterations. In order to determine the first nonvanishing correction to the capacitance caused by roughness, we must find  $A(\mathbf{K})$  up to the second order in  $h$ . Hence

$$A(\mathbf{K}) = A_0(\mathbf{K}) + A_1(\mathbf{K}) + A_2(\mathbf{K}), \quad (9a)$$

where

$$A_0(\mathbf{K}) = (2\pi)^2 \phi_0 \delta(\mathbf{K}), \quad (9b)$$

$$A_1(\mathbf{K}) = \phi_0 q_0 h(\mathbf{K}), \quad (9c)$$

$$A_2(\mathbf{K}) = \frac{1}{2} \phi_0 q_0 \int \frac{d\mathbf{K}'}{(2\pi)^2} h(\mathbf{K} - \mathbf{K}') h(\mathbf{K}') (2q_{K'} - q_0). \quad (9d)$$

$A_0(\mathbf{K})$ , corresponds to the solution for the flat interface, while the next two terms are the corrections due to the surface roughness.

### C. Capacitance

In the linearized Poisson-Boltzmann approximation the charge density distribution is proportional to the potential  $\rho(\mathbf{r}) = -\varepsilon\kappa^2\phi(\mathbf{r})/4\pi$ . The integral charge of the double layer is equal with the sign minus to the charge of the metal surface  $Q$ , so that

$$Q = \frac{\varepsilon\kappa^2}{4\pi} \int d\mathbf{R} \int_{h(\mathbf{R})}^{\infty} dz \phi(\mathbf{r}). \quad (10)$$

Making the lateral Fourier transform of  $\phi(\mathbf{r})$  and using expressions (5) and (9) we obtain the capacitance  $C = Q/\phi_0$  in the form of Eq. (1') with the roughness function

$$\tilde{R}(\kappa) = 1 + \kappa h^2 \int \frac{d\mathbf{K}}{(2\pi)^2} g(\mathbf{K}) [(\kappa^2 + K^2)^{1/2} - \kappa]. \quad (11)$$

Here we introduced the *height-height correlation function*

$$g(\mathbf{K}) \equiv \frac{1}{Sh^2} |\xi(\mathbf{K})|^2. \quad (12)$$

At  $h=0$ , Eq. (11) gives  $R(\kappa)=1$ , reproducing the Gouy-Chapman result for capacitance of a flat interface.

Equation (11) is our central result: it correlates the capacitance with the morphological features of the interface  $h$  and  $g(\mathbf{K})$ . It can describe the effect of both random roughness and periodical corrugation. In the latter case the integral  $\int d\mathbf{K}/(2\pi)^2$  should be replaced by the sum  $S^{-1}\sum_{\mathbf{K}}$ .

### III. LIMITING LAWS

Consider the behavior of expression (11) for two extreme cases: (a) the Debye length  $\kappa^{-1}$  is shorter than the smallest characteristic correlation length of roughness  $l_{\min}$ , and (b)  $\kappa^{-1}$  is greater than the maximal correlation length  $l_{\max}$ . These two limiting cases can be realized experimentally, changing, for instance, the electrolyte concentration. Note that the concept of characteristic correlation length breaks down for fractal surfaces, which we discuss specially in Sec. IV B.

For  $\kappa^{-1} \ll l_{\min}$  one may expand  $(\kappa^2 + K^2)^{1/2}$  in the integrand of Eq. (11) using the smallness of  $(K/\kappa)^2$ , Eq. (11) then reduces to

$$\tilde{R}(\kappa) \approx R \left\{ 1 - \frac{1}{2R} \frac{\langle \mathcal{H}^2 \rangle}{\kappa^2} \right\}. \quad (13)$$

