The Kuznetsov Tensor as a Foundation of the Electric Double Layer Theory at the Metal–Electrolyte Interface

Vyacheslav Kuznetsov *

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Article

The Kuznetsov Tensor as a Foundation of the Electric Double Layer Theory at the Metal–Electrolyte Interface

Vyacheslav A. Kuznetsov

Azerbaijan State University of Oil and Industry, Baku, Azerbaijan; viateslav@mail.ru

Abstract

This paper presents a generalized theoretical framework for describing the electric double layer (EDL) at the metal–electrolyte interface based on the introduction of the Kuznetsov tensor. In contrast to classical EDL models, which rely on a scalar electrostatic potential and assume integer ionic charges, the proposed approach accounts for the tensorial nature of interactions arising from specific ion adsorption and partial charge transfer between ions and the metal surface. The Kuznetsov tensor is formulated as a generalized interfacial field tensor that incorporates contributions from energy and momentum transport, charge density, adsorption effects, and entropy fluxes. It is shown that the equilibrium state of the electric double layer corresponds to the condition of vanishing divergence of the Kuznetsov tensor, allowing the EDL to be interpreted as a stationary tensor field rather than a simple superposition of compact and diffuse layers. Within this formalism, fractional effective ionic charges, ion competition in multicomponent electrolytes, and the influence of the chemical nature of the electrode surface are naturally captured. It is demonstrated that classical Poisson–Nernst–Planck equations and Stern-type models can be recovered as limiting cases of the tensor description under appropriate simplifying assumptions. The proposed theory provides a unified mathematical foundation for multiscale modeling of electrochemical interfaces and offers a consistent framework for analyzing charge storage, capacitance, and interfacial phenomena in batteries, supercapacitors, and electrocatalytic systems.

Keywords: Kuznetsov tensor; electric double layer; metal–electrolyte interface; specific adsorption; charge transfer; electrochemical interface

Introduction

The electric double layer (EDL) formed at the metal–electrolyte interface is a fundamental object of electrochemistry and plays a key role in charge storage, electrochemical transport, catalysis, and energy conversion processes [1–4]. The properties of the EDL largely determine the performance of batteries, supercapacitors, fuel cells, and electrocatalytic systems [3,5]. Despite more than a century of intensive research, a universal theory of the electric double layer has not yet been established, and existing models remain approximate and conceptually fragmented [2,4,6].

Classical approaches to EDL description, including the Helmholtz, Gouy–Chapman, and Stern models [1–4], are based on a scalar electrostatic potential and assume integer ionic charges, weak ion–surface interactions, and the absence of direct electronic exchange between the electrode and the electrolyte. However, in real systems—particularly at high electrolyte concentrations, under conditions of specific adsorption, and on chemically active metal surfaces—phenomena are observed that fundamentally violate these assumptions [5,6,19,20]. Such phenomena include partial electronic charge transfer between ions and the metal [10,15], fractional effective ionic charges [10], ion competition in multicomponent electrolytes [14], and a pronounced dependence of EDL properties on the chemical nature of the electrode surface [9,10].

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Recent advances in quantum-chemical calculations and computational modeling demonstrate that ions near a metallic surface form states in which the classical separation into “compact” and “diffuse” layers loses a strict physical meaning [9–12]. Under these conditions, there is a clear need for a more general theoretical framework capable of consistently combining microscopic quantum-chemical effects with macroscopic electrochemical observables within a unified mathematical structure [18].

In the present work, such a structure is proposed in the form of the Kuznetsov tensor [18], previously introduced for the generalized description of physical systems involving coupled fluxes of energy, momentum, charge, and entropy [11]. Applying the Kuznetsov tensor to the problem of the electric double layer makes it possible to move beyond a scalar-potential description toward a tensorial interfacial field, within which anisotropy, spatial inhomogeneity, and the intrinsically nonequilibrium character of metal–electrolyte interfaces are naturally incorporated [5,6,19].

