

**Anomalous large capacitance of an ionic liquid described by the restricted primitive model**

M. S. Loth, Brian Skinner, and B. I. Shklovskii

*Fine Theoretical Physics Institute, University of Minnesota, Minneapolis, Minnesota 55455, USA*

(Received 9 August 2010; revised manuscript received 12 October 2010; published 2 November 2010)

We use Monte Carlo simulations to examine the simplest model of a room-temperature ionic liquid (RTIL), called the “restricted primitive model,” at a metal surface. We find that at moderately low temperatures the capacitance of the metal-RTIL interface is so large that the effective thickness of the electrostatic double layer is up to three times smaller than the ion radius. To interpret these results we suggest an approach which is based on the interaction between discrete ions and their image charges in the metal surface and which therefore goes beyond the mean-field approximation. When a voltage is applied across the interface, the strong image attraction causes counterions to condense onto the metal surface to form compact ion-image dipoles. These dipoles repel each other to form a correlated liquid. When the surface density of these dipoles is low, the insertion of an additional dipole does not require much energy. This leads to a large capacitance  $C$  that decreases monotonically with voltage  $V$ , producing a “bell-shaped” curve  $C(V)$ . We also consider what happens when the electrode is made from a semimetal rather than a perfect metal. In this case, the finite screening radius of the electrode shifts the reflection plane for image charges to the interior of the electrode, and we arrive at a “camel-shaped”  $C(V)$ . These predictions seem to be in qualitative agreement with experiment.

DOI: [10.1103/PhysRevE.82.056102](https://doi.org/10.1103/PhysRevE.82.056102)

PACS number(s): 89.90.+n, 82.47.Uv, 61.20.Qg

**I. INTRODUCTION**

Room-temperature ionic liquids (RTILs) are molten salts made from ions which are large enough that their Coulomb interaction is relatively small, so that they remain in a fluid state at relatively low temperatures. Essentially, a RTIL is a solvent-free electrolyte, which means that RTILs can be ideally suited for applications which require a thin or intensely concentrated layer of ionic charge. RTILs are already being used for batteries and “supercapacitors” [1], as well as for gating of new electronic materials. It has therefore become a subject of great interest to understand the nature of the interface between a RTIL and a metallic electrode.

In its simplest form, the question of how a RTIL behaves in the vicinity of a charged metal surface seems remarkably straightforward. While real-life experiments probing the structure of the ionic double layer can be marked by a number of complications [2], the essential description is encapsulated in a very simple model: an infinite planar metallic electrode is placed in contact with a semi-infinite volume that contains a total concentration  $N$  of mobile positively and negatively charged hard spheres, each with the same diameter  $a$  and the same absolute value of charge  $e$ . Such a model of the RTIL is called the restricted primitive model (RPM); one can think that it reflects the properties of a real RTIL reasonably well because typical ion sizes in a RTIL,  $a \sim 1$  nm, are much larger than atomic sizes. We set the dielectric constant of the RTIL equal to unity since we are considering a model of nonpolarizable ions in a solvent-free environment. If a voltage  $V$  is applied between the electrode and the bulk of the RTIL, how large is the charge density  $\sigma$  of the metal surface? In other words, what is the capacitance per unit area,  $C(V) = d\sigma/dV$ , of the interface?

The answer to this question is well known in the limit of large temperature and low applied voltage. In this case the ionic double layer is well described as a diffuse screening layer with a characteristic size equal to the Debye-Hückel (DH) screening radius

$$r_{DH} = \sqrt{\frac{k_B T}{4\pi e^2 N}}. \quad (1)$$

Here,  $k_B T$  is the thermal energy [Eq. (1), and the remainder of this paper, uses Gaussian units]. The diffuse layer of countercharge effectively comprises the second half of a parallel-plate capacitor of thickness  $r_{DH}$ , so that the capacitance per unit area is equal to  $C_{DH} = 1/4\pi r_{DH}$ . At large density  $Na^3 \sim 1$  this result for capacitance is valid as long as the temperature is high enough that  $T \gg T_0 \equiv e^2/k_B a$  and the voltage is small enough that  $eV \ll k_B T$ .

More generally, one can characterize the capacitance by the effective thickness of the double layer  $d^* = 1/4\pi C$ . In the DH limit,  $d^* = r_{DH}$ . In realistic situations, however, the characteristic temperature  $T_0$  is very large and the DH approximation fails at room temperature. One can think that as a result ions become more strongly bound to the charged electrode and the size of the double layer shrinks, so that  $d^*$  decreases and the capacitance grows. One may ask, then, how thin the double layer can be or, in other words, how large the capacitance can be. The apparent answer to this question goes back to Helmholtz [3], who imagined that in an extreme case a neutralizing layer of ions could collapse completely onto the electrode surface, thereby forming the second half of a plane capacitor at a distance equal to the ion radius  $a/2$ . The result is a double layer of size  $d^* = a/2$  and a capacitance per unit area equal to the “Helmholtz capacitance”

$$C_H = 1/2\pi a. \quad (2)$$

In classical mean-field theories of the electrostatic double layer [4–6], and in the recent influential theory of the metal-RTIL capacitance which accounts for the excluded volume among ions [7],  $C_H$  plays the role of a maximum possible capacitance per unit area. Monte Carlo (MC) simulations [8–10] seem to confirm this statement. However, these and the majority of other simulations make the simplification of

replacing the metal electrode with a uniformly charged insulating plane. We argue below that in this way the essential physics of image charges in the metal surface is lost (see also Refs. [11–13]).