Here we used the expression for the mean area of a random surface,

$$\frac{S_{\text{real}}}{S} \equiv R = 1 + \frac{h^2}{2} \int \frac{d\mathbf{K}K^2}{(2\pi)^2} g(\mathbf{K}), \quad (14)$$

valid up to the terms of the second order in  $\xi$ , and the definition for the mean square curvature

$$\langle \mathcal{H}^2 \rangle \equiv \frac{h^2}{4} \int \frac{d\mathbf{K}K^4}{(2\pi)^2} g(\mathbf{K}). \quad (15)$$

Equation (13) shows, as expected, that the roughness function  $\tilde{R}(\kappa)$  approaches the geometrical roughness factor  $R$  for the small Debye length  $\kappa^{-1}$  (large  $n$ ). With the increase of  $\kappa^{-1}$  (the decrease of  $n$ ) it decreases with respect to  $R$ , the correction being proportional to the square of the Debye length, i.e., it is inversely proportional to the charge carriers concentration.

In the range of large Debye lengths (low concentrations),  $\kappa^{-1} \gg l_{\max}$ , one may expand the term  $(\kappa^2 + K^2)^{1/2}$  in the integrand of Eq. (11) in  $(\kappa/K^2)^2$  to obtain

$$\tilde{R}(\kappa) \approx 1 + \frac{\kappa h^2}{L} - \kappa^2 h^2. \quad (16)$$

Here the length

$$L \equiv \left\{ \int \frac{d\mathbf{K}}{(2\pi)^2} K g(\mathbf{K}) \right\}^{-1} \quad (17)$$

is of the order of  $l_{\max}$ . As expected, at very low Debye lengths the roughness of the surface is not "seen" in the capacitance. The first correction to the flat surface result is linear in  $\kappa$ .

Approving our expectations, Eqs. (13) and (16) specify how the roughness function approaches the two obvious limits.

## IV. EXAMPLES OF DIFFERENT SURFACE MORPHOLOGIES

### A. Euclidean surfaces

The asymptotic laws for the capacitance at small and large Debye lengths [given by Eq. (1') and Eq. (13) or Eq. (16)] are universal for weak Euclidean roughness. However, the specific form of the roughness function depends on the morphology of the interface. When the roughness may be described by a one scale correlation function,

$$g(\mathbf{K}) = l^2 u(Kl), \quad (18)$$

Eq. (11) can be rewritten as

$$\tilde{R}(\kappa) = 1 + \frac{h^2}{l^2} f(\kappa l), \quad (19)$$

where

$$f(x) = \frac{1}{2\pi} x^2 \int_0^\infty dt tu(t) [(1 + t^2/x^2)^{1/2} - 1]. \quad (20)$$

In this case the roughness induced change of the capacitance is proportional to the square of the "roughness slope"  $h/l$  and the *scaling function*  $f(x)$  of a single variable: the ratio of the correlation length (period) of roughness to the Debye length.

Consider two examples of surface morphologies, which lead to two different scaling functions and represent two types of roughness: deterministic and random.

(1) *Periodical corrugation*:  $\xi(\mathbf{R}) = h \sin(2\pi x/l_s)$ . In this case,  $\mathbf{K} = (2\pi m/l_s, 0)$  and  $\xi(\mathbf{K}) = hS(\delta_{m,1} - \delta_{m,-1})/2i$ , where  $m = 0, \pm 1, \pm 2, \dots$  and  $\delta_{m,\pm 1}$  is the Kronecker symbol.

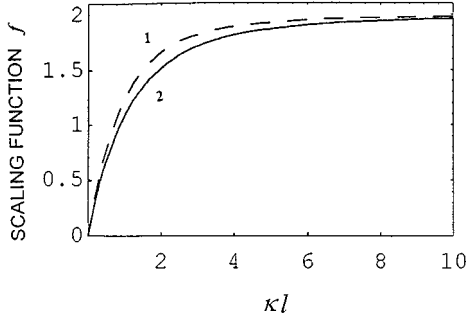


FIG. 1. Scaling functions for rough Euclidean surfaces. (1)  $f(x)/\pi^2$  for sinusoidal corrugation [Eq. (21)], (2)  $f(x)$  for Gaussian roughness [Eq. (22)]. [The factor  $1/\pi^2$  is introduced to compare  $\tilde{R}(\kappa)$  for the two morphologies at the same geometrical roughness factor].