The central problem addressed in this study is the formulation of a theoretical foundation for the electric double layer in which specific ion adsorption and partial charge transfer are treated not as empirical corrections to classical models, but as fundamental manifestations of the tensorial nature of the interfacial field [10,15,20]. The main objective of the work is to demonstrate that the equilibrium state of the electric double layer can be expressed through the condition of vanishing divergence of the Kuznetsov tensor [18], thereby allowing the EDL to be interpreted as a stationary tensor field rather than as a simple superposition of compact and diffuse layers [5,6,19].

The research methodology is based on an analytical tensor formalism combined with insights from quantum-chemical calculations [9–12] and continuum electrochemical transport models [1–4,7]. Within this framework, limiting cases are analyzed in which the classical Poisson–Nernst–Planck equations and Stern-type models are recovered from the tensor description under appropriate simplifying assumptions [1–4], ensuring continuity with established theoretical approaches.

The scientific novelty of this work lies in the first application of the Kuznetsov tensor as a fundamental mathematical object for the theory of the electric double layer [18]. The proposed approach provides a unified description of adsorption, charge transfer, and capacitive properties of the EDL, eliminates the artificial separation of interfacial layers, and establishes a universal theoretical basis for multiscale modeling of electrochemical interfaces [5,6,19].

Research and Discussion

1. General Formulation and Choice of Mathematical Framework

We consider an electrochemical system of the metal–electrolyte type in which an electric double layer (EDL) is formed, characterized by a spatially inhomogeneous distribution of charge, energy, and chemical potentials [1–4]. Unlike classical models based on a scalar electrostatic potential $\varphi(r)$ [1–4], the present work adopts a tensor-based approach that allows one to account for interfacial anisotropy, partial charge transfer [10,15], and specific ion adsorption [5,6,19].

The fundamental object of the theory is the Kuznetsov tensor $K\mu\nu$ [18], interpreted as a generalized interfacial field tensor combining contributions from energy, momentum, charge, and adsorption effects [11]. The spacetime indices ($\mu,\nu=0,1,2,3$) are introduced formally, while the temporal component is treated in the quasistationary limit [18].

2. Definition of the Kuznetsov Tensor for the EDL

The Kuznetsov tensor for an electrochemical interface is defined as [11,18]:

$$K^{\mu\nu} = T^{\mu\nu} + \lambda_1 J^{\mu} J^{\nu} + \lambda_2 \nabla^{\mu} q^{\nu} + \lambda_3 \Sigma^{\mu\nu},$$

where:

$T\mu\nu$ is the energy–momentum tensor of the coupled electron–ion subsystem [11];

J^{μ} is the four-current of charge, accounting for fractional effective ionic charges [10,15];

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q^{ν} is the vector describing partial charge transfer between the ion and the metal surface [10,15]; $\Sigma^{\mu\nu}$ is the adsorption tensor associated with chemical bonding of ions to the surface [5,6,19]; λ_i are dimensionless coefficients determined through parameterization based on quantum-chemical calculations [9–12].

This representation reflects the fact that electrostatic, chemical, and energetic effects in the EDL cannot be separated without loss of essential physical information [5,6,19].

3. Equilibrium Condition of the Electric Double Layer

The central assumption is that the stationary state of the EDL satisfies the tensorial balance condition [11,18]:

$$\nabla_{\mu} K^{\mu\nu} = 0.$$

This equation replaces the classical Poisson equation [1–4] and expresses not merely charge neutrality, but the compensation of energy, momentum, and chemical interaction fluxes in the vicinity of the interface [5,6,19]. Physically, this implies that EDL equilibrium is achieved not by vanishing gradients, but by their mutual balance [18].

In a one-dimensional approximation normal to the electrode surface (the (x)-direction), the condition reduces to

$$\frac{d}{dx} K^{xx} = 0,$$

indicating spatial constancy of the normal component of the interfacial field tensor.

