

**Electrostatic correlations in electrolytes:  
Contribution of screening ion interactions to the  
excess chemical potential**

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## ABSTRACT

A new theory for the electrostatic component of the chemical potential for homogeneous electrolytes modeled with the primitive model is developed. This Mean Countershell Approximation (MCSA) is an analytic theory derived by including the interactions between the ions' screening clouds. At molar concentrations, these contribute substantially to the excess chemical potential but are absent in classical Debye-Hückel and Mean Spherical Approximation (MSA) theories. Simulations show MCSA is highly accurate, including at the low dielectric constants of ionic liquids. While sharing a mathematical framework with MSA, MCSA has simpler formulas and is qualitatively more accurate when there is ion size asymmetry.

## INTRODUCTION

A number of technologies are based on electrolytes (e.g., supercapacitors,<sup>1</sup> energy conversion mechanisms,<sup>2,3</sup> analytic tools<sup>4</sup>). Moreover, today's fabrication techniques produce such devices with new surface properties<sup>5</sup> and nanometer length scales<sup>6</sup> where ion correlations dominate and create new device functionalities.<sup>7,8</sup>

Two important types of ion correlations are due to excluded volume and electrostatic screening. The former correlations are due to ions having finite size so they cannot occupy the same space. The physics of this is generally understood, and theories describe it well.<sup>9-11</sup> The physics of the latter correlations, due to ions rearranging around each other to most optimally screen the individual ions' charges, is less well understood. These screening correlations produce counterintuitive phenomena like charge inversion, where the sign of the electrostatic potential can change,<sup>12-14</sup> resulting in ionic current changing sign also<sup>15,16</sup> or reversing the flow of electrophoretically-driven fluids.<sup>7,17,18</sup>

While simulations capture these phenomena,<sup>12,18-22</sup> elucidating the physics behind the ionic correlations requires a physical theory, preferably one with explicit analytic formulas. However, even for the simplest systems with excluded volume and screening correlations, creating such theories is challenging. Take, for example, the primitive model of electrolytes, in which ions are charged hard spheres in a dielectric medium. Although simple in concept, even for a homogeneous bulk system where ion concentrations are uniform, there are few analytic theories for this model that accurately describe the excess chemical potential due to screening correlations.

Integral equation theories describe the homogeneous primitive model well,<sup>23</sup> but usually require numerical solutions of the Ornstein-Zernike (OZ) equation. Exceptions include the Mean Spherical Approximation (MSA)<sup>24-32</sup> and the generalized MSA (GMSA),<sup>33-36</sup> which are analytic solutions of the OZ equation, specifically for the direct and total correlation functions. Both still require numerical solutions to algebraic equations, with the GMSA having 13 unknowns<sup>36</sup> while the MSA has only one. Therefore, despite its thermodynamic inconsistencies,<sup>33-35</sup> the MSA is more commonly used, and its simple formulas do capture much of the underlying physics.

The MSA has been used to study electrolytes in various systems<sup>37-39</sup> and is the basis for many theories of inhomogeneous systems.<sup>40-45</sup> Those inhomogeneous theories have, in turn, been used to describe (and predict) experimental results in systems where ion correlations play a dominant role, like biological ion channels<sup>46-49</sup> and nanofluidic channels.<sup>50,51</sup> Their real-world success comes despite the fact that the primitive model is an oversimplification of a real electrolyte and that the MSA describes that model only approximately.

Thus, a simple accurate analytic theory for the homogeneous primitive model is highly desirable. This is not only true for application modeling, but also for basic physics: without understanding the physics of a relatively simple system like the primitive model, one cannot understand more complex and realistic models of electrolytes.

Here, we present such a theory, which we call the Mean Countershell Approximation (MCSA). The derivation is based in large part on Blum and Rosenfeld's reexamination of the underlying assumptions of MSA.<sup>52</sup> They found that the MSA can be obtained (to leading order) using three physical assumptions. The MCSA is derived by adding the interactions between the ions' screening clouds to Blum and Rosenfeld's three pillars. In the end, the MCSA adds a simple term to the MSA's excess chemical potential, while at the same time simplifying the MSA equations in general. We show that MCSA is very accurate compared to simulations and a qualitative improvement over the MSA with lower computational cost.

## **THEORY**

### ***Review of MSA***

The MSA was derived by assuming a closure relationship with which the OZ equation can be solved exactly.<sup>24-26</sup> If the ions of species  $i$  have density  $\rho_i$ , diameter  $\sigma_i$ , radius  $R_i$ , and valence

$z_i$  and are immersed in a fluid with relative permittivity (dielectric constant)  $\varepsilon$ , then that closure leads to a Helmholtz free energy density of the form  $A = A^{\text{HS}} + A^{\text{MSA}}$ .  $A^{\text{HS}}$  is the Helmholtz free energy for a fluid of uncharged hard spheres with Percus-Yevick equation of state.<sup>9,11,23,53</sup>

Here, we briefly summarize the MSA equations related to  $A^{\text{MSA}}$  (reviewed in Ref. <sup>39</sup>). This screening contribution splits into two terms:  $A^{\text{MSA}} = E^{\text{MSA}} - TS^{\text{MSA}}$ . The screening excess electrostatic energy density is

$$\beta E^{\text{MSA}} = -\frac{\lambda_B}{2} \sum_i \frac{z_i^2 \rho_i}{b_i} - \frac{\lambda_B}{2} \eta \sum_i \frac{z_i \rho_i \sigma_i}{b_i \Gamma} \quad (1)$$

where  $\lambda_B = \beta e_0^2 / 4\pi\varepsilon\varepsilon_0$  is the Bjerrum length,  $e_0$  the fundamental charge,  $\varepsilon_0$  the permittivity of free space,  $k$  the Boltzmann constant,  $T$  the temperature,  $\beta = 1/kT$ , and