This leads to the roughness factor  $R = 1 + 2\pi^2 h^2/l_s^2$  and to the scaling function of argument  $\kappa l_s$ ,

$$f(x) = x^2 \left\{ \left( 1 + \frac{4\pi^2}{x^2} \right)^{1/2} - 1 \right\}. \quad (21)$$

(2) *Gaussian roughness.* The most widely used approximation for a random Euclidean roughness is the isotropic Gaussian model. It characterizes the roughness spectrum by two parameters: the rms height  $h$  and the tangential correlation length  $l$ . In this case  $g(\mathbf{K}) = \pi l_G^2 \exp(-l_G^2 K^2/4)$  [i.e.,  $u(t) = \pi \exp(-t^2/4)$ ], the roughness factor  $R = 1 + 2h^2/l_G^2$ , and the mean square curvature  $\langle \mathcal{H}^2 \rangle = 8h^2/l_G^4$ . The scaling function of  $\kappa l_G$  here takes the form

$$f(x) = 2\sqrt{\pi} x \exp(x^2/4) [1 - \Phi(x/2)], \quad (22)$$

where  $\Phi(z)$  is the probability function [31].

Note that the meaning of the characteristic lateral length may be different for different types of roughness. For example, at the same rms  $h$ , the same geometrical roughness factor  $R$  would correspond to  $l_s = \pi l_G$ . Then, according to Eq. (19), one should compare the Gaussian scaling function with the sinusoidal scaling function divided by  $\pi^2$ . Such a comparison (Fig. 1) shows a small difference in the range of intermediate  $\kappa l$ . Naturally, both models reproduce the limiting laws (13) and (16) [32]. The roughness function for the Gaussian model is shown in Fig. 2. The framework of the perturbation theory (7) does not allow us to consider the region of large  $\kappa$ ,  $\kappa h \gg 1$ . However, as we see from Fig. 2, far before this range the roughness function levels off to the geometrical factor  $R$ . Therefore this condition is not critical.

### B. Self-affine fractal surfaces

In the above given examples the roughness spectrum was characterized by a single in-plane correlation length  $l$ . However, recent efforts aimed at understanding the properties of rough solid surfaces have demonstrated that a wide class of them is well represented by a self-affine model of roughness [33]. In this case, within a certain confined range of distances there is no characteristic scale, i.e., the height-difference correlation function,  $\langle |h(\mathbf{R}' + \mathbf{R}) - h(\mathbf{R}')|^2 \rangle$ , follows a power law

$$\langle |h(\mathbf{R}' + \mathbf{R}) - h(\mathbf{R}')|^2 \rangle \sim (R/l)^{2H}, \quad l_{\min} \ll R \ll l. \quad (23)$$

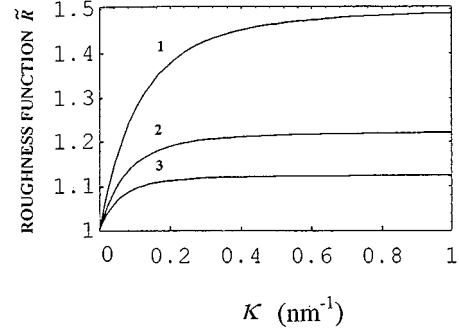


FIG. 2. Roughness function  $\tilde{R}$  versus the inverse Debye length,  $\kappa$  [Eqs. (19), (22)] for the random Gaussian surfaces.  $\epsilon = 80$ ,  $h = 5$  nm,  $l = (1) 10$ , (2) 15, (3) 20 nm.