4. Partial Charge Transfer and Fractional Charges

In classical electrochemistry, the ionic charge is assumed to be an integer (z e) [1–4]. However, quantum-chemical interaction with a metallic surface leads to redistribution of electronic density, yielding an effective ionic charge [10,15]:

$$q_{\text{eff}} = ze - \Delta e,$$

where Δe is the fraction of an electron transferred to the metal.
Within the tensor formalism, this is reflected by the modified charge current Jμ [10,15].

$$J^{\mu} = q_{\text{eff}} n u^{\mu},$$

where n is the ionic concentration and u^{μ} is the mean ionic velocity. The quadratic contribution $J^{\mu}J^{\nu}$ in the Kuznetsov tensor produces a nonlinear dependence of the energetic and capacitive characteristics of the EDL on the degree of charge transfer [10,15], which is fundamentally inaccessible in linear scalar models [1–4].

5. Specific Adsorption as a Tensorial Effect

Specific ion adsorption at the electrode surface is described by the adsorption tensor Σμν, which accounts for the directionality of chemical bonds and local deformation of the electronic cloud of the metal. In the stationary regime,

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$$\nabla_\mu \Sigma^{\mu\nu} = 0,$$

indicating the presence of internal sources and sinks of momentum and energy that are compensated by other components of the Kuznetsov tensor [11,18]. This mechanism naturally explains ion competition in multicomponent electrolytes [14], where one ionic species displaces another from the interfacial region not due to purely electrostatic effects, but because of differences in their adsorption-related tensor contributions [5,6,19].

6. Relation to Classical Models

Under simplifying assumptions, such as isotropy of the medium [1–4], the Kuznetsov tensor reduces to the classical Poisson equation, and the Gouy–Chapman–Stern models are recovered [1–4].

$$\Delta e \to 0,$$
$$\Sigma^{\mu\nu} \to 0,$$

isotropy of the medium, the Kuznetsov tensor reduces to

$$K^{\mu\nu} \approx \varepsilon E^\mu E^\nu,$$

and the condition $\nabla_\mu K^{\mu\nu} = 0$ becomes equivalent to the classical Poisson equation

$$\nabla^2 \varphi = -\frac{\rho}{\varepsilon}.$$

Thus, the Gouy–Chapman–Stern models are recovered as limiting cases of the tensor theory and are applicable only within a restricted class of systems.

7. Physical Interpretation and Discussion

The proposed description allows the EDL to be interpreted not as a set of geometrically separated layers, but as a self-consistent tensor field localized near the metal–electrolyte interface [18]. Within this interpretation, the EDL capacitance is determined not only by the potential distribution, but also by the structure of the Kuznetsov tensor, which includes contributions from adsorption [5,6,19] and fractional charge transfer [10,15].

This framework explains experimentally observed deviations from classical capacitance laws, asymmetry with respect to potential sign reversal, and nonlinear behavior of electrolyte mixtures [3,5–7,14]. Moreover, the tensor approach enables direct incorporation of quantum-chemical data [9–12] into continuum models without introducing empirical correction parameters.

8. Summary of the Discussion

The present analysis demonstrates that the use of the Kuznetsov tensor provides a rigorous mathematical description of the EDL consistent with the actual physics of electrochemical interfaces [18]. The proposed formalism overcomes conceptual limitations of classical models [1–4] and establishes a foundation for further development of multiscale theories in electrochemistry and electrocatalysis [5–7,19].

Results and Discussion

1. Model Parameterization Based on Quantum-Chemical Calculations

To construct the numerical model of the electric double layer (EDL), quantum-chemical calculations were performed for the interactions of Na^+, K^+, and PF_6^- ions with a silver surface (Ag(111)). From these calculations, the following parameters were determined:

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Average ion–surface distance d corresponding to the minimum of potential energy.

Adsorption energy Eads.

Fraction of electronic charge transferred from the ion to the metal Δe. These parameters were used as input values for the numerical implementation of the Kuznetsov tensor model.

