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Influence of self-affine interface roughness on the charge capacitance between two dielectric media

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In this paper we investigate the influence of the interface roughness on the charge capacitance between two different dielectric media. Assuming the roughness fluctuations to be self-affine, it is shown that the roughness exponent H, which characterizes short wavelength roughness fluctuations, plays the dominant role with respect to the rms roughness amplitude w and the lateral correlation length ξ. Furthermore, it is shown that any evolution of the interface roughness under conditions leading to time variant local interface slope will have significant influence on charge capacitance properties.

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I. INTRODUCTION

A wide variety of important topics in electrochemistry,[1] colloid science,[2] biophysics,[3] and semiconductor technology[4] are based on the Gouy-Chapman (GC)[5,6] theory of electrolyte plasma near a flat charged wall. For a long period in electrochemistry, studies were performed on the liquid mercury drop electrode, and later on GaTi, Ga, and InGa electrodes.[7] Moreover, studies on solid electrodes (i.e., Cd, Bi, Cu, Pb) revealed problems that were associated with metal/electrolyte interface roughness, which is a problem that has been extensively addressed in various comprehensive studies.[8] Indeed, for rough metal/solution interfaces we cannot replace the flat surface area with that of the rough one because characteristic lateral roughness length scales can compete with system characteristic length scales leading to different functional dependence on potential and electrolyte concentration.[8]

However, in contrast to metal/solution interfaces, very little is known about the structure of dielectric liquid/liquid interfaces. One approach is that the solvents form a sharp boundary and a compact layer of solvent molecules, which the ions cannot further penetrate.[9] Another approach is that it exists a mixed layer of the solutions.[10] Furthermore, the interfacial structure of liquid-liquid interfaces is different from metal/solution interfaces without specific adsorption. The measured capacity at low electrolyte concentrations is found to be higher than the GC capacity.[11] In addition, besides experimental investigations, computer simulations of dielectric liquid/liquid interfaces[12,13] show that there is a sharp interface at which the two liquids do not mix, whereas recent calculations based on the density functional formalism predict a mixed solvent layer.[14] This is also confirmed within a simple lattice gas model.[15] Including ions in this approach, it was also possible to explain the higher capacity compared to the GC capacity by the existence of a mixed boundary layer, whose thickness extends over several solvent diameters. The extent of this boundary layer depends on the solubility of one solvent in the other.

Furthermore, for rough liquid/liquid interfaces a recent theory has been proposed[16] for the case of the linear Gouy-Chapman theory for a rough interface between two immiscible electrolytes. In this work the authors derived a roughness function of the capacitance in terms of the Fourier transform of the height-height correlation function of the interface.[16] It was shown that the capacity of the interface could be significantly higher than the value predicted by the GC theory. The deviation from the GC prediction depends on the competition among the Debye lengths for the two electrolyte solutions and the height and characteristic length of the rough interface modulation.[16] Nevertheless, so far the calculations were performed for the simple case of periodic rough interfaces, which possess only one lateral period. On the other hand, random rough interfaces possess roughness over various length scales rather than over a single one.

In this paper we extend the present theory to investigate the case of random self-affine rough interfaces, which can cover the case of thermal fluctuations in the limit of roughening exponents equal to zero (within the harmonic approximation for thermally induced capillary fluctuations).[17–19] This is quite a general description and it can be also applied to semiconductor/metal, semiconductor/electrolyte, and metal/electrolyte interfaces within the linear Poisson-Boltzmann (PB) equation.[16]

II. CAPACITANCE THEORY

In this work we denote with “1” the side of medium with dielectric constant ε_1 and $y > h(x)$, while with “2” the medium side with dielectric constant ε_2 and $y < h(x)$ [Fig. 1(a), where for simplicity the one-dimensional case is considered]. Also assume that the rough interface can be described by a single valued random function $y = h(x)$ of the in-plane position distance x so that $\langle h(x)\rangle = 0$. The linear PB equation has the form[16]

$$\nabla^2 \mathbf{\Phi} - k_{Di}{}^2 \mathbf{\Phi} = c_i \quad (i = 1,2), \tag{1}$$

where c_i is a constant usually set to zero in one side, k_{Di} $(=1/\lambda_{Di})$ and $\beta = 1/k_B T$ with T as the system temperature. The boundary conditions used to solve Eq. (1) in a perturbative approach are the following $\mathbf{\Phi}(x, -\infty) = \mathbf{\Delta\Phi}$ and $\mathbf{\Phi}(x,$