It is the purpose of this paper to demonstrate that capacitance  $C > C_H$  is possible or, in other words, that the effective thickness of the double layer can be smaller than the ion radius. Our previous work [14] has demonstrated that capacitance  $C > C_H$  can occur for highly asymmetric RTILs (where the cation has a much smaller radius than the anion, or vice versa). Here, we show that even in the RPM, where cations and anions have equal diameter, capacitance significantly larger than the Helmholtz value is possible. As we describe below, the metallic nature of the electrode—specifically, the ability of ions to form image charges in the metal surface—plays a key role in the development of large capacitance. We present the results of MC simulations of the restricted primitive model of a RTIL at various temperatures and densities, and we suggest a basic theoretical explanation of these results based on the weak repulsion between dipoles composed of bound ions and their images in the metal surface.

We note that the critical role of image charges for the structure of the double layer has in fact been recognized by previous authors [15], who performed similar simulations which account explicitly for the electronic polarization of the electrode. However, Ref. [15] explored only very low ion density  $Na^3=0.01$ , where  $C(V=0) < C_H$ . Another paper [16] studied the capacitance of a RTIL between two identical metal plates and obtained large capacitance  $C(0) \sim 2C_H$ , but this study used a much more complicated model of the RTIL.

The remainder of this paper is organized as follows. In Sec. II we present our MC results for  $C(T)$  at small voltage and describe our MC procedure. Section III is devoted to our analytical theory, including both temperature and voltage dependences of the capacitance  $C(V, T)$ . Section IV considers the role of the electrode material on  $C(V, T)$ . We conclude in Sec. V with a summary of our main results.

## II. TEMPERATURE DEPENDENCE OF THE CAPACITANCE AND MONTE CARLO SIMULATION METHOD

Figure 1 shows the zero voltage capacitance  $C(0)/C_H$ , as measured by our MC simulations, as a function of reduced temperature  $T^*=T/T_0$  for three different dimensionless ion densities  $Na^3$ . The points correspond to results from the MC simulation and solid lines are a fit to the form  $C/C_H=A(T^*)^{-1/3}$ , where  $A$  is a numerical constant. The motivation for this  $(T^*)^{-1/3}$  dependence is explained in Sec. III. For all three values of the density that we examined, the capacitance at low temperature is significantly higher than the Helmholtz value.

These results should be contrasted with previous simulation studies [8,9] of the capacitance of the RPM, in which the metallic electrode was replaced with a charged insulator with uniform charge density  $\sigma$ . These studies report a capacitance  $C(V=0, T)$  that grows with decreasing  $T^*$  before reaching a peak at  $T^*=T_p^*$  and then collapsing rapidly at  $T^* < T_p^*$ . For  $Na^3=0.08$  and  $0.64$ ,  $T_p^* \approx 0.17$  and  $0.28$ , respectively.

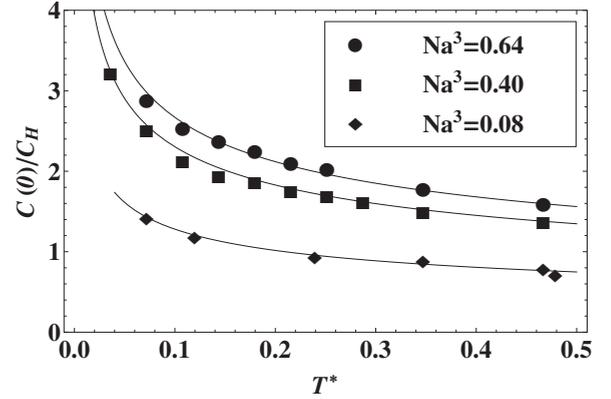


FIG. 1. The capacitance of the metal-RTIL double layer at zero voltage as a function of the dimensionless temperature  $T^*$ , plotted for three values of the dimensionless ion density  $Na^3$ . Symbols represent results from the MC simulation and solid lines show a best fit to the form  $C/C_H=A(T^*)^{-1/3}$  for each density. Error bars are smaller than the symbol size.

The collapse of the capacitance at low temperatures  $T^* < T_p^*$  was interpreted by the authors of Refs. [8,9] as the result of strong binding of positive and negative ions to form neutral pairs. Such binding leads to an extreme sparsity of free charges in the RTIL, so that their total concentration  $N_f \ll N$ . Substituting  $N_f$  for  $N$  into Eq. (1) at  $T^* \ll 1$ , we arrive at a large screening radius  $r_{DH}$  and therefore much smaller capacitance  $C(0)$ . These arguments are generic and convincing. Why, then, does the capacitance in Fig. 1 continue to grow with decreasing temperature?