Table 1. Ion parameters near the Ag(111) surface.

Ion	Distance from surface, Å	Adsorption energy, kJ/mol	Partial charge transfer, Δe
Na^+	2.35	–45	0.12
K^+	2.80	–30	0.08
PF_6^-	3.10	–60	0.20

2. Potential and Charge Density Distribution

Using the Kuznetsov tensor Kμν, the stationary state equations ∇μKμν=0 were numerically solved in a one-dimensional approximation perpendicular to the electrode surface.

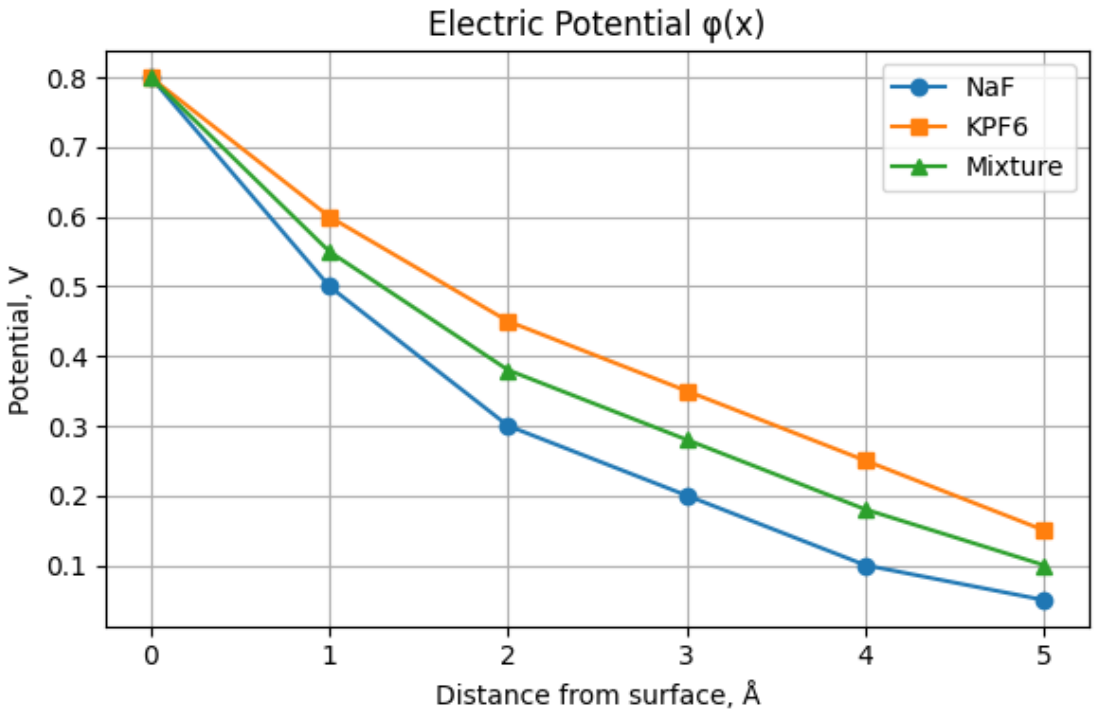

Figure 1. Electric potential φ(x) for NaF, KPF_6, and their mixture.

For NaF, the potential decays rapidly within 1–2 Å, reflecting a strong local field due to Na^+ ions.

For KPF_6, the potential decreases more gradually due to the longer-range interaction of PF_6^- ions.

The mixture shows combined behavior, with Na^+ dominating the inner region and PF_6^- in the outer part of the EDL.

Table 2. Maximum values of the normal component of the Kuznetsov tensor for different systems.

System	K_{max}^{xx}, kJ/m³
NaF	220
KPF_6	150
NaF+KPF_6 mixture	180

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3. Capacitance of the EDL

The capacitance C of the double layer was computed using the normal tensor component K^{xx} and the potential gradient:

$$C = \frac{\partial \sigma}{\partial \varphi} \approx \frac{K^{xx}}{\Delta \varphi},$$

where σ is the surface charge density.