$+\infty)=0$, where $\Delta\mathbf{\Phi}$ is the total potential drop across the interface.[16] The quantity that can be independently controlled in an experiment is the total potential drop $\Delta\mathbf{\Phi}$ across the interface, since someone has no direct influence on the interface position itself. Moreover, if $\vec{n}(x)$ is the normal vector to the interface (pointing within side 1) then it is assumed that the displacement vector $\vec{D}_i=-\varepsilon_i\vec{\nabla}\Phi_i$ obeys the constraint $\vec{n}\cdot(\vec{D}_1-\vec{D}_2)=0$ (zero charge density in absence of nonelectrostatic contribution from adsorption of ionic species). Finally, the potential continuity at the interface yields $\mathbf{\Phi}_1[x,y=h(x)]=\mathbf{\Phi}_2[x,y=h(x)]$.[16]

For weak roughness ($|\nabla h|<1$) the charge capacitance C is given by[16]

$$C = C_{GC}A_{flat}R_{rough},$$

$$R_{rough} = R^G + \frac{1}{C_{GC}\Delta\mathbf{\Phi}}\int_{-Q_c<k<Q_c}\beta(k)\langle|h(k)|^2\rangle\frac{dk}{(2\pi)} \qquad (2)$$

with R^G as the geometrical roughness factor (ratio of real rough area over the average flat interface area). The GC capacitance for a flat interface is given by $C_{GC}=[(\varepsilon_1 k_{D1})^{-1}+(\varepsilon_2 k_{D2})^{-1}]^{-1}$. The other functions in Eq. (2) are given by[16]

$$\beta(k) = \frac{C^2{}_{GC}\Delta\mathbf{\Phi}}{2\varepsilon_1}f_1(k) + \frac{C^2{}_{GC}\Delta\mathbf{\Phi}}{2\varepsilon_2}f_2(k) + \frac{C_{GC}\hat{a}_1(k)}{2\varepsilon_1}f_{g1}(k) - \frac{C_{GC}\hat{a}_2(k)}{2\varepsilon_2}f_{g2}(k), \qquad (3)$$

$$f_i(k) = 1 - \left\{[2r_i(k)-1] - \frac{k^2}{k_{Di}{}^2}\left[\frac{2}{r_i(k)}-1\right]\right\},$$

$$r_i(k) = \sqrt{1+(k^2/k_{Di}{}^2)}, \qquad (4)$$

$$f_{gi}(k) = 1 - \left[r_i(k) - \frac{k^2}{k_{Di}{}^2 r_i(k)}\right], \qquad (5)$$

$$\hat{a}_{i(=1,2)}(k) = \frac{C_{GC}{}^2\Delta\mathbf{\Phi}}{\varepsilon_2}\left[\frac{1}{r_2(k)}-1\right] - \frac{C_{GC}{}^2\Delta\mathbf{\Phi}}{\varepsilon_1}\left[\frac{1}{r_1(k)}-1\right]. \qquad (6)$$

In any case, for the calculation of the charge capacitance C in terms of Eq. (2) a model for the roughness spectrum $\langle|h(k)|^2\rangle$ is necessary. This will defined in the following section.

III. INTERFACE ROUGHNESS MODEL

A self-affine morphology is characterized by a finite correlation length ξ, a rms roughness amplitude $w=\sqrt{\langle|h|^2\rangle}$, and a roughness exponent H ($0<H<1$), which is a measure of the degree of surface irregularity.[17] Small values of H (~ 0) characterize extremely jagged or irregular surfaces, while large values H (~ 1) surfaces with smooth hills and valleys.[17] For self-affine fractals the roughness spectrum $\langle|h(k)|^2\rangle$ is characterized by the power law scaling behavior $\langle|h(k)|^2\rangle\propto k^{-1-2H}$ *if* $k\xi\gg 1$ and $\langle|h(k)|^2\rangle\propto$ const if $k\xi\ll 1$.[17] This scaling behavior is satisfied by the simple Lorentzian model for $\langle|h(k)|^2\rangle$:[18,19]