$$b_i \equiv R_i + \frac{1}{2\Gamma} \quad (2)$$

the capacitance radius. As described later, the quantity

$$\eta = \frac{\frac{\pi}{2} \sum_i \frac{z_i \rho_i \sigma_i}{\Gamma \sigma_i + 1}}{\frac{\pi}{2} \sum_i \frac{\rho_i \sigma_i^3}{\Gamma \sigma_i + 1} + 1 - \frac{\pi}{6} \sum_i \rho_i \sigma_i^3} \quad (3)$$

contributes only when there is ion size asymmetry. The entropy's screening component is

$$S^{\text{MSA}} = -\frac{k}{3\pi} \Gamma^3. \quad (4)$$

The quantity  $\Gamma$  is a reciprocal length where  $(2\Gamma)^{-1}$  is the MSA's screening length.  $\Gamma$  is defined by the variational principle  $\partial A^{\text{MSA}} / \partial \Gamma = 0$ , which gives an implicit formula for  $\Gamma$ :

$$\Gamma^2 = \pi \lambda_B \sum_i \rho_i \left( \frac{z_i - \eta \sigma_i^2}{1 + \Gamma \sigma_i} \right)^2. \quad (5)$$

Intuitively,  $(2\Gamma)^{-1}$  is a generalization of the familiar Debye screening length  $\kappa^{-1}$  that includes ion sizes; in the limit of point-sized ions,  $(2\Gamma)^{-1} \rightarrow \kappa^{-1}$ .

With this, the screening component of the excess chemical potential is  $\mu_i^{\text{MSA}} \equiv dA^{\text{MSA}} / d\rho_i = \partial A^{\text{MSA}} / \partial \rho_i + \partial A^{\text{MSA}} / \partial \Gamma \cdot \partial \Gamma / \partial \rho_i = \partial E^{\text{MSA}} / \partial \rho_i$  (see Table S1 in the Supplementary Material for formula). The latter equality uses that  $\partial A^{\text{MSA}} / \partial \Gamma = 0$ . The pressure is

$$\begin{aligned}\beta P^{\text{MSA}} &\equiv \sum_i \frac{d\beta A^{\text{MSA}}}{d\rho_i} \rho_i - \beta A^{\text{MSA}} \\ &= -\frac{\Gamma^3}{3\pi} - \frac{2\lambda_B \eta^2}{\pi}.\end{aligned}\tag{6}$$

For the special case when all ions have the same size (called the restricted primitive model),  $\eta = 0$  because the numerator in Eq. (3) is 0 from charge neutrality when  $\sigma_i = \sigma$  for all  $i$ . However, even when ions do not all have the same size,  $\eta\sigma_i^2$  is small and  $\eta$  terms produce only small corrections to the leading order (i.e.,  $\eta = 0$ ) for  $E^{\text{MSA}}$ ,  $\Gamma$ ,  $\mu_i^{\text{MSA}}$ , and  $P^{\text{MSA}}$ .<sup>39,52</sup>

## Derivation of MCSA

Here, we derive the screening component of the excess chemical potentials not by using a new closure for the OZ equation, but by using several properties of MSA's leading order ( $\eta = 0$ ) internal energy and entropy that were found after the MSA's original derivation:

1. As described by Wei and Blum,<sup>54</sup> the form of the first term in  $E^{\text{MSA}}$  in Eq. (1) is the same as the internal energy of Debye-Hückel theory, but for a capacitance radius  $b_i$  with  $\kappa^{-1}$  instead of  $(2\Gamma)^{-1}$  in Eq. (2).<sup>55</sup> Therefore, a term of this form can be derived generally with the same Guntelberg charging process<sup>56</sup> used to derive Debye-Hückel theory in textbooks.<sup>57-60</sup> We call this the Debye-Hückel-Guntelberg term (with  $\Gamma$  as yet unspecified):

$$\beta E^{\text{DHG}} = -\frac{\lambda_B}{2} \sum_i \frac{z_i^2 \rho_i}{R_i + (2\Gamma)^{-1}}.\tag{7}$$

2. As described by Blum and Rosenfeld,<sup>52</sup> the requirement that  $\partial A / \partial \Gamma = 0$  defines the screening length in a way that minimizes the Helmholtz free energy.
3. Blum and Rosenfeld<sup>52</sup> also showed that the entropy in Eq. (4) can be derived using a general argument that follows from the previous two ideas. Specifically, one assumes: 1)  $S$  is solely a function of  $\Gamma$ ; 2)  $E$  has the Debye-Hückel-Guntelberg form in Eq. (7); 3)  $A$  is minimized by  $\Gamma$ . A dimensionality argument shows that only a term proportional to  $\Gamma^3$  has the correct units, and enforcing the known low-density Debye-Hückel limit gives Eq. (4).<sup>52,61</sup> We will also define entropy this way.

4. For the restricted primitive model, Blum and Rosenfeld<sup>52</sup> showed that the MSA's second-order direct correlation function<sup>62</sup>  $c_{ij}^{(2)}(r)$ , when  $r < R_i + R_j$ , is  $-\beta\psi_{ij}^{ss}(r)$ . Here,  $\psi_{ij}^{ss}(r)$  is the interaction potential of two infinitely-thin spherical shells with surface charge density  $z_k e_0 / 4\pi b_k^2$  and radius  $b_k$  ( $k = i, j$ ), separated by center-to-center separation  $r$ .

The arguments in the first three points are quite general and sufficient to recover the leading order ( $\eta = 0$ ) MSA.<sup>52</sup> Here, we combine these three pillars with a fourth one. Specifically, we assume that the ion screening cloud around a central ion with charge  $z_i e_0$  is a shell of charge with radius  $b_i$ , like that described by the  $c_{ij}^{(2)}(r)$  function. We call this the ‘‘countershell’’ because we give the shell total charge  $-z_i e_0$ .