Here,  $l$  is the crossover length from the self-affine to saturated roughness, and its interplay with  $\kappa^{-1}$  is important. The minimum self-affinity scale would not enter the results if  $\kappa^{-1} > l_{\min}$ , which is usually the case for  $l_{\min}$  of atomic dimensions and  $\kappa^{-1}$  for solutions of moderate concentrations. The height-difference correlation function is related to the height-height correlation function, introduced above, as

$$\langle |h(\mathbf{R}' + \mathbf{R}) - h(\mathbf{R}')|^2 \rangle = 2h^2 [1 - g(R)], \quad (24)$$

where  $g(R)$  is obtained from  $g(\mathbf{K})$  by an inverse Fourier transform.

The roughness exponent  $H$ ,  $0 < H \leq 1$ , determines the surface texture (the degree of surface irregularity), and is associated with a local fractal dimension,  $D = 3 - H$  [33]. Small values of  $H$  correspond to extremely jagged or irregular surfaces, while large values of  $H$  describe surfaces with smooth hills and valleys. As our approach is valid only for slightly rough surfaces, it would not be wise to consider  $H < 1/2$ .

The height-difference correlations of any real surface must saturate at sufficiently large tangential lengths to the value  $2h^2$ . A ‘‘reduced’’ self-affine scaling law has been proposed [34] that has such a long-length cutoff

$$\langle |h(\mathbf{R}' + \mathbf{R}) - h(\mathbf{R}')|^2 \rangle = 2h^2 \{ 1 - \exp[-(R/l)^{2H}] \}. \quad (25)$$

For  $H = 1$  Eq. (25) reduces to the Gaussian correlation function discussed above. The 2D-Fourier transform of this function cannot be calculated analytically, except for the cases of  $H = 1$  and  $H = 0.5$ . Therefore it is convenient to directly approximate the function  $g(\mathbf{K})$  (which we need for the calculation of capacitance). For  $1/2 \leq H < 0.8$ , the approximation

$$g(\mathbf{K}) = \frac{2\pi l^2}{(1 + K^2 l^2 / 2H)^{H+1}}, \quad (26)$$

suggested in Ref. [35], reproduces fairly well the Fourier transform of the correlation function  $g(R)$  for self-affine fractal surfaces. The use of approximation (26) leads to the scaling function

$$f(x) = (x)^{2(1-H)} \pi (2H)^{H+1} \frac{\Gamma(H-1/2)}{\Gamma(H+1/2)} \times F(H+1, H-\frac{1}{2}, H+\frac{1}{2}, 1-2H/x^2), \quad (27)$$

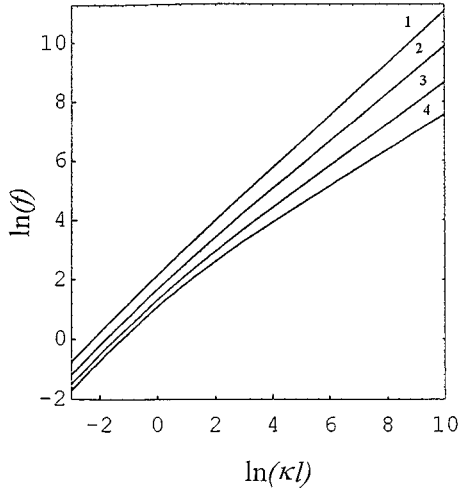


FIG. 3. Scaling functions for the self-affine fractal surfaces [Eqs. (27)]. The roughness exponent  $H=(1) 0.55$ , (2) 0.6, (3) 0.65, (4) 0.7.

where  $\Gamma(z)$  is the Euler gamma function and  $F(\alpha, \beta, \gamma, z)$  is the Gauss hypergeometrical function [31]. As before, the  $\kappa$  dependence of the roughness function is determined by the one-parameter scaling function. However, the asymptotic behavior of  $R(\kappa)$  for  $\kappa^{-1} \ll l$

$$\tilde{R}(\kappa) = 1 + \frac{h^2}{l^2} (\kappa l)^{2(1-H)} \sqrt{\pi} (2H)^H \times \Gamma(1-H) \Gamma(H-1/2), \quad \kappa^{-1} \ll l \quad (28)$$