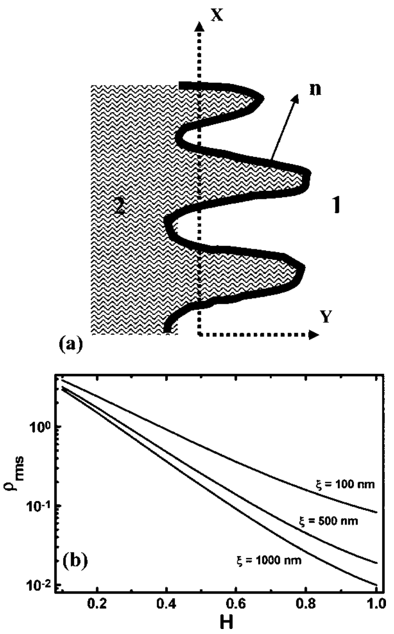

FIG. 1. (a) Schematic of the interface system under consideration. (b) Local interface slope vs roughness exponent H for various correlations lengths ξ as indicated.

$$\langle|h(k)|^2\rangle = \frac{2\pi w^2\xi}{(1+a|k|\xi)^{1+2H}} \qquad (7)$$

with $a=(1/H)[1-(1+aQ_c\xi)^{-2H}]$ if $0<H<1$, and $a=2\ln(1+aQ_c\xi)$ if $H=0$.[18,19] This form differs from the form of the power spectrum for liquid-liquid interfaces[20] for roughness exponents $H>0$. However, for roughness exponents $H=0$ (logarithmic roughness) the corresponding two-dimensional counterpart of Eq. (7) $[\langle|h|^2\rangle\propto(1+ak^2\xi^2)^{-(1+H)}]$ reproduces that of thermally induced capillary fluctuations $[\langle|h|^2\rangle\propto(1+k^2\xi^2)^{-1}]$ in liquids within the harmonic approximation.[21] On the other hand, the one-dimensional form of the power spectrum is suited to describe solid-liquid and solid-solid interfaces where the theory discussed in Sec. II can also be applied for semiconductor/metal, semiconductor/electrolyte, and metal/electrolyte interfaces within the linear PB equation.[16]

IV. RESULTS—DISCUSSION

The geometrical roughness factor can be more accurately computed for the case of Gaussian roughness fluctuations[20] by the knowledge of the local interface slope. Indeed, since $R^G=\langle\int\sqrt{1+|\nabla h|^2}\rangle$ (with $\langle\cdots\rangle$ an ensemble average over possible roughness configurations) we have for Gaussian fluctuations[22]

$$R^G = \int_0^{+\infty} (1 + \rho_{rms}{}^2 u)^{1/2} e^{-u} du. \tag{8}$$

Equation (8) accommodates the roughness influence due to geometric roughness for both weak ($\rho_{rms} < 1$) or strong ($\rho_{rms} > 1$) roughness. Indeed, for weaker roughness ($\rho_{rms} < 1$) expansion of Eq. (9) yields the series formula for the geometric factor

$$R^G = 1 + \frac{1}{2}\rho_{rms}{}^2 + \sum_{n=2}^{+\infty} S(n)\rho_{rms}{}^{2n} \tag{9}$$

with $S(n)=\{1\cdot 1\cdot 3\cdot 5\cdots(2n-3)\}(-1)^{n-1}/2^n$. Note that up to second order terms the result is independent of any nature of the interface fluctuations, while the higher order terms are only valid for Gausian fluctuations. The average local slope ρ_{rms} is given in terms of the roughness spectrum $\langle |h(k)|^2\rangle$ by the relation

$$\rho_{rms} = \left\{ 2\int_{0<k<Q_c} k^2 \langle |h(k)|^2\rangle \frac{dk}{(2\pi)} \right\}^{1/2} \tag{10}$$

with $Q_c = \pi/c$ and c as a lower length scale cutoff of the order of atomic dimensions. The local slope shows a strong dependence on the roughness exponent.[23] This is also displayed in Fig. 1(b) where a variation of the roughness exponent H within its nominal range from 0 to 1 (which is approximately an order of magnitude) leads to local slope variations by more than three orders of magnitude. Therefore the influence of the roughness exponent H is significantly stronger than the effect of the lateral correlation length ξ [as Fig. 1(b) shows], and in more general sense of the long wavelength roughness ratio w/ξ.