We combine these four pillars to define the MCSA's Helmholtz free energy density  $A^{\text{MCSA}} = E^{\text{MCSA}} - TS^{\text{MCSA}}$  and screening parameter  $\Gamma$  (which differs slightly from the MSA  $\Gamma$ ). As detailed below, the internal energy density  $E^{\text{MCSA}} = E^{\text{DHG}} + E^{\text{ss}}$  will have a Debye-Hückel-Güntelberg term  $E^{\text{DHG}}$  (Eq. (7)) and a countershell-countershell interaction term  $E^{\text{ss}}$ . This latter term is a new additional internal energy term in the MCSA that is absent in Debye-Hückel and MSA. The entropy  $S^{\text{MCSA}}$  will be given by Eq. (4) and  $\Gamma$  defined by  $\partial A / \partial \Gamma = 0$ . Thus, all terms except  $E^{\text{ss}}$  come from the first three points described above.

To derive  $E^{\text{DHG}}$ , we note that the electrostatic potential inside the countershell is constant with value  $-z_i e_0 / 4\pi\epsilon\epsilon_0 b_i$ .<sup>63</sup> The work to charge up the central ion seated inside the countershell via the Güntelberg charging process is  $-z_i^2 e_0^2 / 8\pi\epsilon\epsilon_0 b_i$ .<sup>56-60</sup> This is obtained by giving the central ion charge  $z_i e_0 \xi$  and increasing it from  $\xi = 0$  to  $\xi = 1$  via integration. Charging  $N_i$  ions of species  $i$  with this process gives the energy density in Eq. (7) since  $\rho_i = N_i / V$  where  $V$  is the volume of the system. As in Debye-Hückel and MSA theories, this term is the ion-counterion contribution to the internal energy density.

Next, we add the fourth pillar by taking the idea of charged countershells one step further by including their interactions with each other. For the new  $E^{\text{ss}}$  term, we include the shell-shell interactions in the mean-field approximation. This is motivated by the fact that ion-ion interactions are often included in a mean-field way. For example, Poisson-Boltzmann theory (upon which the

Debye-Hückel theory is based) includes the ion-ion interactions in an inhomogeneous system via the mean-field expression (i.e., approximating radial distribution functions by 1)

$$\frac{1}{2} \sum_{i,j} \int_{\square^3} \int_{\square^3} \rho_i(\mathbf{x}) \rho_j(\mathbf{x}') \psi_{ij}^C(|\mathbf{x} - \mathbf{x}'|) d\mathbf{x} d\mathbf{x}'. \quad (8)$$

Here,  $\beta\psi_{ij}^C(r) = \lambda_B z_i z_j r^{-1}$  is the Coulomb interaction potential of two point charges separated by distance  $r = |\mathbf{x} - \mathbf{x}'|$ . In a homogeneous system with charge neutrality, however, this energy is 0.

We include the interactions of two countershells in a similar way for our system with constant densities (superscripted “ss” for shell-shell):

$$E^{ss} = \frac{1}{2} \sum_{i,j} \rho_i \rho_j \int_{\square^3} \int_{\square^3} \psi_{ij}^{ss}(|\mathbf{x} - \mathbf{x}'|) d\mathbf{x} d\mathbf{x}'. \quad (9)$$

Here, again  $\psi_{ij}^{ss}(r)$  is the interaction potential of two charged shells described above.  $\psi_{ij}^{ss}(r)$  can be written compactly in terms of the Coulomb potential and a function of the shells’ center-to-center separation  $r$ :<sup>64</sup>

$$\beta\psi_{ij}^{ss}(r) = \beta\psi_{ij}^C(r) + \begin{cases} 0 & r > b_{ij} \\ -\lambda_B \frac{z_i z_j}{4b_i b_j r} (r - b_{ij})^2 & |\Delta b_{ij}| \leq r \leq b_{ij} \\ \lambda_B z_i z_j \left( \max(b_i, b_j)^{-1} - r^{-1} \right) & 0 < r < |\Delta b_{ij}| \end{cases} \quad (10)$$

where  $b_{ij} = b_i + b_j$  and  $\Delta b_{ij} = b_i - b_j$ . (The three conditionals, from top to bottom, define the shells’ interaction when the shells are far apart and their interaction is Coulombic, when the shells overlap, and when the small shell is completely inside the large shell.)

Performing the integration in Eq. (9) gives<sup>64</sup>

$$\beta E^{ss} = -\frac{\pi}{3} \lambda_B \sum_{i,j} z_i z_j \rho_i \rho_j (b_i^2 + b_j^2). \quad (11)$$

Interestingly,

$$\begin{aligned} \beta E^{ss} &= -\frac{\pi}{3} \lambda_B \sum_i z_i \rho_i \sum_j z_j \rho_j (b_i^2 + b_j^2) \\ &= -\frac{2\pi}{3} \lambda_B \left( \sum_i z_i \rho_i \right) \left( \sum_j z_j \rho_j b_j^2 \right) \\ &= 0. \end{aligned} \quad (12)$$

because charge neutrality makes the first factor 0. However, its derivative is generally nonzero:

$$\frac{\partial \beta E^{\text{ss}}}{\partial \rho_i} = -\frac{2\pi}{3} \lambda_B z_i \sum_j z_j \rho_j b_j^2. \quad (13)$$

Thus,  $E^{\text{ss}}$  does not contribute to the internal energy because the system is charge neutral, but it contributes to the chemical potential because this counts ions added in a non-charge-neutral way.