differs essentially from the case of Euclidean surfaces, given by Eq. (13). The reason for this is quite obvious. For  $\kappa^{-1} \ll l$  the roughness function should be close to the geometrical roughness factor  $R = S_{\text{real}}/S$ , but for the fractal surfaces the value of the true area  $S_{\text{real}}$  depends on the resolution ( $\kappa^{-1}$ ) of an instrument used for the measurements. As we have already mentioned Eq. (28) cannot be used for the description of the surfaces with the roughness exponent  $H$  close to unity. The reflection of this drawback is the function  $\Gamma(1-H)$  on the right-hand side of Eq. (28), which has a pole for  $H=1$ .

The asymptotic behavior of the roughness function for  $\kappa^{-1} \gg l$

$$\tilde{R}(\kappa) = 1 + \frac{h^2}{l^2} (\kappa l) \sqrt{2} (\pi H)^{3/2} \frac{\Gamma(H-1/2)}{\Gamma(H+1)}, \quad \kappa^{-1} \gg l \quad (29)$$

is similar to the case of Euclidean surfaces. Due to the saturation of the rms roughness at large lateral distances the double layer does not feel fractal features of the surface when the ‘‘yard stick’’  $\kappa^{-1}$  exceeds  $l$ .

The scaling function  $f(\kappa l)$  is shown in Fig. 3 over the wide range of  $\kappa l$  values. In agreement with Eq. (28), the fractional power law is observed in the self-affine regime,  $\kappa l > 1$ . Typical curves of the roughness function for self-affine surfaces are plotted in Fig. 4.

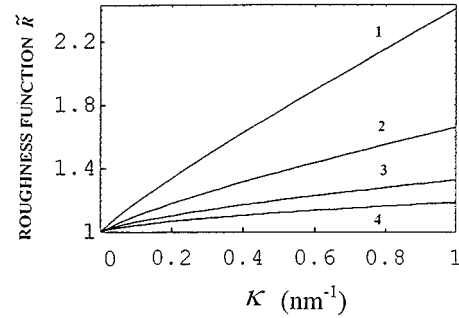


FIG. 4. Roughness function  $\tilde{R}$  versus the inverse Debye length  $\kappa$  [Eqs. (19), (27)] for the self-affine fractal surfaces.  $\epsilon=80$ ,  $h=5$  nm,  $l=100$  nm,  $H=(1) 0.55$ , (2) 0.6 (3) 0.65, (4) 0.7.

#### IV. COMPACT LAYER CONTRIBUTION

By extending the linearized version of the Gouy-Chapman theory to rough surfaces we have established how the space charge linear response capacitance at rough interfaces (metal-electrolyte, metal-semiconductor, or semiconductor-electrolyte) differs from the one for the flat surfaces. In semiconductors the concentration of charge carriers is relatively small and when the contact is perfect the space charge entirely determines the net interfacial capacitance. In the context of the metal-electrolyte interface, we have considered, essentially, the so called *diffuse layer* capacitance. A common assumption in electrochemistry is that one must also introduce the contribution of the *compact layer* with the capacitance  $C_H$ , connected in series with the diffuse layer contribution. The total capacitance is then given by

$$\frac{1}{C_{\text{tot}}} = \frac{1}{C_H} + \frac{1}{C}. \quad (30)$$

This ansatz was first suggested by Grahame [36], who combined the ideas of Helmholtz about the existence of a monomolecular layer on the electrode with the Gouy-Chapman theory. It was assumed that electrolyte ions do not penetrate into the compact layer and its capacitance does not depend on their concentration.

The validity of the Gouy-Chapman-Grahame theory is usually checked by drawing the *Parsons-Zobel plots*:  $1/C_{\text{tot}}$  versus  $1/C_{\text{GC}}$  for different electrolyte concentrations [37]. The straight line with the unit slope approves the Gouy-Chapman theory for the diffuse layer, and the corresponding intercept determines the value of  $1/C_H$ . Slopes lower than 1 are usually attributed to the geometrical roughness factor [9]. Deviations from the straight line are regarded as indications of specific adsorption of ions [9].