In general, the charge capacitance will have a simpler dependence on the roughness amplitude w since $\langle |h(k)|^2\rangle \propto w^2$ (assuming weak roughness), while any more complex dependence will arise from the roughness parameters H and ξ for self-affine roughness. Our calculations were performed for lower roughness cutoff $c = 0.3$ nm where we have to point out that the lower roughness cutoff ($c = 0.3$ nm in the present calculations) corresponds to a typical lattice constant for metals. However, a lower value might be necessary for a physical system (depending on the material) since the actual smallest step height might be smaller than the lattice constant.

Figure 2 shows the dependence of the roughness factor $R_{rou} = R_{rough} - 1$ on the roughness amplitude w. Indeed, the factor R_{rou} subtracts any effect from the flat interface contribution ($C = C_{GC} + C_{GC}R_{rou}$). This becomes more obvious if we substitute Eq. (10) into Eq. (2), which yields the simpler expression for R_{rou}:

$$R_{rou} = \frac{1}{2}\rho_{rms}{}^2 + \sum_{n=2}^{+\infty} R(n)\rho_{rms}{}^{2n} + \frac{2}{C_{GC}\Delta\Phi}\int_{0<k<Q_c} \beta(k)\langle |h(k)|^2\rangle \frac{dk}{(2\pi)}. \tag{11}$$

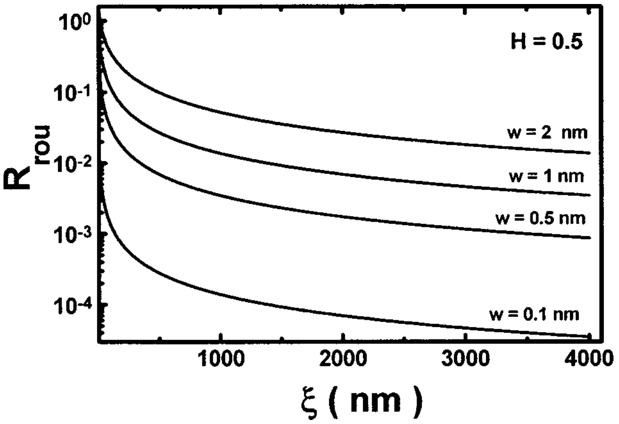

FIG. 2. Roughness ratio R_{rou} vs roughness correlation length ξ for $\lambda_{D1} = 0.5$ nm, $\varepsilon_1 = 12$, $\lambda_{D2} = 20$ nm, $\varepsilon_2 = 80$, $H = 0.5$, and various roughness amplitudes w as indicated.

At any rate as Fig. 2 shows R_{rou} decays rather fast with increasing correlation length ξ, while with increasing roughness amplitude w a nonlinear increment takes place. This is due to the surface term ($\sim R^G$) in Eq. (11), where since $\rho_{rms} \sim w$ we obtain a dependence on w with higher powers than 1 if we consider the terms with $n > 2$. The potential dependent term (integral term) has a simple dependence on w since $\langle |h|^2\rangle \propto w^2$.

Furthermore, Fig. 3 shows that the roughness contribution R_{rou} to the charge capacitance is highly sensitive to changes of the roughness exponent H. This is also clearly depicted in direct plots of R_{rou} versus roughness exponent H in Fig. 4 for various correlation lengths ξ, and in Fig. 5 for various roughness amplitudes w. Notably, as Fig. 4 indicates the roughness factor R_{rou} shows a variation in decay rate with varying correlation length ξ. If we compare the influence of all the roughness parameters (w, ξ, and H), as the roughness exponent H changes by an order of magnitude within its nominal range of values, the variation of the factor R_{rou} can be more than an order of magnitude. As a result the effect of the roughness exponent H, which quantifies short range roughness fluctuations, is more dominant than that of the roughness ratio w/ξ that quantifies the long wavelength roughness characteristics (length scales $> \xi$).

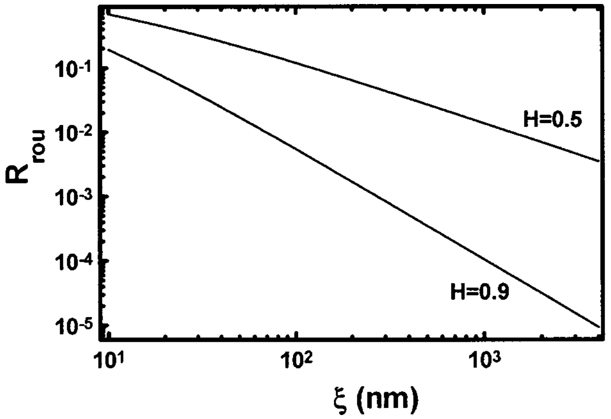

FIG. 3. Roughness ratio R_{rou} vs roughness correlation length ξ for $\lambda_{D1} = 0.5$ nm, $\varepsilon_1 = 12$, $\lambda_{D2} = 20$ nm, $\varepsilon_2 = 80$, $w = 0.1$ nm, and roughness exponents H as indicated.