We now have all the components to define the MCSA theory for the screening component:

$$A^{\text{MCSA}} = E^{\text{MCSA}} - TS^{\text{MCSA}} \quad (14)$$

$$\beta E^{\text{MCSA}} = -\frac{\lambda_B}{2} \sum_i \frac{z_i^2 \rho_i}{b_i} + \beta E^{\text{ss}} \quad (15)$$

$$S^{\text{MCSA}} = -\frac{k}{3\pi} \Gamma^3 \quad (16)$$

and  $b_i = R_i + (2\Gamma)^{-1}$ . Since  $\partial E^{\text{ss}} / \partial \Gamma = 0$  and by requiring  $\partial A^{\text{MCSA}} / \partial \Gamma = 0$ , the MCSA screening parameter  $\Gamma$  is defined implicitly:

$$\Gamma^2 = \pi \lambda_B \sum_i \frac{z_i^2 \rho_i}{(1 + \Gamma \sigma_i)^2}. \quad (17)$$

(Note that this equation has exactly one positive root for  $\Gamma$ .) The screening component of the excess chemical potential then is

$$\beta \mu_i^{\text{MCSA}} = -\frac{\lambda_B}{2} \frac{z_i^2}{b_i} - z_i \beta \mu^{\text{ss}} \quad (18)$$

where<sup>64</sup>

$$\beta \mu^{\text{ss}} = \frac{2\pi}{3} \lambda_B \sum_j z_j \rho_j b_j^2 \quad (19)$$

The pressure is

$$\beta P^{\text{MCSA}} = -\frac{\Gamma^3}{3\pi}. \quad (20)$$

In Eq. (15) we formally include  $E^{\text{ss}}$  even though  $E^{\text{ss}} = 0$  as a reminder of where the new  $\mu^{\text{ss}}$  term in Eq. (18) originated.

# RESULTS AND DISCUSSION

## *Properties of MCSA*

Comparing the MCSA thermodynamic quantities to the corresponding MSA terms (recapitulated in Table S1), we see the MCSA equations are the MSA equations with  $\eta$  formally set to 0 (and thus a good measure simpler). The sole exception is the new  $\mu^{\text{ss}}$  term in  $\mu_i^{\text{MCSA}}$ . Thus, except for the excess chemical potential, the formulas for the internal energy, entropy, screening parameter, and pressure are identical to the MSA formulas after formally setting  $\eta = 0$ . (Note that the output of the MCSA and MSA are *not* identical since usually  $\eta \neq 0$ . We merely point out the similarity in the formulas.) As we will see later, however, this single adjustment to the excess chemical potential significantly increases its accuracy.

The MSA is known to satisfy various thermodynamic relations and have known limiting values. Here, we list some of these and show that the MCSA also satisfies these fundamental relations but sometimes has different asymptotic values:

1. For both the MSA and MCSA, the Gibbs free energy density's screening component is given by  $G \equiv A + P = \sum_i \mu_i \rho_i$ , where the respective theories' values are used (Table S1).
2. From this form of  $G$  it follows that the Gibbs-Duhem equation  $\sum_i \rho_i \cdot d\mu_i = -S \cdot dT + dp$  is satisfied by the MCSA.<sup>55</sup> The MSA is already known to satisfy it.
3. The MCSA preserves the MSA's correct low-density Debye-Hückel limits of the Helmholtz energy and excess chemical potential as  $\rho_i \rightarrow 0$ . In that limit,  $\eta \rightarrow 0$  in the MSA, while  $\mu^{\text{ss}} \rightarrow 0$  in the MCSA (Eq. (18)), so  $E^{\text{MCSA}} \rightarrow E^{\text{MSA}}$  and  $\mu_i^{\text{MCSA}} \rightarrow \mu_i^{\text{MSA}}$ .
4. In the low temperature limit ( $T \rightarrow 0$ ), also called the asymptotic high coupling limit where  $\Gamma \rightarrow \infty$ , both  $E^{\text{MSA}}$  and  $E^{\text{MCSA}}$  approach the Onsager limit, an exact lower bound for the internal energy of a charged, hard sphere system.<sup>65,66</sup>
5. In the high temperature limit ( $T \rightarrow \infty$ ),  $\Gamma \rightarrow 0$  and  $E^{\text{MCSA}} \rightarrow 0$  while  $E^{\text{MSA}} \rightarrow -\left(e_0^2 / 4\pi\epsilon\epsilon_0\right)\eta(\Gamma = 0)\sum_i z_i \rho_i \sigma_i$ .

6. In the MCSA, the electrostatic energy to insert an *uncharged* particle into a *charged* system is 0. This is in contrast to the MSA where  $\mu_i^{\text{MSA}} \neq 0$  for a species with  $z_i = 0$  when  $\eta \neq 0$ , although this is generally very small (on the order of  $\sim 0.01 kT$ ).

Besides these thermodynamic limits and relations, other similarities and differences between the two theories include that the MSA and MCSA are identical in the restricted primitive model. This is because then  $\eta = 0$  in the MSA and  $\mu^{\text{ss}} = 0$  in the MCSA by charge neutrality. It follows from this and the concentration dependence of  $\mu^{\text{ss}}$  that differences between the MSA and MCSA are biggest with large ion size asymmetries and high concentrations. Moreover, these differences are amplified by large valences, given the valence dependence of the second term in  $\mu_i^{\text{MCSA}}$  (Eq. (18)). This point is significant for the very asymmetric electrolytes used in some experiments<sup>15,16</sup> (e.g., aqueous Cobalt(III) sepulchrate trichloride, whose trivalent cation is  $\sim 0.9$  nm in diameter<sup>67,68</sup> and monovalent anion  $\sim 0.36$  nm in diameter<sup>69</sup>).

Lastly, we note that the value for the MCSA  $\Gamma$  is different from, but very close to, the MSA  $\Gamma$  because of the relatively small contribution made by  $\eta$  in the MSA (Table S1). In all the cases we studied (detailed below), the MCSA  $\Gamma$  differed from the MSA  $\Gamma$  by  $< 0.6\%$ . Therefore, the MCSA pressure also differed little ( $< 2.7\%$ ).

## **Comparisons to simulations**

To assess the MCSA, we computed the screening component of the excess chemical potential with Grand Canonical Monte Carlo (GCMC) simulations. Each ion species' chemical potential  $\mu_i$  is the sum of ideal gas, hard-sphere, and screening components. In the simulations, values for  $\mu_i$  are iterated until the desired ion concentrations  $\rho_i$  are achieved,<sup>70</sup> defining both  $\mu_i$  and the ideal gas component. Thus, once the hard-sphere component is determined, so is the screening component (by subtraction). The hard-sphere component is computed from the acceptance/rejection ratio of attempts to inset *uncharged* hard sphere “ions,” as previously described.<sup>71</sup> High packing fractions for large ions limited the maximum concentrations we could simulate; higher concentrations required unreasonably large simulation boxes. More details are provided in the Supplementary Material.