This question is the main focus of our discussion in Sec. III. The remainder of the present section is devoted to describing our Monte Carlo procedure and may safely be skipped by those not interested in the details of our simulation method.

In our MC simulations, a canonical ensemble of  $M_a$  anions and  $M_c$  cations is placed in a square prism cell of dimensions  $L \times L \times L/2$  and corresponding volume  $\Omega=L^3/2$ . The metallic electrode coincides with one of the cell's square faces. Every charge within the cell forms an electrostatic image in the electrode surface ( $z=0$ ), i.e., a charge  $q=\pm e$  at position  $(x, y, z)$  has an image charge  $-q$  located at  $(x, y, -z)$ . The total electrostatic energy  $\mathcal{E}$  of the cell is calculated as 1/2 times the energy of a system twice as large composed of the real charges and their images, so that

$$\mathcal{E} = \frac{1}{2} \sum_{\{i,j\}}^{M_t} u(d_{i,j}), \quad (3)$$

where the indices  $i, j$  label the set of all particles in the system (ions and images),  $M_t=2(M_a+M_c)$  is the total number of these particles,  $d_{i,j}$  is the distance between particles  $i$  and  $j$ , and the two-particle interaction energy  $u(d_{i,j})$  is

$$u(d_{i,j}) = \begin{cases} \infty, & d_{i,j} < a \\ q_i q_j / d_{ij}, & d_{i,j} > a. \end{cases} \quad (4)$$

Here,  $q_i = \pm e$  is the charge of particle  $i$ .

The charge of the electrode is varied by changing the number of anions  $M_a$  and cations  $M_c$  in the system by equal and opposite amounts, so that the total number of ions  $M_a + M_c = N\Omega$  remains fixed for a given overall density  $N$ . The corresponding electronic charge (in the form of image charges) in the electrode is  $Q = e(M_a - M_c)$  and the capacitance  $dQ/dV$  can be determined from the resulting voltage. We use the system size  $L = 20a$  everywhere.

At the beginning of each simulation, positive and negative ions are placed within the simulation cell in such a way that they do not overlap with each other or with the metal surface. The MC program then selects an ion at random and attempts to reposition it to a random position within a cubic volume of  $(2a)^3$  centered on the ion's current position. The change in the energy  $\mathcal{E}$  associated with this move is then calculated, and the move is accepted or rejected based on the standard Metropolis algorithm. For one in every 100 attempted moves, the MC program chooses the random position from within a larger volume  $(10a)^3$  as a means of overcoming the effects of any large local energy barriers. The simulation cell is given periodic boundaries, so that an ion exiting one face of the cell reenters at the opposite face. To ensure thermalization, 2500 moves per ion are attempted before any simulation data are collected. After thermalization, simulations attempt  $2 \times 10^4$  moves per ion, of which 15–50 % are accepted.

The voltage of the electrode is measured by defining a “measurement volume” near the back of the simulation cell—occupying the range  $-L/4 < x < L/4$ ,  $-L/4 < y < L/4$ , and  $L/4 < z < 3L/8$ , where the origin  $(x, y, z) = (0, 0, 0)$  is located at the center of the electrode surface—inside of which the electric potential is measured. After performing thermalization, the total electric potential is measured at 500 equally spaced points within the measurement volume after every  $3(M_a + M_c)$  attempted moves. These measured values of potential are then averaged both temporally and spatially to produce a value for the voltage  $V$  of the electrode relative to the bulk. There was no noticeable systematic variation in electric potential across the measurement volume. The capacitance  $C(V=0)$  is determined from the discrete derivative  $\Delta Q/\Delta V$  at sufficiently small values of  $Q$  that the relationship  $Q$  vs  $V$  is linear.

Our results are shown in Fig. 1. For all  $Na^3$  studied, the lowest value of  $T^*$  in Fig. 1 is larger than the corresponding liquid-gas or liquid-solid coexistence temperature. For comparison, the triple point in the phase diagram of the RPM ionic liquid is located at  $Na^3 = 0.5$  and  $T^* = 0.025$ , while the gas-liquid critical point is at  $Na^3 = 0.02$  and  $T^* = 0.05$  [17]. We verified for each simulation that there was no phase separation within the simulation cell.

In order to quantify the finite-size effects of our simulation cell, we examined the capacitance at zero voltage,  $C(0, T^*)$ , obtained from three simulation volumes of sizes  $L = 10a$ ,  $20a$ , and  $30a$ . For  $Na^3 = 0.4$ ,  $C(0, T^*)$  was seen to scale linearly with  $1/L$  at all values of the temperature that we examined ( $T^* = 0.042$ ,  $0.072$ , and  $0.14$ ). In each case, the value of  $C(0, T^*)$  obtained by extrapolation to infinite system size was within 20% of the value of  $C(0, T^*)$  corresponding to  $L = 20a$ . These results allow us to conclude that the simulation cell with  $L = 20a$  provides a reasonable approximation

of an infinite system. All MC results presented below correspond to this choice.