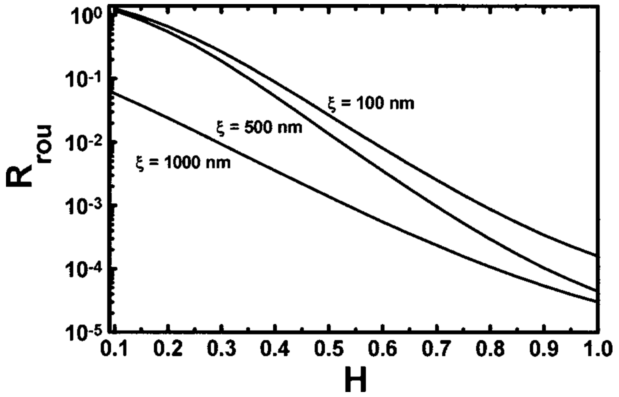

FIG. 4. Roughness ratio R_{rou} vs roughness exponent H for $\lambda_{D1}=0.5$ nm, $\varepsilon_1=12$, $\lambda_{D2}=20$ nm, $\varepsilon_2=80$, $w=1$ nm, and correlation lengths ξ as indicated.

For the cases of solid-solid and solid-liquid interfaces it is likely to modify or fabricate in advance the interface roughness characteristics (w, ξ, and H) by different thin film deposition processes where depending on the growth conditions and material properties the roughness can evolve as a function of growth time.[17] Therefore, as a secondary consequence (not by considering any simultaneous temporal system evolution that would require solution of time dependent equations of motion) we will consider how separately the evolution of interface roughness can influence the roughness contribution to the charge capacitance. Indeed, if both roughness parameters w and ξ evolve with some growth time τ as $w \propto \tau^{\beta}$ and $\xi \propto \tau^{1/z}$ with $z=2H/\beta$, then the evolution of the roughness factor R_{rou} for various times τ is clearly evident in Fig. 6(a). The choice of the so-called dynamic exponent z so that $z \neq H/\beta$ leads to an evolution of the local interface slope. Indeed, since $\rho_{rms} \propto w/\xi^{H}$ we obtain for $z=2H/\beta$ the temporal evolution $\rho_{rms} \propto \tau^{\beta}$. Note that for $z=H/\beta$ the local slope is time invariant ($\partial\rho_{rms}/\partial\tau=0$). Indeed, the effect of the temporal evolution as depicted by Fig. 6(a) is more prominent for low roughness exponents ($H<0.5$) or equivalently when the interface becomes more irregular at short wavelengths ($<\xi$). On the other hand, if we consider the case of interface smoothing as for example the case of $z=H/2\beta$, which leads to local slope decrement as $\rho_{rms} \propto \tau^{-\beta}$, the roughness contribution decreases [Fig. 6(b)] with still, however, the strongest influence appearing at small roughness exponents H (<0.5).

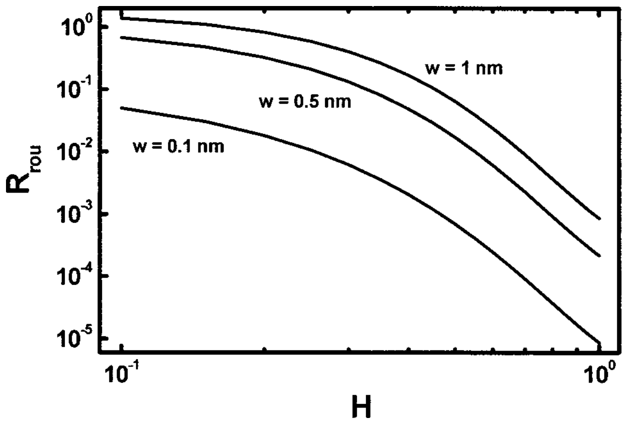

FIG. 5. Roughness ratio R_{rou} vs roughness exponent H for $\lambda_{D1}=0.5$ nm, $\varepsilon_1=12$, $\lambda_{D2}=20$ nm, $\varepsilon_2=80$, $w=1$ nm, correlation length $\xi=100$ nm, and roughness amplitudes w as indicated.