In our calculations of both the MCSA and MSA, we updated  $A^{\text{HS}}$  to the more accurate one based on the Boublik-Mansoori-Carnahan-Starling-Leland equation of state.<sup>72,73</sup>

In the Supplementary Material, we provide an overview of the accuracy of the MCSA. Specifically, we show how the MCSA screening excess chemical potential for 24 different electrolytes compares to GCMC simulations and MSA as cation concentration, diameter, and valence vary. Here in the main text, we highlight specific significant aspects.

Fig. 1 shows the accuracy of the MCSA for large ion size asymmetry and high valences. In Fig. 1(a), the MCSA correctly predicts the trivalent cation screening contribution (solid black line versus black symbols) and is significantly better than MSA (dashed black line). MCSA also correctly predicts the upturn for the anion (solid red line versus red symbols) that is missed by the MSA (dashed red line).

The results in Fig. 1(b) for a 2:2 electrolyte are significant in a different way. At first glance it may appear that the MSA and the MCSA are comparably correct. However, a closer look reveals that the MSA's anion result (dashed red line) follows the GCMC and MCSA cation results (black symbols and solid black line, respectively). Conversely, the MSA's cation result (dashed black line) incorrectly follows that the others' anion results (red symbols and solid red line). Thus, for this case, the MCSA corrects a qualitatively incorrect trend of the MSA. For this 2:2 electrolyte,

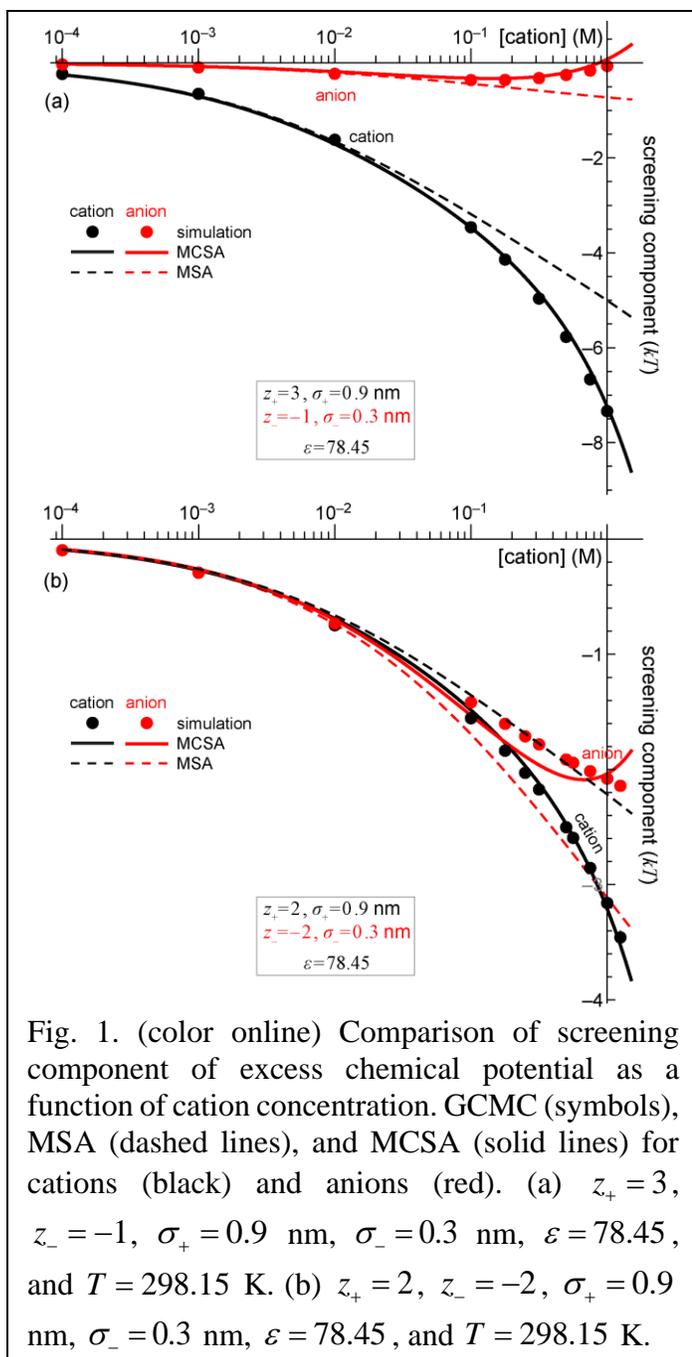


Fig. 1. (color online) Comparison of screening component of excess chemical potential as a function of cation concentration. GCMC (symbols), MSA (dashed lines), and MCSA (solid lines) for cations (black) and anions (red). (a)  $z_+ = 3$ ,  $z_- = -1$ ,  $\sigma_+ = 0.9$  nm,  $\sigma_- = 0.3$  nm,  $\epsilon = 78.45$ , and  $T = 298.15$  K. (b)  $z_+ = 2$ ,  $z_- = -2$ ,  $\sigma_+ = 0.9$  nm,  $\sigma_- = 0.3$  nm,  $\epsilon = 78.45$ , and  $T = 298.15$  K.