The whole concept, based on the division of the compact and diffuse layer parts, was always a matter of concern in view of molecular dimensions of the compact layer [38]. However, the contribution to capacitance, independent of electrolyte concentration, i.e., the finite value of the intercept on the Parsons-Zobel plot, is an experimental fact. Furthermore, the molecular theory of the electrolyte near a charged hard wall [39] and the phenomenological nonlocal electrostatic theory [40] both predict such a contribution without an artificial introduction of any ‘‘compact layers.’’ This results as an effect of the short range structure of the solvent [41].

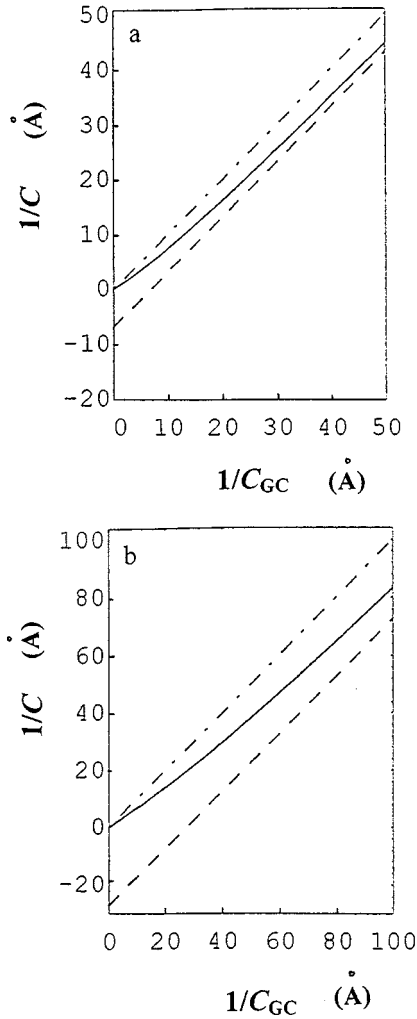


FIG. 5. Parsons-Zobel plots: inverse space-charge capacitance for the random Gaussian surfaces versus the inverse Gouy-Chapman capacitance [Eq. (1)]. Curves: (—) the plot, calculated via Eqs. (1'), (19), (22); (---) Gouy-Chapman plot; (-·-·-) the large Debye length (small  $C_{GC}$ ) asymptotic law.  $h=5$  nm,  $l=10$  nm,  $\epsilon=(a) 80$ , (b) 20.

Experimental data for a set of simple metals and polar solvents give typical values of the compact layer capacitance [9,38],  $(4\pi C_H/S_{\text{real}})^{-1}=0.1-0.8$  Å.

Equations (1') and (11) suggest that roughness leads to deviations of Parsons-Zobel plots from linearity. Figure 5 demonstrates it for the case of the Gaussian roughness, without a compact layer contribution (the intercept is kept at zero). Adding the compact layer one should bear in mind that  $C_H$  would also vary with the variation of  $R$ .

Several conclusions follow from these figures.

(1) "Negative" intercept. Extrapolation of the curves in Fig. 3(a) from the small  $\kappa$  range to the limit of large  $\kappa$  ( $1/C_{GC} \Rightarrow 0$ ) gives an "apparent" negative intercept. Equation (16) derived for Euclidean surfaces gives the value of the intercept  $-4\pi h^2/\epsilon LS$ . The intercept with account for a compact layer is given by

$$\frac{1}{C_{\text{tot}}^{(\text{extrap})}} = \frac{1}{C_H} - \frac{4\pi h^2}{\epsilon LS}. \quad (31)$$

For  $h=50$  Å,  $l=100$  Å our calculations give  $4\pi h^2/\epsilon LS=6.5$  Å of the intercept. Since the experimental values of the intercept are usually positive, that means that the negative extrapolation value is compensated by the compact layer contribution. Thus in order to get a value of  $C_{\text{tot}}^{(\text{extrap})} \geq 20$   $\mu\text{F}/\text{cm}^2$ , which is typically observed, one must have  $C_H < 10$   $\mu\text{F}/\text{cm}^2$ . Therefore the evaluation of the true compact layer contribution from the extrapolated intercept needs an essential correction for rough surfaces.