### III. INTERPRETATION OF THE CAPACITANCE GROWTH AT SMALL VOLTAGE AND TEMPERATURE

Our goal is to interpret the large capacitance of the metal-RTIL interface at  $T^* \ll 1$ . In this section we suggest an analytical semiquantitative theory of a mechanism which produces such large capacitance. This theory operates in the limited range of temperature  $0.05 < T^* < 1$ , where the RTIL does not freeze. Thus, our theory (as any theory of the liquid state) does not have any true asymptotically small parameters and should be considered only semiquantitative.

We begin by observing that when the electrode is metallic, the energy of an ion binding to its image charge,  $-e^2/2a$ , is exactly half the energy of a bound ion pair,  $-e^2/a$ . This fact implies that if an ion pair is separated in the bulk and then both ions are brought to the metal surface there is no net change in electrostatic energy. Thus, even in the absence of applied voltage there are plenty of free charges at the metallic surface. Roughly speaking, this allows the double layer to be very thin and leads to the large capacitance shown in Fig. 1.

The zero-energy process of ion pairs dissociating and sticking to their images on the metal surface implies that at low temperatures  $T^* \ll 1$  effectively all ions in the system are either paired in the bulk or bound to their images on the electrode [18]. At zero applied voltage, equal numbers of positive and negative ions are bound to the metal surface. The area density  $n_0$  of these ions can be estimated from the requirement that the chemical potential of pairs in the bulk is equal to the chemical potential of ions at the surface, which gives  $\ln(2/Na^3) = 2 \ln(1/n_0a^2)$ , so that  $n_0 = \sqrt{N/2a}$ .

As the voltage  $V$  of the electrode is increased from zero, some number of pairs in the system is separated, so that the free counterion can come to neutralize the electrode surface. The corresponding density of these “excess ions”  $\delta n$  on the metal surface is related to the charge density  $\sigma$  by  $\delta n = |\sigma|/e$ . If  $\sigma > 0$ , then  $\delta n$  represents an excess of anions on the surface; if  $\sigma < 0$  the excess ions are cations. Naturally, excess ions condensed onto the metal surface repel each other. Since each ion on the metal surface is separated by a distance  $a$  from its image charge in the metal, ions and their images constitute compact ion-image dipoles with dipole moment  $ea$ , and so excess ions repel each other via a dipole-dipole interaction

$$u_{dd}(\delta n) = \frac{e^2 a^2 (\delta n)^{3/2}}{2}. \quad (5)$$

Excess ions at the metal surface are surrounded by  $n_0$  other ions per unit area, which effectively neutralize each other by forming  $n_0/2$  bound pairs. These  $n_0/2$  bound pairs, along with bound pairs in the bulk, may serve to modify the effective dielectric constant for the interaction of excess ions. We comment on this possibility later in this paper.

At low temperatures, the excess ions will seek to maximize their distance from each other while maintaining a given density  $\delta n$ . One can hypothesize a zero-temperature

description of the resulting positional correlations, where excess ions form a strongly correlated liquid reminiscent of a two-dimensional Wigner crystal. The corresponding total electrostatic energy per unit area of the system is

$$U = \alpha \delta n u_{dd}(\delta n) - e \delta n V, \quad (6)$$

where  $\alpha$  is a numerical coefficient which describes the structure of the lattice of excess ions; for a triangular lattice,  $\alpha \approx 4.4$  [19]. The term  $-e \delta n V$  describes the work done by the voltage source.

The voltage  $V$  which corresponds to a given charge density  $\sigma = e \delta n$  can be found by the equilibrium condition  $\partial U / \partial (e \delta n) = 0$ , which gives

$$V = \frac{5\alpha e a^2}{4} (\delta n)^{3/2}. \quad (7)$$

The resulting capacitance per unit area  $C = d\sigma / dV = e [dV / d(\delta n)]^{-1}$  is

$$C(\delta n) = \frac{8}{15\alpha a \sqrt{\delta n a^2}}. \quad (8)$$

Substituting Eq. (7) into Eq. (8) gives the capacitance in terms of voltage:

$$C(V) = \frac{8}{3} \left( \frac{1}{10\alpha} \right)^{2/3} \left( \frac{e}{aV} \right)^{1/3} \frac{1}{a} \approx 1.3 \left( \frac{e}{aV} \right)^{1/3} C_H. \quad (9)$$

The expression of Eq. (9) implies that  $C$  can be significantly larger than  $C_H$  when  $V$  is small. At such small voltages, the fractional coverage of excess ions on the electrode surface  $\delta n a^2 \ll 1$ , so that it is incorrect to think of the double layer in the mean-field way: as a series of uniform layers of charge. Rather, the neutralizing ionic charge consists of discrete ion-image dipoles. The correlated nature [20] of these dipoles allows for lower energy than what is possible in mean-field descriptions and therefore larger capacitance that is not limited by the physical distance  $a/2$  between the electrode and its countercharge.

Of course, the validity of Eqs. (5)–(9) is limited to the range of voltage where  $\delta n a^2 \ll 1$ . By Eq. (7), this corresponds to a dimensionless voltage  $V^* = V / (e/a) \ll 5\alpha/4 \approx 5.5$ . At large enough voltages that  $\delta n a^2 \approx 1$ , excess ions constitute a uniform layer of charge, and therefore the capacitance approaches  $C_H$ . At even larger voltages, the capacitance declines as complete layers of counterions accumulate next to the electrode and the double layer becomes thicker. This leads to a mean-field capacitance  $C \propto V^{-1/2}$  at large voltages, as described in Ref. [7].