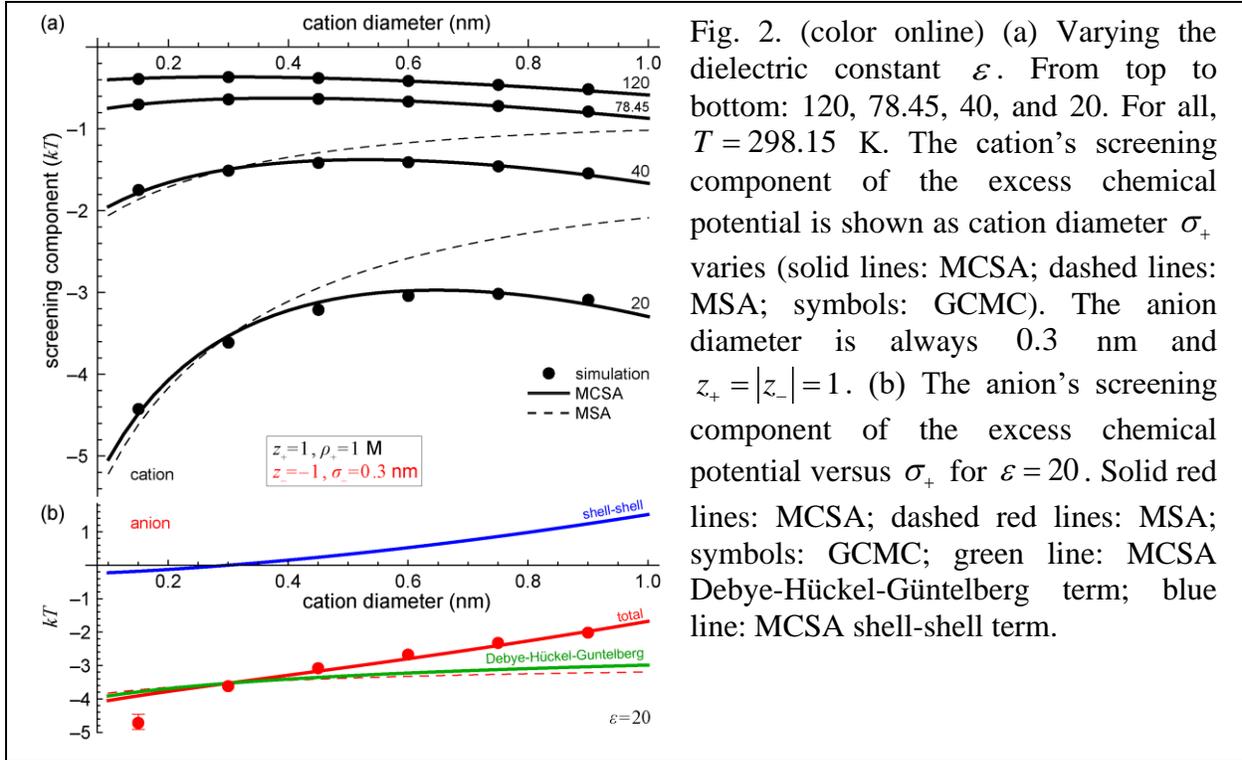


Fig. 2. (color online) (a) Varying the dielectric constant  $\epsilon$ . From top to bottom: 120, 78.45, 40, and 20. For all,  $T = 298.15$  K. The cation's screening component of the excess chemical potential is shown as cation diameter  $\sigma_+$  varies (solid lines: MCSA; dashed lines: MSA; symbols: GCMC). The anion diameter is always 0.3 nm and  $z_+ = |z_-| = 1$ . (b) The anion's screening component of the excess chemical potential versus  $\sigma_+$  for  $\epsilon = 20$ . Solid red lines: MCSA; dashed red lines: MSA; symbols: GCMC; green line: MCSA Debye-Hückel-Güntelberg term; blue line: MCSA shell-shell term.

the MCSA predicts a minimum for the anion, like that in Fig. 1(b) (solid red line), which is not present in the GCMC simulation results. Since the GCMC simulations no longer produce reliable results above 1.25 M for this case due to high packing fractions, we are currently unable to determine whether the MCSA result is incorrect or if the minimum occurs at a higher concentration in the simulations (as they do for 1:1 electrolytes, as shown in the Supplementary Material).

The figures in the Supplementary Material place the comparisons in Fig. 1 into a broader context. Besides showing the onset of the nonmonotonicity of the anion curve, they also verify that the differences between the MSA and MCSA increase with cation size asymmetry and ion valences.

Fig. 2 confirms that the MCSA scales correctly with the system's dielectric constant. Not only are the screening excess chemical potentials quantitatively accurate, but Fig. 2(a) shows that the MCSA correctly predicts that the cation screening component has a maximum as cation diameter increases.

Fig. 2(b) focuses on the anion, and breaks out the Debye-Hückel-Güntelberg and shell-shell terms of Eq. (18) to highlight both the importance of the latter new contribution and that the two components can have opposite signs. The relatively large magnitude of the shell-shell term shown here is particularly relevant because room temperature ionic liquids have static dielectric

constants<sup>74,75</sup> of ~8–20 and because the dielectric constant of aqueous electrolytes varies with ion concentration.<sup>76</sup> In addition, a positive anion shell-shell term like the one in Fig. 2(b) (blue line) drives the increase in the anion screening component at high concentrations seen in Fig. 1 (solid red lines), creating the minimum as it works against the negative Debye-Hückel-Güntelberg term.

Taken as whole, Figs. 1 and 2 show that MCSA is systematically accurate over a very wide range of electrolyte parameters (from monovalent to trivalent, from micromolar to >1 M, from very small (0.15 nm diameter) to very large (0.9 nm), from low (20) to high (120) dielectric constant). The figures in the Supplementary Material further support the MCSA's accuracy.

### ***Physical insights and interpretation***

The physical interpretation of the MCSA shell-shell term is that the interactions of the two clouds of screening ions around two central ions contribute significantly to the energetics of an electrolyte. For ionic liquids, with their high concentration, ion size asymmetry, and low dielectric constant, these interactions' contributions are on par with the traditional Debye-Hückel-Güntelberg term (Fig. 2(b)). For aqueous electrolytes, the shell-shell interactions are also significant, as they produce a minimum in the screening component of the excess chemical potential with concentration (Fig. 1(a) and Supplementary Material) that, to our knowledge, has not been explained before.

While this work applies to the primitive model of electrolytes, the energetic contributions of counterion cloud interactions are likely to be important for more complex models of electrolytes as well. Moreover, the derivation technique we employed to define internal energy, entropy, and the screening length is potentially a new methodology to create theories for other models of electrolytes beyond the primitive model.