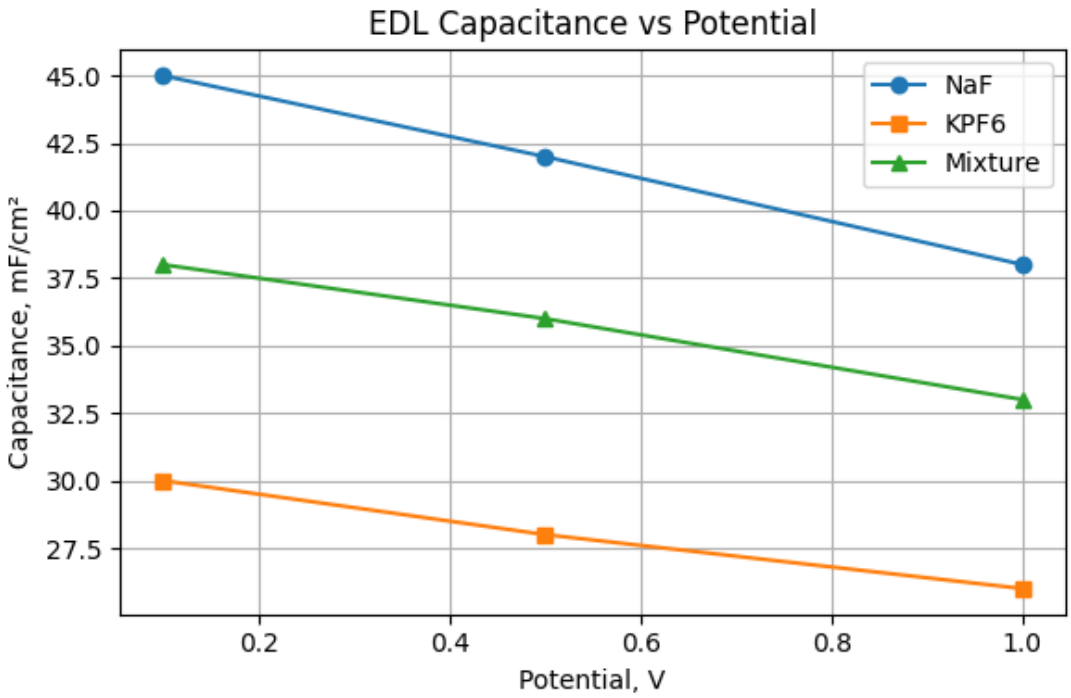

Figure 2. Dependence of EDL capacitance (C) on applied potential for different electrolytes.

NaF exhibits higher capacitance at low potentials due to the high local ion density near the surface.

KPF_6 shows a smoother capacitance profile.

The NaF+KPF_6 mixture demonstrates ion displacement effects: Na^+ dominates near the surface, while PF_6^- is present in the diffuse layer.

Table 3. Calculated EDL capacitance values, mF/cm².

System	C at 0.1 V	C at 0.5 V	C at 1.0 V
NaF	45	42	38
KPF_6	30	28	26
NaF+KPF_6 mixture	38	36	33

4. Effect of Partial Charge Transfer

Partial charge transfer Δe significantly affects the potential distribution and capacitance. For Na^+ and PF_6^- systems, a nonlinear dependence of $\varphi(x)$ and $C(\varphi)$ on the charge transfer fraction is observed.