Formally, Eq. (9) diverges as the voltage goes to zero. Of course, this expression neglects entropic effects of the excess ions, which tend to destroy the lattice structure of excess ions on the metal surface. Such effects will truncate the low-voltage divergence of Eq. (9), resulting in a finite capacitance at zero voltage. Intuitively, one would expect that the value of this capacitance maximum can be estimated by evaluating the capacitance at the point where  $u_{dd}(\delta n) = k_B T$ . This procedure gives

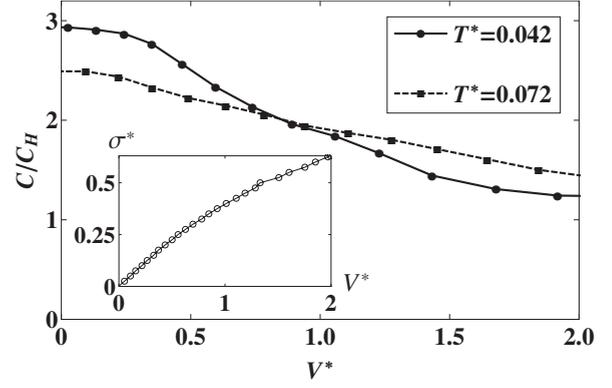


FIG. 2. The capacitance as a function of the dimensionless voltage  $V^* = V / (e/a)$  at two different temperatures for a system with ion density  $Na^3 = 0.4$ . The inset shows a plot of the dimensionless charge density  $\sigma^* = \sigma a^2 / e$  as a function of the voltage  $V^*$  measured by the MC simulation at the temperature  $T^* = 0.042$ .

$$C_{\max}(T) = \frac{A}{(T^*)^{1/3}} C_H, \quad (10)$$

where  $A \approx 0.6$ . In other words, the effective thickness  $d^* = a(T^*)^{1/3} / 2A$ . At  $T^* \ll 1$ , we find that  $d^* \ll a$ . The corresponding voltage at which the capacitance plateaus is  $V_c^* \approx 11T^*$ .

Figure 2 shows the capacitance as a function of  $V^*$ , as measured by our MC simulation, at density  $Na^3 = 0.4$  and at two values of the temperature  $T^*$ . The inset shows the dimensionless charge density  $\sigma^* = \sigma a^2 / e$  of the electrode as a function of the voltage  $V^*$  for the temperature  $T^* = 0.042$ . The capacitance is determined by a numerical derivative of the  $\sigma$  vs  $V$  curve. Here,  $e/a^2$  is the maximal density for a square lattice of ions on the metal surface, so that  $\sigma^*$  can be interpreted as a filling factor of the first layer of ions. Note that the capacitance drops substantially even at low filling factor  $\sigma^*$ , so that the capacitance is already reduced by a factor of 2 at  $\sigma^* = 0.5$ . This suggests that for  $V^* \lesssim 2$  the decline in capacitance is not driven by the excluded volume effects emphasized in the theory of Ref. [7].

The conclusion  $C_{\max}(T) \propto (T^*)^{-1/3}$  can also be reached by an analytical description of the metal surface which is appropriate for small charge density  $\sigma$ , where the excess ions can no longer be described as a strongly correlated liquid. When the density of excess ions is small enough that  $\delta n a^2 \ll (T^*)^{2/3}$ , the total free energy  $F$  per unit area can instead be written using a virial expansion:

$$F \approx F_{id} + (\delta n)^2 k_B T B(T) - e \delta n V. \quad (11)$$

Here,  $F_{id} = \delta n k_B T \ln(\delta n a^2)$  is the free energy of a two-dimensional ideal gas,  $B(T)$  is the second virial coefficient, and  $-e \delta n V$  is the source work term.  $B(T)$  is calculated from the dipole-dipole interaction energy  $u_{dd}(r)$  between two ion-image dipoles as

$$B(T) = \frac{1}{2} \int_0^\infty (1 - e^{-u_{dd}(r)/k_B T}) 2\pi r dr \quad (12)$$

$$\approx 2.65 \left( \frac{e^2 a^2}{k_B T} \right)^{2/3}. \quad (13)$$

As before, we can use the equilibrium condition  $\partial F / \partial (e \delta n) = 0$  to define the voltage with respect to the density of excess ions  $\delta n$ , which gives

$$V^* \approx T^* [5.3 \delta n a^2 (T^*)^{-2/3} - \ln(1/\delta n a^2)]. \quad (14)$$

In the limit  $V^* \rightarrow 0$ , the two terms on the right-hand side of Eq. (14) become equal, and the corresponding capacitance  $d(e \delta n)/dV$  is  $C_{\max}(T) \approx AC_H/(T^*)^{1/3}$ . Hence, this approach arrives at the same conclusion as that of Eq. (10), although it gives a somewhat different estimate for the constant  $A \approx 1.2$ .

