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The mystery of anomalously long-ranged screening in concentrated ionic systems

1. **Ionic liquids behave as dilute electrolyte solutions**
   Authors: M. A. Gebbie, M. Valtiner, X. Banquy, E. T. Fox, W. A. Henderson, and J. N. Israelachvili
   Proc. Natl. Acad. Sci. U.S.A 110, 9674 (2013).
2. **The electrostatic screening length in concentrated electrolytes increases with concentration**
   Authors: A. M. Smith, A. A. Lee, and S. Perkin
   J. Phys. Chem. Lett. 7, 2157 (2016).
3. **Underscreening in concentrated electrolytes**
   Authors: A. A. Lee and C. S. Perez-Martinez and A. M. Smith and S. Perkin
   Faraday Discuss. 199, 239 (2017).

Recommended with a Commentary by Christian Holm (Institute for Computational Physics, University of Stuttgart, Germany) and Svyatoslav Kondrat (Institute for Computational Physics, University of Stuttgart, Germany, and the Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland)

It is textbook knowledge that electrostatic interactions between two ions of an electrolyte are exponentially screened. This screening, known as Debye screening, arises from a cloud of screening counter-ions surrounding each ion and can be formally obtained as the solution of the linearized Poisson-Boltzmann equation, also known as the Debye-Hückel equation. Applied to an electrolyte confined between two charged parallel plates separated by distance D, it leads to an effective force acting between the planes that decays exponentially as

$$f(D) \sim \mathrm{e}^{-D/\lambda_D}, \tag{1}$$

where

$$\lambda_D = \sqrt{\frac{\epsilon_0 \epsilon_r k_B T}{e^2 \rho}} = (4\pi\lambda_B \rho)^{-1/2} \tag{2}$$

is the Debye screening length. Here, $\rho = \rho_+ + \rho_-$ is the salt concentration ($\rho_+ = \rho_-$ is the cation and anion concentrations), ϵ_0 is the vacuum permittivity, ϵ_r is the relative permittivity, k_B is the Boltzmann constant and T temperature, e the proton charge, and $\lambda_B = e^2/(4\pi\epsilon_0\epsilon_r k_B T)$ is the Bjerrum length.

Note that λ_D is inversely proportional to the square root of the ion concentration and the Bjerrum length. Taking the dielectric constant of water $\epsilon_r = 78$ at room temperature $T = 298\,\mathrm{K}$ ($\lambda_B \approx 0.71\,\mathrm{nm}$), we find $\lambda_D \approx 303\,\mathrm{nm}$ for a concentration of $\rho = 1\,\mu\mathrm{M}$ and $96\,\mathrm{nm}$ for $10\,\mu\mathrm{M}$. Increasing the concentration to $0.3\,\mathrm{mM}$, which means the average distance between the ions $\ell \approx \rho^{1/3} \approx 17.7\,\mathrm{nm}$, the Debye length becomes $\lambda_D \approx 17.5\,\mathrm{nm}$, that is, comparable to the inter-ion separation. Thus, the notion of an ion cloud above this concentration becomes questionable.

Ionic liquids are a particular interesting class of organic molten salts which have a melting point below 100 °C (373,15 K). Taking 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[\mathrm{C}_4\ \mathrm{C}_1\ \mathrm{Im}]^+[\mathrm{NTf}_2]^-$) as an example that has a relative permittivity $\epsilon_r \approx 9.1$ and density $\rho \approx 3.6\,\mathrm{M}$ at room temperature [1], we obtain $\lambda_D \approx 0.6\,\mathrm{nm}$, which is comparable to the ion size. Thus, the beautiful and physically intuitive Debye picture breaks down for concentrated electrolytes and ionic liquids.

Screening in such concentrated ionic systems was thoroughly analysed in mid 1990th [4, 5], resulting in a fairly generic picture, which we show schematically in Fig. 1 by green lines in the plane of scaling variables $\sigma_{\text{ion}}/\lambda_D$ and λ_D/ξ. Here, σ_{ion} is the ion diameter, and ξ is the screening length. There are three regimes. In the first regime, the leading order decay is exponential. The decay length is Debye-like at low concentrations (corresponding to low $\sigma_{\text{ion}}/\lambda_D$) but deviates from it when the concentration increases (*i.e.*, ξ/λ_D deviates from unity). At the Kirkwood point, the leading order decay is determined by damped oscillations, *i.e.*

$$f(D) \sim \cos(2\pi D/p)e^{-D/\xi} \tag{3}$$

where p is the period of oscillations and the screening length ξ *increases* with concentration (and hence with $\sigma_{\text{ion}}/\lambda_D$), thus 'underscreening' the interactions compared to the Debye screening. Still, electrostatic interactions dominate this regime. At yet higher concentrations, there is a crossover to hard-core repulsion that provide an even longer decay length.

In 2013, Gebbie et al. [6] reported unusually long electrostatic screening lengths in a room-temperature ionic liquid (RTIL) $[\mathrm{C}_4\mathrm{mim}]^+[\mathrm{NTf}_2]^-$, followed by studies of several other RTILs [7]. A systematic analysis for different concentrated electrolytes and RTILs revealed [2] that "the electrostatic screening length in concentrated electrolytes increases with concentration". As we know from classical theories, this is expected. However, the mystery was (and remains) the plain values of these screening lengths, which exceed the ones predicted by classical theories by an order of magnitude (symbols in Fig. 1). Shortly afterwards, Lee et al. [3] reported that all available experimental data collapsed on a single 'master' curve showing a cubic scaling, *viz.*

$$\xi/\lambda_D \sim (\sigma_{\text{ion}}/\lambda_D)^n \tag{4}$$

with $n = 3$. The authors of Ref. [3] termed their findings *underscreening*. It could instead be called *anomalous underscreening* [8] because an increase in the screening length over the Debye length was predicted decades ago.