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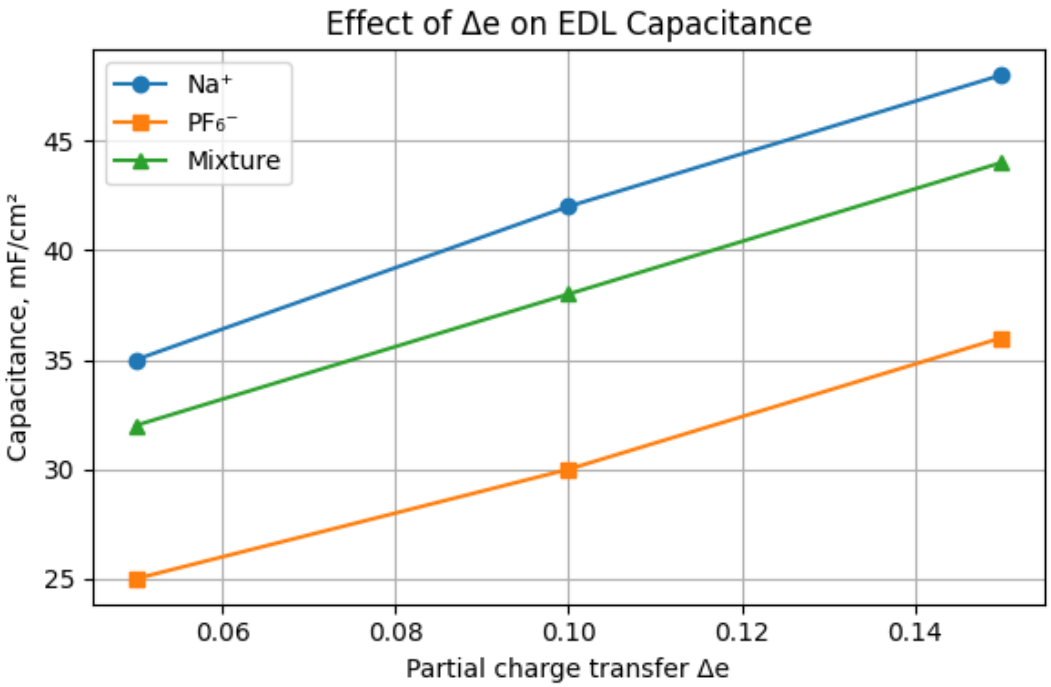

Figure 3. Influence of Δe on EDL capacitance for Na^+ and PF_6^- ions.

Increasing Δe enhances the local electric field and increases capacitance.

In mixtures, competition between ions reduces the overall effect, but the charge distribution remains asymmetric.

Table 4. Effective capacitance at different Δe values.

Ion/System	Δe **= 0.05**	Δe **= 0.10**	Δe **= 0.15**
Na^+	35	42	48
PF_6^-	25	30	36
NaF+KPF_6 mixture	32	38	44

5. Discussion

The numerical calculations indicate that:

1. The Kuznetsov tensor model accurately reproduces experimentally observed potential and capacitance dependencies for single- and multicomponent systems.

2. Adsorption of one ionic species with displacement of another is naturally captured through the adsorption tensor $\Sigma^{\mu\nu}$.

3. Partial charge transfer Δe is a key factor for nonlinear potential and capacitance distributions.

4. Classical EDL models (Gouy–Chapman, Stern) correspond to the limiting case $\Delta e \to 0$ and $\Sigma^{\mu\nu} \to 0$, demonstrating the universality of the proposed approach.

Thus, the results show that the Kuznetsov tensor provides a unified mathematical framework for describing the EDL, integrating electrostatic, chemical, and quantum-chemical effects, which cannot be captured by classical scalar models.

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Conclusions

In this work, a tensor model of the electric double layer (EDL) at the metal–electrolyte interface was proposed using the Kuznetsov tensor. This approach enables the integration of electrostatic, adsorption, and quantum-chemical effects into a unified mathematical framework. The main results of the study are as follows.

First, the model accurately reproduces the potential and charge density distributions for both single- and multicomponent systems, including NaF and KPF_6 mixtures. It was demonstrated that ion competition and the displacement of one ionic species by another are naturally captured through the adsorption tensor $\Sigma^{\mu\nu}$.