The prediction of Eq. (10) provides a good fit to the capacitance measured by our MC simulation over a range of ion densities, as shown in Fig. 1. The value of the coefficient  $A$  is found to be 0.6, 1.1, and 1.2 for  $Na^3 = 0.08, 0.4,$  and  $0.64$ , respectively, which is consistent with our earlier estimates. The dependence of the constant  $A$  on the ion density, which produces larger capacitance at larger  $Na^3$ , is perhaps an indication that the dipole interaction suggested in Eq. (5) is weaker at higher ion density. One possible explanation is that at high densities ion pairs in the vicinity of two excess ions can polarize in the direction of the electric field, thereby producing an effective dielectric constant between them. If such a dielectric constant  $\epsilon'$  is added to Eq. (5), then we find that  $A \approx 0.6(\epsilon')^{2/3}$ . The values of the constant  $A$  from above suggest that for bulk densities  $Na^3 = 0.08, 0.4,$  and  $0.64$ , the value of  $\epsilon'$  is 1.0, 2.4, and 2.9, respectively. These values are consistent with our interpretation that the effective dielectric constant should increase with ion density, driving the capacitance upward. This increase is also reflected in Fig. 2, where the capacitance at finite voltage is somewhat larger than predicted by Eq. (9), consistent with the increase in the constant  $A$ .

Based on our arguments from this section about the dependence of the capacitance on voltage and temperature, we can hypothesize a general scaling relationship  $C(V^*, T^*)$  which reproduces Eqs. (9) and (10):

$$\frac{C(V^*, T^*)}{C_H} = \frac{\beta_1}{[(\beta_2 T^*)^2 + (V^*)^2]^{1/6}}. \quad (15)$$

Here,  $\beta_1$  and  $\beta_2$  are numerical coefficients. Applying this fit to the curves shown in Fig. 2 gives a reasonably good fit with  $\beta_2 \approx 8$ , suggesting the capacitance plateaus at about  $V^* = 8T^*$ , as compared to the theoretically estimated value  $V_c^* = 11T^*$ .

#### IV. ELECTRODE MATERIAL: FROM PERFECT TO POOR METAL

So far we have assumed that the electrode is a perfect metal or, in other words, that the screening radius  $b$  of the metal is much smaller than the ion diameter  $a$ . This assumption is justified for RTILs with large ions and electrodes made from a good metal. Experiments on such systems have indeed reported large capacitance that declines with absolute

value of voltage [21] (the  $C$ - $V$  curve is ‘‘bell shaped’’). However, for smaller ions and for electrodes made from semimetals, such as graphite or glassy carbon, experimental values of  $C(V=0)$  are smaller and the  $C(V)$  curves are ‘‘camel shaped,’’ i.e., the capacitance grows parabolically near  $V=0$  [21–23].

In order to interpret this difference qualitatively, let us recall that in such poor metals the density of states at the Fermi level is relatively small, and the screening radius  $b$  of the metal may become comparable to  $a/2$ . As a result, the image potential changes. When  $b < a/2$  one can think that the electric field produced by ions at the metal surface is relatively weak and slowly varying. In such a case the screening charge of the metal is effectively situated at the distance  $b$  away from the metal surface, i.e., at  $z = -b$ . Therefore, the reflection plane for the image charge is at  $z = -b$ , so that an ion at distance  $z$  from the surface experiences a smaller attraction  $-e^2/4(z+b)$  to the surface, rather than the standard  $-e^2/4z$  for a perfect metal. At the distance of closest approach  $z = a/2$ , the ion-to-surface attraction energy becomes  $-e^2/2(a+2b)$ . This leads to a finite energy cost  $E_0$  for dissociating a bulk ion pair and bringing it to the metal surface, given by  $E_0 = e^2/[a^{-1} - (a+2b)^{-1}]^{-1}$ . Thus, a finite voltage is necessary to break pairs in the bulk and obtain free ions which can provide screening. This means that, for an electrode with finite screening radius  $b$ , the bell shaped  $C(V)$  curve splits into two peaks located at  $V = \pm E_0/e$ , thereby becoming camel shaped, in agreement with the above-mentioned data.

The capacitance  $C(V)$  at  $V > E_0/e$  can be estimated with the help of the theory in Sec. III leading up to Eq. (9). In this case, however, the voltage  $V$  in Eq. (9) should be replaced with  $V - E_0/e$  and the dipole arm  $a$  should be replaced with the longer arm  $a + 2b$ . These substitutions give

$$C(V) = 1.3 \left( \frac{e}{(a+2b)(V - E_0/e)} \right)^{1/3} \frac{a}{a+2b} C_H, \quad (16)$$

for  $V > E_0/e$ . Since the dipole-dipole repulsion is much stronger due to the longer dipole arm,  $C(V)$  is substantially smaller and reaches its geometrical limit  $C_H(b) = C_H a / (a + 2b)$  at a smaller voltage  $V - E_0/e = 5ae/4(a+2b)$  or  $V^* - E_0/(e^2/a) \approx 5.5/(1+2b/a)$ . Starting from this voltage the capacitance saturates at the level of  $C_H(b)$ .