## **CONCLUSION**

Within the primitive model, the MCSA is an analytic theory that provides a very accurate excess chemical potential. Moreover, it is significantly more accurate than the commonly used MSA theory (which is more accurate than Debye-Hückel), especially for electrolytes with large ion size asymmetries. It does so using the MSA mathematical framework, but with simpler formulas for all components. However, the MCSA is only theory of free energy and the quantities

derived that. It does not, for example, output correlation functions, and other theories like GMSA<sup>33-</sup>  
<sup>36</sup> are needed for these.

## **SUPPLEMENTARY MATERIAL**

The Supplementary Material file contains comparisons of the MCSA theory to GCMC simulations for 24 different electrolytes, a table of MSA and MCSA formulas, and further details about the simulations.

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## **AUTHOR DECLARATIONS**

### ***Conflict of interest***

The authors have no conflicts to disclose.

## **DATA AVAILABILITY**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## REFERENCES

- <sup>1</sup>P. Simon and Y. Gogotsi, *Nature Nanotech.* **7**, 845 (2008).
- <sup>2</sup>F. H. J. van der Heyden, D. J. Bonthuis, D. Stein, C. Meyer, and C. Dekker, *Nano Lett.* **7**, 1022 (2007).
- <sup>3</sup>M. Janssen, A. Härtel, and R. van Roij, *Phys. Rev. Lett.* **113**, 268501 (2014).
- <sup>4</sup>J. M. Sustarich, B. D. Storey, and S. Pennathur, *Physics of Fluids* **22**, 112003 (2010).
- <sup>5</sup>S. Boden, P. Karam, A. Schmidt, and S. Pennathur, *Appl. Phys. Lett.* **110**, 181605 (2017).
- <sup>6</sup>C. Duan and A. Majumdar, *Nature Nanotech.* **5**, 848 (2010).
- <sup>7</sup>J. Loessberg-Zahl, K. G. H. Janssen, C. McCallum, D. Gillespie, and S. Pennathur, *Anal. Chem.* **88**, 6145 (2016).
- <sup>8</sup>D. Gillespie, *Nano Lett.* **12**, 1410 (2012).
- <sup>9</sup>M. S. Wertheim, *Phys. Rev. Lett.* **10**, 321 (1963).
- <sup>10</sup>Y. Rosenfeld, *Phys. Rev. Lett.* **63**, 980 (1989).
- <sup>11</sup>R. Roth, *J. Phys.: Condens. Matter* **22**, 063102 (2010).
- <sup>12</sup>G. M. Torrie and J. P. Valleau, *J. Chem. Phys.* **86**, 3251 (1982).
- <sup>13</sup>S. Y. Mashayak and N. R. Aluru, *J. Chem. Phys.* **148**, 214102 (2018).
- <sup>14</sup>A. Voukadinova and D. Gillespie, *J. Chem. Phys.* **150**, 154706 (2019).
- <sup>15</sup>F. H. J. van der Heyden, D. Stein, K. Besteman, S. G. Lemay, and C. Dekker, *Phys. Rev. Lett.* **96**, 224502 (2006).
- <sup>16</sup>Y. He, D. Gillespie, D. Boda, I. Vlassiuk, R. S. Eisenberg, and Z. S. Siwy, *J. Am. Chem. Soc.* **131**, 5194 (2009).
- <sup>17</sup>K.-H. Chou, C. McCallum, D. Gillespie, and S. Pennathur, *Nano Lett.* **18**, 1191 (2018).
- <sup>18</sup>R. Qiao and N. R. Aluru, *Phys. Rev. Lett.* **92**, 198301 (2004).
- <sup>19</sup>S. Lamperski and L. B. Bhuiyan, *J. Electroanal. Chem.* **540**, 79 (2003).
- <sup>20</sup>M. Valiskó, D. Boda, and D. Gillespie, *J. Phys. Chem. C* **111**, 15575 (2007).
- <sup>21</sup>G. M. Torrie and J. P. Valleau, *J. Chem. Phys.* **73**, 5807 (1980).
- <sup>22</sup>D. Boda, M. Valiskó, and D. Gillespie, *Entropy* **22**, 1259 (2020).
- <sup>23</sup>J. M. G. Barthel, H. Krienke, and W. Kunz, *Physical Chemistry of Electrolyte Solutions: Modern Aspects.* (Springer, New York, 1998).
- <sup>24</sup>L. Blum, *Mol. Phys.* **30**, 1529 (1975).
- <sup>25</sup>L. Blum and J. S. Høye, *J. Phys. Chem.* **81**, 1311 (1977).
- <sup>26</sup>L. Blum, *J. Stat. Phys.* **22**, 661 (1980).
- <sup>27</sup>D. Henderson and W. R. Smith, *J. Stat. Phys.* **19**, 191 (1978).
- <sup>28</sup>J. S. Høye and G. Stell, *J. Chem. Phys.* **67**, 439 (1977).
- <sup>29</sup>R. Triolo, J. R. Grigera, and L. Blum, *J. Phys. Chem.* **80**, 1858 (1976).
- <sup>30</sup>R. Triolo, L. Blum, and M. A. Floriano, *J. Chem. Phys.* **67**, 5956 (1977).
- <sup>31</sup>R. Triolo, L. Blum, and M. A. Floriano, *J. Phys. Chem.* **82**, 1368 (1978).
- <sup>32</sup>J. S. Høye and J.-P. Simonin, *Mol. Phys.*, e1969045 (2021).
- <sup>33</sup>J. S. Høye, J. L. Lebowitz, and G. Stell, *J. Chem. Phys.* **61**, 3253 (1974).
- <sup>34</sup>G. Stell and S. F. Sun, *J. Chem. Phys.* **63**, 5333 (1975).
- <sup>35</sup>J. S. Høye and G. Stell, *J. Chem. Phys.* **67**, 524 (1977).
- <sup>36</sup>M. C. Abramo, C. Caccamo, and G. Pizzimenti, *Il Nuovo Cimento B (1971-1996)* **66**, 187 (1981).
- <sup>37</sup>A. F. Khater, D. Henderson, L. Blum, and L. B. Bhuiyan, *J. Phys. Chem.* **88**, 3682 (1984).
- <sup>38</sup>J.-P. Simonin, L. Blum, and P. Turq, *J. Phys. Chem.* **100**, 7704 (1996).
- <sup>39</sup>W. Nonner, L. Catacuzzeno, and B. Eisenberg, *Biophys. J.* **79**, 1976 (2000).
- <sup>40</sup>Y. Rosenfeld, *J. Chem. Phys.* **98**, 8126 (1993).
- <sup>41</sup>E. Kierlik and M. L. Rosinberg, *Phys. Rev. A* **44**, 5025 (1991).
- <sup>42</sup>D. Gillespie, W. Nonner, and R. S. Eisenberg, *J. Phys.: Condens. Matter* **14**, 12129 (2002).
- <sup>43</sup>D. Gillespie, W. Nonner, and R. S. Eisenberg, *Phys. Rev. E* **68**, 031503 (2003).