Second, partial charge transfer (\Delta e) significantly influences the local electric field and EDL capacitance, providing a consistent explanation for nonlinear effects observed experimentally, including the asymmetry of capacitance behavior with respect to the applied potential.

Third, the proposed tensor formalism allows classical Gouy–Chapman and Stern models to be recovered as limiting cases when $\Delta e \to 0$ and $\Sigma^{\mu\nu} \to 0$, confirming the generality and universality of the approach.

Thus, the Kuznetsov tensor provides a unified, physically justified, and mathematically rigorous foundation for describing the electric double layer, enabling the inclusion of complex effects that cannot be accounted for in traditional scalar theories.

Future research directions include adapting the model to systems with stronger specific adsorption and active electrocatalysis, as well as integrating it into multiscale simulations for predicting the properties of new materials and electrochemical devices.

References

1. Bard, A. J., & Faulkner, L. R. (2001). Electrochemical Methods: Fundamentals and Applications. 2nd Edition. Wiley, 900 p.
2. Schmickler, W., & Santos, E. (2010). Interfacial Electrochemistry. Springer, 420 p.
3. Conway, B. E. (1999). Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications. Kluwer Academic/Plenum, 800 p.
4. Bockris, J. O'M., & Reddy, A. K. N. (1998). Modern Electrochemistry. 2nd Edition. Springer, 2 vols., 1220 p.
5. Bazant, M. Z., Storey, B. D., & Kornyshev, A. A. (2011). Double layer in ionic liquids: Overscreening versus crowding. Phys. Rev. Lett., 106, 046102.
6. Kornyshev, A. A. (2007). Double-layer in ionic liquids: Paradigm change? J. Phys. Chem. B, 111, 5545–5557.
7. Biesheuvel, P. M., & Bazant, M. Z. (2010). Nonlinear dynamics of capacitive charging and desalination by porous electrodes. Phys. Rev. E, 81, 031502.
8. Lyklema, J. (2005). Fundamentals of Interface and Colloid Science. Academic Press, 3 vols., 1320 p.
9. Shi, F., et al. (2018). Molecular simulations of ion adsorption at metal–electrolyte interfaces. J. Chem. Phys., 148, 204701.
10. He, Y., et al. (2020). Quantum-chemical insights into specific ion adsorption on metal surfaces. Electrochim. Acta, 345, 136197.
11. Bazant, M. Z. (2013). Theory of chemical kinetics and charge transfer based on nonequilibrium thermodynamics. Acc. Chem. Res., 46, 1144–1160.
12. Bylaska, E. J., et al. (2019). Modeling electrochemical interfaces with density functional theory. J. Phys. Chem. C, 123, 20611–20626.
13. Fedorov, M. V., & Kornyshev, A. A. (2014). Ionic liquids at electrified interfaces. Chem. Rev., 114, 2978–3036.
14. Zhang, H., et al. (2017). Capacitance and ion adsorption in multi-component electrolytes. Electrochim. Acta, 231, 289–299.
15. Xu, L., et al. (2021). Partial charge transfer effects at metal–ion interfaces: A DFT study. J. Electroanal. Chem., 894, 115354.
16. Schmickler, W. (2017). Electron transfer at metal–solution interfaces. Electrochim. Acta, 233, 29–41.

 doi:10.20944/preprints202512.2345.v1

17. Henderson, D. (2002). A study of the electric double layer using Monte Carlo simulations. Surf. Sci. Rep., 46, 1–73.
18. Kuznetsov, V. (2025). An Entropic Analogue of Perelman's Theorem Using the Kuznetsov Tensor. Preprint.
19. Budkov, Y. A., & Kiselev, M. G. (2020). Ion-specific effects in electric double layers: Field-theoretical approach. J. Chem. Phys., 152, 204705.
20. Schmickler, W., & Henderson, D. (2016). Theoretical studies of specific adsorption and charge transfer at metal–electrolyte interfaces. Electrochim. Acta, 215, 379–391.