

## Erratum: Double Layer in Ionic Liquids: Overscreening versus Crowding [Phys. Rev. Lett. 106, 046102 (2011)]

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(Received 19 July 2012; published 5 October 2012)

DOI: 10.1103/PhysRevLett.109.149903

PACS numbers: 82.45.Gj, 82.47.Uv, 88.80.fh, 99.10.Cd

We have found that our Letter [1] needs two corrections to the details of the example calculation which does not alter any of the conclusions of the Letter.

(1) Although our model successfully represents short-range Coulomb correlations and ion exclusion effects in the ionic liquid, as a step towards a more subtle account for the atomic structure of the interface, we added in series an interfacial “compact layer” contribution to capacitance. This is a standard approximation in electrochemical modeling, and, in this case, it introduces no new parameters, since we take the width of the compact layer to be the distance of closest approach of the ions (i.e., the ionic radius) with the same long-wavelength dielectric constant as in the bulk ionic liquid. This procedure serves its purpose, providing additional reduction of capacitance at the potential of zero charge. However, to be consistent, this requires a recalculation of the potential drop in the diffuse double layer through the total potential drop across the whole double layer (composed of the voltage across the compact layer and the diffuse layer). In Fig. 4 of Ref. [1], we have actually shown the overall double-layer differential capacitance as a function of the diffuse layer voltage instead of the total voltage. Only the latter is a controllable variable, and the drop across the diffuse layer should be expressed through it.

(2) A factor  $\gamma$  (the ratio of the bulk ion density to the maximum possible density) was missing in our modified Debye screening length,  $\lambda_D$ . The proper definition of  $\lambda_D$  should read  $\lambda_D = \sqrt{\epsilon k_B T \nu / (z^2 e^2 \gamma)}$ . This definition of the Debye length is consistent with setting the bulk concentration to  $c = \gamma/2\nu$ , where  $\nu = 0.83a^3$ , as is explained in the Letter.

Both inaccuracies are rectified in the plots shown below in Fig. 1. The dimensionless parameters used to match the molecular dynamics simulations remain  $\gamma = 1/2$  and  $\delta_c = 10$ . The physical parameters for the ionic liquid remain:  $a = 10 \text{ \AA}$ ,  $T = 450 \text{ K}$ , and  $\epsilon = 5\epsilon_0$ . However, the proper definition of the Debye length gives  $\lambda_D = 1.34 \text{ \AA}$  and thus the Debye capacitance of  $C_D = 33.2 \mu\text{F/cm}^2$ . The corrected definition of the Debye length implies that the correlation length is  $\ell_c = 1.33a$ . We continue to account for a Stern layer of width  $a/2$  with the same value of the dielectric constant of fast degrees of freedom, as in the bulk liquid. The Stern layer has a constant capacitance of  $C_s = 8.85 \mu\text{F/cm}^2$ . Below, in Fig. 1 we recalculate the voltage across the diffuse layer through the total voltage and show the capacitance as a function of the latter.

The correction in the Debye length quantitatively changes Fig. 3 of Ref. [1] but does not change any conclusions drawn from this figure. Together with the proper voltage on the  $x$  axis, the correction also quantitatively changes Fig. 4. However, all the conclusions of the Letter remain. Moreover, with these two corrections, the model of Ref. [1] shows even better agreement with the molecular dynamics simulation data [2]. In particular, our theory of electrostatic correlations now leads

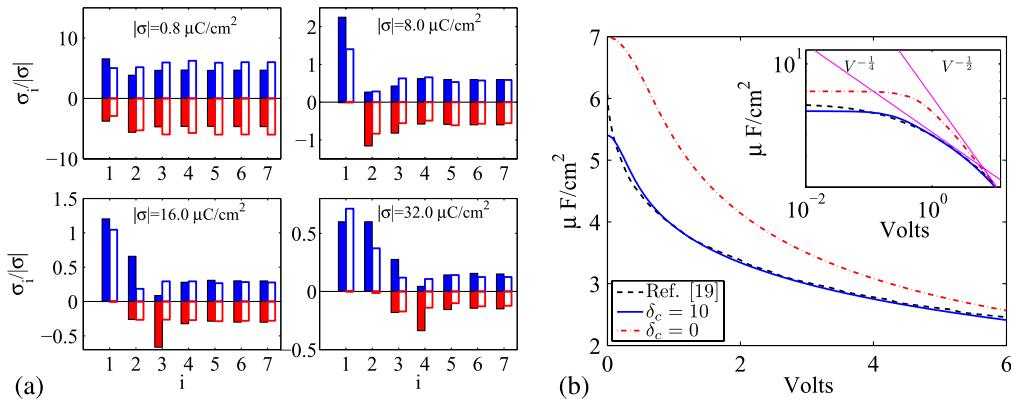


FIG. 1 (color online). (a) Corrected Fig. 3. Distributions of cations (above) and anions (below) sorted into monolayer bins  $i = 1, 2, \dots$  for different surface charges  $\sigma$ , as predicted by our model (solid bars) in qualitative agreement with simulations (Fig. 2 of Ref. [2], open bars). (b) Corrected Fig. 4. Double-layer differential capacitance  $C_d$  from our model (solid line) compared with simulations [2] (dashed line), mean-field theory [3] (dash-dotted line), and our asymptotic scalings (inset).

to a remarkably good fit of the calculated values of capacitance at low voltages with the simulation data and thus corrects an established shortcoming of the mean-field theory.

The authors wish to thank R. Qiao and X. K. Jiang of Clemson University who brought the first of the two inaccuracies to our attention.

- [1] M. Z. Bazant, B. D. Storey, and A. A. Kornyshev, [Phys. Rev. Lett. 106, 046102 \(2011\)](#).
- [2] M. V. Fedorov and A. A. Kornyshev, [Electrochim. Acta 53, 6835 \(2008\)](#).
- [3] A. A. Kornyshev, [J. Phys. Chem. B 111, 5545 \(2007\)](#).