Only at even larger voltage  $V^* - E_0/(e^2/a) \geq [5.5a^2 + 8\pi b(a+b)]/[a(a+2b)]$  do counterions comprise a full layer at the surface, after which the theory of multilayer arrangement of ions [7] becomes applicable. This same behavior for  $C(V)$  is expected in the case where a good metal is covered by a thin insulating layer, for example, its own oxide.

In order to verify this theory we repeated our MC calculations for  $T^* = 0.04$  and  $Na^3 = 0.5$  using a relatively large  $b = a/2$ , which is at the limit of applicability for linear screening by the electrode surface. For simplicity, we have also assumed that the metal ion lattice has the same dielectric constant as our RTIL. Results are shown in Fig. 3, plotted as a function of  $V^*$  and  $\sigma^*$ . As expected, the peak at  $V=0$  is split into a camel-like structure (we show only the positive half of

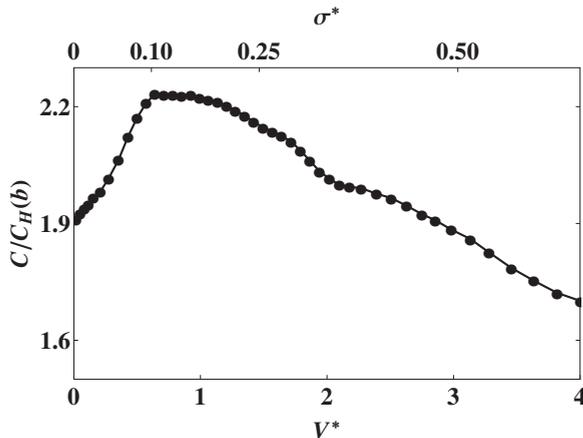


FIG. 3. The ratio of the capacitance of the metal-RTIL interface  $C$  to the geometrical capacitance  $C_H(b)$ , plotted as a function of dimensionless voltage  $V^*$  (bottom axis) and charge density  $\sigma^*$  (top axis) for a system with ion density  $Na^3=0.4$  and metal screening radius  $b=a/2$ . The capacitance is determined by a numerical derivative of the  $\sigma$  vs  $V$  data obtained from a MC simulation at temperature  $T^*=0.042$ .

the symmetric  $C$ - $V$  curve). The characteristic dimensionless voltage of the peak is  $V_p^* \approx 0.5$ , in agreement with the above estimate for  $E_0=e^2/2a$ . Note that the capacitance maximum occurs at  $\sigma^*=0.1$  and is apparently not related to excluded volume effects among counterions. As predicted by Eq. (16), the peak capacitance  $C(V_p^*)$  is approximately 2.5 times smaller than at  $b=0$  [recall that  $C_H(b)$  in Fig. 3 is twice smaller than  $C_H$  in Fig. 2].

## V. CONCLUSION

To summarize, this paper is concerned with Monte Carlo simulations of the restricted primitive model of a RTIL at a metal interface. Within this model, we obtain capacitance at zero voltage as large as  $3C_H$ . We also find that for a good metallic electrode at small voltage,  $C$  decreases with  $T$  as  $T^{-1/3}$ . When the temperature is fixed and is relatively small,  $C(V)$  decreases as  $1/V^{1/3}$  (the  $C$ - $V$  curve is bell shaped). On the other hand, when the electrode is made from a semimetal the  $C$ - $V$  curve is camel shaped, meaning that the capacitance

first grows with  $V$  and then goes through a maximum and decays as  $1/V^{1/3}$ . We interpret these results with the help of a semiquantitative analytical theory based on the weak repulsion between ion-image dipoles. Our conclusions are in qualitative agreement with experimental data.

While there are a number of effects ignored by the primitive restricted primitive model—asymmetry of anion and cation sizes, polarizability of ions, and disorder at the electrode surface, to name a few—our results may be quite relevant for real-world experiments on room-temperature ionic liquids. A typical ionic liquid has anions and cations with diameter  $a \sim 1$  nm, which apparently corresponds to a Helmholtz capacitance  $C_H \sim 2 \mu\text{F}/\text{cm}^2$  and a dimensionless temperature  $T^* \sim 0.02$ . This temperature is extremely low, and within the assumptions of the RPM would imply crystallization of ions in the bulk. However, in real RTILs the ions are polarizable, which means that the bulk of the RTIL has a dielectric constant  $\epsilon > 1$  that reduces the magnitude of interactions at long distances; typically  $\epsilon \sim 3$ . Thus,  $T^*$  should generally be replaced with  $\epsilon T^* \sim 0.06$  and  $C_H$  with  $\epsilon C_H \sim 6 \mu\text{F}/\text{cm}^2$ . In this sense, our result that in the RPM the capacitance can be as large as  $3C_H$  should be taken as an indication that polarizable RTILs can have  $C \sim 3\epsilon C_H = 18 \mu\text{F}/\text{cm}^2$ , a value that is in agreement with typical capacitance measurements on RTILs [21–23]. The typical electrochemical stability window of about 6 V corresponds to  $\epsilon|V^*| \lesssim 12$ , which is well within the range of our predictions [24].