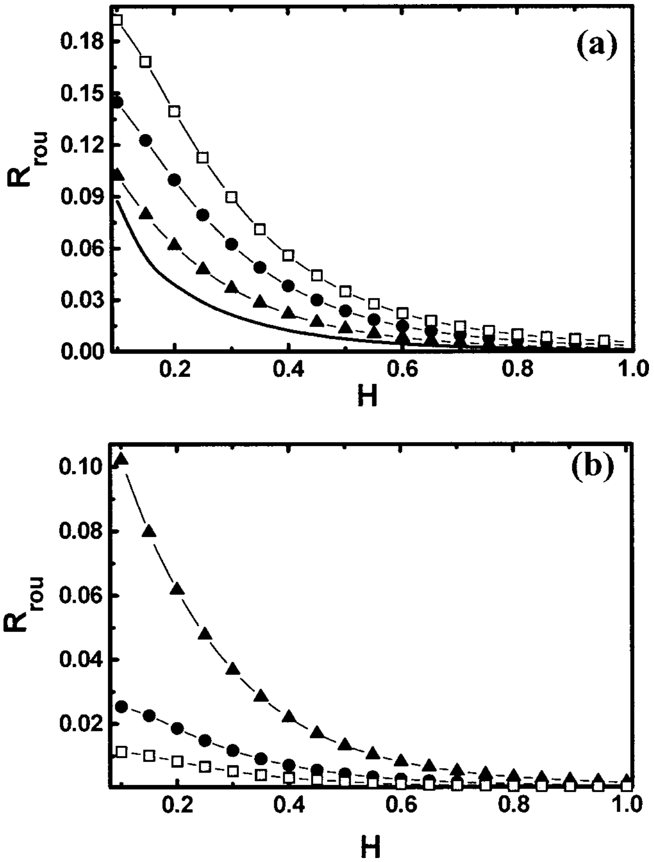

FIG. 6. Roughness ratio R_{rou} vs roughness exponent H for $\lambda_{D1}=1$ nm, $\varepsilon_1=12$, $\lambda_{D2}=20$ nm, $\varepsilon_2=80$. (a) $w=0.1\tau^{\beta}$, $\xi=10\tau^{1/z}$ ($\beta=0.25$, $z=2H/\beta$). Solid line: $\tau=0.1$, solid triangles: $\tau=1$, solid circles: $\tau=10$, open squares: $\tau=50$. (b) $w=0.1\tau^{\beta}$, $\xi=10\tau^{1/z}$ ($\beta=0.25$, $z=H/2\beta$). Solid triangles: $\tau=1$, solid circles: $\tau=10$, open squares: $\tau=50$.

V. CONCLUSIONS

In this paper we investigate the influence of the interface roughness on the charge capacitance between two different dielectric media. Assuming self-affine roughness fluctuations, it is shown that the roughness exponent H that characterizes short wavelength roughness fluctuations plays the dominant role with respect to the rms roughness amplitude w and the lateral correlation length ξ. Furthermore, it is shown that any temporal evolution of the interface roughness under conditions leading to a temporally variant local interface slope will have significant impact on charge capacitance properties and should be carefully taken into consideration. In all cases, the roughness leads to capacitance values larger than the GC prediction. If the roughness function is known for various electrolyte concentrations, one can get information about the height-height correlation function of the interface. On the other hand, this result can be verified in a simple geometry system by means of x-ray reflectivity, which allows probing of interface fluctuations including also liquid-liquid interfaces.[17]

At any rate, because our results are derived from a quite general formalism that can be applied to a variety of interfaces (semiconductor/metal, semiconductor/electrolyte, and metal/electrolyte interfaces[16]), their applicability is expected also to be more general. We should, however, point out that in many cases at dielectric liquid-liquid interfaces[20] not only does the interfacial roughness influence the potential distribution at the interface, but also the potential influences the interface roughness correlation function. As a result both effects have to be taken into account in capacitance calculations with the potential distribution and the correlation function being determined self-consistently.[20] However, such an effect is not expected to be of significance for solid-liquid and solid-solid interfaces and it was omitted in the present treatment.

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