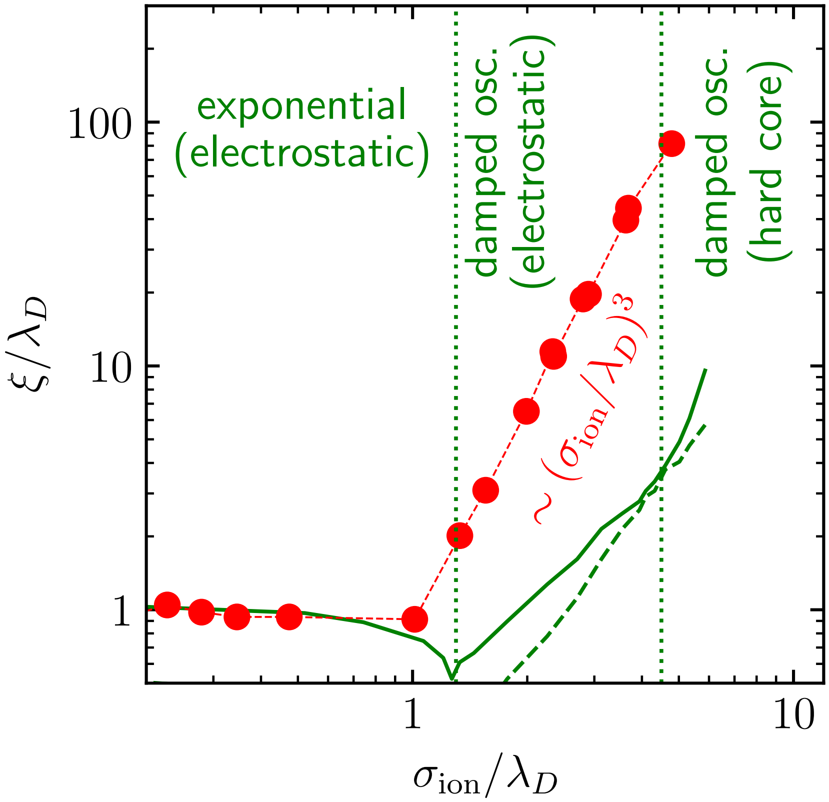

Figure 1: **Ionic screening lengths.** Classical theories predict exponential and damped oscillatory screening dominated by electrostatic interactions followed by a damped oscillatory screening dominated by hard-core repulsion as the ion concentration increases. The solid line shows the largest and the dashed line the second largest screening length. The symbols correspond to the experimental data for various ionic liquids and aqueous electrolytes from Ref. [2]. According to Ref. [3], all values approximately collapse on a single 'master curve' displaying a cubic scaling, Eq. (4) with $n = 3$, for $\sigma_{\text{ion}}/\lambda_D \gtrsim 1$.

Some theoretical [3, 9] and simulation [8] studies have reported consistency with "anomalous underscreening". However, their used parameter ranges were different from those used in experiments, either with ion concentration or electrostatic coupling. All other studies, including theory [10, 11, 12] and simulations in bulk [13, 1, 14] and under confinement [14] show no appearance of unusually large screening lengths, producing screening lengths of the same order of magnitude as classical liquid state theories. Also, there is no clear evidence of a universal scaling of the screening lengths with concentration, as different studies report different scaling exponents, *viz.*, $n = 1$ [1], $n = 2$ [1, 10], $n \approx 1.3$ [13], and $n = 1.5$ [11, 12]. It remains to be seen which exponent is correct and whether there is a single well-defined scaling exponent at all.

While other experiments support anomalous underscreening (*e.g.* Ref. [15, 16]), there are also experiments (particularly AFM experiments) reporting either no anomalous underscreening [17, 18] or only at elevated temperatures [19]. There are also experiments reporting anomalously large screening lengths, but without cubic scaling [20]. Moreover, it is still debated whether anomalous underscreening arises as a bulk property of concentrated ionic systems or due to surface effects[21]. Thus, even from an experimental perspective, anomalous underscreening remains a mystery, and additional studies are needed to comprehend the physical mechanisms underlying the reported anomalously long screening lengths.

The present situation reminds us of the time when like-charge attraction was a hot research topic, sparking an enormous wave of investigations of the interactions between charged macromolecules. Ise et al. [22] and others observed void structures and clusters in colloidal suspensions, suggesting unknown attractive interactions and motivating work on electrostatic interactions between colloids in confinement, first performed by Crocker and Grier [23] and Kepler and Fraden [24]. Standard Poisson-Boltzmann-like theories could not explain their results, which led to faulty explanations based on numerical calculations published in high-impact journals (*e.g.*, by Bowen and Sharif [25] and Sogami and Ise [26]), debugged later by rigorous mathematical theorems [27, 28]. However, it brought us a much better understanding of how Coulomb correlations can induce attractions [29, 30, 31] and how we can treat them beyond mean-field [32, 33].

Similarly, the studies by Gebbie et al.[6] and Smith et al. [2] have sparked enormous renewed research activities in the field of concentrated electrolytes, which already led to an improved understanding of their behaviour. We anticipate and hope that additional experiments, theory, and simulations will soon find a conclusive answer to this apparently anomalous underscreening paradox.

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