Finally, we note that if both ionic species have the same polarizability, then our basic description of the interface remains valid. Polarizability of ions modifies both the attraction energy between ions and the attraction energy between an ion and its image. However, the attraction energy of a pair of oppositely charged polarizable ions in the bulk is still equal to the sum of the attraction energies of the two ions to the metal surface, so that at zero voltage the metal surface is highly populated by dissociated ions. At small finite voltage, excess ions seek to maximize their distance from each other, and the resulting correlations allow  $C > C_H$  in the way described by Sec. III.

## ACKNOWLEDGMENTS

We are grateful to D. Boda, M. M. Fogler, Y. Levin, P. A. Madden, and M. B. Partenskii for helpful discussions.

- 
- [1] M. Galiński, A. Lewandowski, and I. Stępiak, *Electrochim. Acta* **51**, 5567 (2006).
  - [2] J. O'M. Bockris, A. K. N. Reddy, and M. Gamboa-Aldeco, *Modern Electrochemistry 2A* (Kluwer Academic, New York, 2000), Chap. 6.
  - [3] H. L. F. von Helmholtz, *Ann. Phys. (Leipzig)* **165**, 353 (1853); *Proc. IEEE* **92**, 868 (2004).
  - [4] G. Gouy, *J. Phys. Theor. Appl.* **9**, 457 (1910).
  - [5] D. L. Chapman, *Philos. Mag.* **25**, 475 (1913).
  - [6] O. Stern, *Z. Elektrochem.* **30**, 508 (1924).
  - [7] A. A. Kornyshev, *J. Phys. Chem. B* **111**, 5545 (2007).
  - [8] D. Boda, D. Henderson, K.-Y. Chan, and D. T. Wasan, *Chem. Phys. Lett.* **308**, 473 (1999).
  - [9] D. Boda, D. Henderson, and K.-Y. Chan, *J. Chem. Phys.* **110**, 5346 (1999).
  - [10] M. V. Fedorov and A. A. Kornyshev, *J. Phys. Chem. B* **112**, 11868 (2008).
  - [11] M. B. Partenskii and P. C. Jordan, *J. Chem. Phys.* **99**, 2992 (1993); *Phys. Rev. E* **77**, 061117 (2008).
  - [12] S. Lamperski, C. W. Outhwaite, and L. B. Bhuiyan, *J. Phys. Chem. B* **113**, 8925 (2009).
  - [13] D. Henderson, S. Lamperski, C. W. Outhwaite, and L. B.

- Bhuiyan, *Collect. Czech. Chem. Commun.* **75**, 303 (2010).
- [14] M. S. Loth, B. Skinner, and B. I. Shklovskii, *Phys. Rev. E* **82**, 016107 (2010).
- [15] M. Alawneh, D. Henderson, C. W. Outhwaite, and L. B. Bhuiyan, *Mol. Simul.* **34**, 501 (2008).
- [16] M. Pounds, S. Tazi, M. Salanne, and P. A. Madden, *J. Phys.: Condens. Matter* **21**, 424109 (2009).
- [17] Y. Levin and M. E. Fisher, *Physica A* **225**, 164 (1996); B. Smit, K. Esselink, and D. Frenkel, *Mol. Phys.* **87**, 159 (1996).
- [18] This statement is correct even in a relatively dense liquid, where a significant fraction of ion pairs in the bulk form larger neutral clusters, and ions sticking to the metal may be decorated by one or more neutral pairs. Let us imagine a bulk cluster made of  $2m$  ions, where  $m$  is an odd number—for example,  $m=3$ . If the cluster is sufficiently symmetric, then it can be dissociated into two smaller clusters, one positive and one negative, which have an equal number  $m$  of ions and which differ only by the inversion of the charge of each ion. When these two charged clusters stick to their images in the metal surface, they also recover the energy spent on their dissociation. Thus, we are dealing with a statistical physics problem of very high degeneracy, which may have a beautiful exact solution. (Less symmetric clusters may have a small contribution to the partition function of the system.) In this paper we use the term “excess ions” to refer to all charged objects at the surface, regardless of whether they are decorated by neutral pairs.
- [19] J. Topping, *Proc. R. Soc. London, Ser. A* **114**, 67 (1927).
- [20] In principle, the correlations among excess ions on the metal surface can be identified from MC data. This process is made difficult, however, by the large number of neutral pairs and larger neutral clusters present on the metal surface at small voltages. A more exhaustive MC investigation of the surface correlations will be the subject of future work.
- [21] Md. M. Islam, M. T. Alam, and T. Ohsaka, *J. Phys. Chem. C* **112**, 16568 (2008).
- [22] Md. M. Islam, M. T. Alam, T. Okajima, and T. Ohsaka, *J. Phys. Chem. C* **113**, 3386 (2009).
- [23] V. Lockett, R. Sedev, J. Ralston, M. Horne, and T. Rodopoulos, *J. Phys. Chem. C* **112**, 7486 (2008).
- [24] M. Armand, F. Endres, D. R. MacFarlane, H. Ohno, and B. Scrosati, *Nature Mater.* **8**, 621 (2009).