- <sup>44</sup>R. Roth and D. Gillespie, *J. Phys.: Condens. Matter* **28**, 244006 (2016).
- <sup>45</sup>L. Mier-y-Teran, S. H. Suh, H. S. White, and H. T. Davis, *J. Chem. Phys.* **92**, 5087 (1990).
- <sup>46</sup>D. Gillespie, *Biophys. J.* **94**, 1169 (2008).
- <sup>47</sup>D. Gillespie and M. Fill, *Biophys. J.* **95**, 3706 (2008).
- <sup>48</sup>D. Gillespie, J. Giri, and M. Fill, *Biophys. J.* **97**, 2212 (2009).
- <sup>49</sup>D. Gillespie, L. Xu, and G. Meissner, *Biophys. J.* **107**, 2263 (2014).
- <sup>50</sup>D. Gillespie, A. S. Khair, J. P. Bardhan, and S. Pennathur, *J. Colloid Interface Sci.* **359**, 520 (2011).
- <sup>51</sup>J. Hoffmann and D. Gillespie, *Langmuir* **29**, 1303 (2013).
- <sup>52</sup>L. Blum and Y. Rosenfeld, *J. Stat. Phys.* **63**, 1177 (1991).
- <sup>53</sup>J. J. Salacuse and G. Stell, *J. Chem. Phys.* **77**, 3714 (1982).
- <sup>54</sup>D. Wei and L. Blum, *J. Phys. Chem.* **91**, 4342 (1987).
- <sup>55</sup>D. A. McQuarrie, *Statistical Mechanics*, 2 ed. (University Science Books, 2000).
- <sup>56</sup>E. Güntelberg, *Zeitschrift für Physikalische Chemie* **123U**, 199 (1926).
- <sup>57</sup>S. R. Berry, S. A. Rice, and J. Ross, *Physical Chemistry*, 2nd ed. (Oxford, New York, 2000).
- <sup>58</sup>J. O. Bockris and A. K. N. Reddy, *Modern Electrochemistry I: Ionics*, 2nd ed. ed. (Plenum Press, New York, 1998).
- <sup>59</sup>J. Newman and K. E. Thomas-Alyea, *Electrochemical Systems*, 3rd ed. ed. (Jon Wiley & Sons, Inc., Hoboken, New Jersey, 2004).
- <sup>60</sup>W. R. Fawcett, *Liquids, Solutions, and Interfaces: From Classical Macroscopic Descriptions to Modern Microscopic Details*. (Oxford University Press, New York, 2004).
- <sup>61</sup>B. B. Laird and A. D. J. Haymet, *J. Chem. Phys.* **100**, 3775 (1994).
- <sup>62</sup>K. Hiroike, *Mol. Phys.* **33**, 1195 (1977).
- <sup>63</sup>R. P. Feynman, R. B. Leighton, and M. Sands, *The Feynman Lectures on Physics*. (Addison-Wesley Publishing Co., New York, 1989).
- <sup>64</sup>J. Jiang and D. Gillespie, *J. Chem. Theory Comput.* **17**, 2409–2416 (2021).
- <sup>65</sup>L. Onsager, *J. Phys. Chem.* **43**, 189 (1939).
- <sup>66</sup>Y. Rosenfeld and L. Blum, *J. Chem. Phys.* **85**, 1556 (1986).
- <sup>67</sup>A. Bacchi, F. Ferranti, and G. Pelizzi, *Acta Crystallographica Section C* **49**, 1885 (1993).
- <sup>68</sup>J. M. Harrowfield, A. J. Herlt, A. M. Sargeson, and T. D. Donno, in *Inorg. Synth.* (1980), pp. 85.
- <sup>69</sup>R. D. Shannon and C. T. Prewitt, *Acta Crystallogr.* **B25**, 925 (1969).
- <sup>70</sup>A. Malasics and D. Boda, *J. Chem. Phys.* **132**, 244103 (2010).
- <sup>71</sup>D. Boda, J. Giri, D. Henderson, R. S. Eisenberg, and D. Gillespie, *J. Chem. Phys.* **134**, 055102 (2011).
- <sup>72</sup>T. Boublik, *J. Chem. Phys.* **53**, 471 (1970).
- <sup>73</sup>G. A. Mansoori, N. F. Carnahan, K. E. Starling, and T. W. Leland, *J. Chem. Phys.* **54**, 1523 (1971).
- <sup>74</sup>C. Wakai, A. Oleinikova, M. Ott, and H. Weingärtner, *J. Phys. Chem. B* **109**, 17028 (2005).
- <sup>75</sup>C. Daguinet, P. J. Dyson, I. Krossing, A. Oleinikova, J. Slattery, C. Wakai, and H. Weingärtner, *J. Phys. Chem. B* **110**, 12682 (2006).
- <sup>76</sup>J. Barthel, R. Buchner, and M. Münsterer, *Electrolyte Data Collection, Part 2: Dielectric Properties of Water and Aqueous Electrolyte Solutions, (Chemistry Data Series, Vol. XII, Part 2)*. (Dechema, Frankfurt/M., 1995).