(2) *Extended region of non-Gouy-Chapman behavior.* Considerable curvature of the plot is seen, e.g., in Fig. 3 in the region of  $\kappa l \sim 1$ . However, generally, the Parsons-Zobel plots are not convenient for the characterization of the surface roughness. More convenient would be the plot of  $\tilde{R}(\kappa) \approx \{1/C_{\text{tot}} - 1/C_H\}^{-1} \{C_{GC}\}^{-1}$  versus  $\kappa$ . If the accuracy would allow, the limiting laws (13) and (16) may be studied, giving important roughness parameters:  $\langle \mathcal{H}^2 \rangle$  and  $h^2/L$ . A nonlinear regression fit of the whole curve would give  $l$ . In the case of self-affine surfaces the measurements of  $\tilde{R}(\kappa)$  versus  $\kappa$  in the region of high concentrations would give the roughness exponent  $H$ .

(3) *Compensation of deviations from the Gouy-Chapman theory at large concentrations.* The interference between the solvent structure and Debye length rounds the Parsons-Zobel plot down from the straight line in the high concentration region [41]. The roughness effect does the opposite. The two effects may compensate each other for very small  $l$ , and the Parsons-Zobel plot will appear "more straight" than it should be for an ideally flat surface.

## V. CONCLUSION AND OUTLOOK

We have developed a theory of the space-charge double layer capacitance at rough surfaces. The interplay between the Debye length and the lengths characterizing surface roughness was studied. The derivation of the main formulae was limited to the case of weak roughness, i.e., when the amplitude of height fluctuations  $h$  is smaller than the correlation length  $l$ . Extension on the case of strong roughness would require laborious efforts. However, the two limiting laws of small and large Debye lengths, obtained in the present work, should retain for the case of strong roughness. Thus as an interpolation, one may extend our present results to the case of  $h \sim l$ . However, at  $h \gg l$  the form of the roughness function may differ considerably from the obtained expressions.

A method for the study of surface roughness by the measurements of the space charge double layer capacitance at varied Debye length is suggested. Within the framework of the linearized Poisson-Boltzmann approximation used, the Debye length variation is provided by the variation of the density of charge carriers. The effective Debye length can also vary with the variation of electrode potential. The form and the magnitude of this effect depend on the system (the trends could be different for liquid and solid electrolytes [30]). The nonlinear Poisson-Boltzmann variant of the theory is currently in progress.

The suggested method for the study of surface roughness should be first tested on surfaces with roughness characteristics known from alternative conventional studies, such as, electron microscopy in UHV, *in situ* scanning tunnel micro-

scope (STM) or optical methods. It would also be interesting to test the theory predictions on electrodes with deterministic, designed roughness, e.g., on a sinusoidally corrugated surface. In such experiments one may vary not only the Debye length, but the corrugation period in a series of samples.

As an *in situ* method, it will be of special value when the medium bounding the metal is nontransparent for radiation and inaccessible to STM. This would be the cases of metal-semiconductor or metal-solid electrolyte interfaces, in particular. Strictly speaking, we would need the nonlinear variant of the theory, to have a framework for the interpretation of the data, based on the potential variation of the Debye length. Meanwhile, one may focus on the experiments on the capacitance of the metal-electrolyte interface at the small

surface charges at varied ionic strength of the surface inactive electrolytes. It would be fascinating if this classical technique of electrochemistry shed light on the microroughness of metal surfaces. Since the interpretation here is transparent and unambiguous, we believe that this method will soon be in common use.

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