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Development and application of fluid density functional theory for novel electrochemical interfaces

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Electrochemical interfaces exist in diverse electrochemical devices, and the performance of these devices is directly related to the physical and chemical properties of the interface. However, it is difficult to in situ measure and characterize the structure and properties of electrochemical interfaces in experimental conditions. It is necessary to develop methods that can describe interface behavior to reveal the relationship between electrochemical interfaces and device performance. Fluid density functional theory (FDFT) stands out for its function to accurately describe the complex interface phenomena during the electrochemical process. A series of research methods based on FDFT continues to emerge. In this perspective, the development history and applications in various fields of FDFT are summarized, including time-dependent FDFT, reactioncoupled FDFT, and quantum density functional theory combined FDFT (i.e. joint density functional theory). By comparing the similarities and differences of different methods. we hope our work could further promote the long-term development of electrochemical interface models and methods.

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Introduction

The conversion of electrical energy and chemical energy is inseparable from the electrochemical interface that is ubiquitous in nature [1], such as energy storage [2], electroplating [3], electrolysis [4], and corrosion [5]. In energy storage and conversion equipment, for example, batteries, their capacity and cycle performance are closely associated with the microstructure of the electrochemical interface [6]. The electrochemical interface is the multiphase environment where the main physical and chemical processes involved in the energy transformation take place [7]. The interface structure fundamentally determines the conduct of the electrochemical process. A novel interface involving electrification, chemical reaction, and mass transfer, relates to not only the properties of the bulk-phase substances, but also the physical structure and electronic state of the substances in the interface area [8] (Figure 1).

Facing novel electrochemical interface, traditional thermodynamic methods are not fully applicable [9]. The traditional Poisson-Boltzmann (PB) method has been put forward for decades, which has established the substance structure distribution at the interface with a theoretical model for the first time [10]. However, the PB method is only applicable to the dilute solution at low voltage, and has a large deviation in other cases [11,12]. In terms of dynamics, the emergence of Poisson-Nernst-Planck (PNP) equations also extends the evolution process of the interface structure in dynamics, but it is also difficult to deal with complex situations, such as intermolecular interaction, polymer, and electrostatic correlation [13]. As an alternative to the PB equation, fluid density functional theory (FDFT) is proposed to describe the interface structure and thermodynamic properties of confined ion systems for novel complex interfaces [14]. FDFT is a method developed in statistical mechanics and suitable for grand-canonical ensemble [15]. Combined with the transfer equation, FDFT can be extended to describe time-dependent phenomena, and developed to time-dependent fluid density functional theory (TD-FDFT) [16]. It can be used to explore the dynamic relaxation process of novel electrochemical interfaces and reveal the mechanism of the charge and discharge process [17]. In addition, the reaction kinetics model can also be combined with FDFT to develop new reaction-coupled FDFT, which eventually develops into joint density functional theory (JDFT) that combines quantum density functional theory (QDFT) and FDFT to explore the properties of electrochemical interfaces under reaction circumstances [18]. The thriving FDFT provides a new perspective for the study of complex novel electrochemical interfaces.





Schematic diagram of a novel electrochemical interface, including surface structure, reaction, and transport.

FDFT has been developed for decades, but still faces many challenges. Some researchers doubted its accuracy and efficiency compared with traditional methods. In order to adapt to different conditions and solve complex problems of novel electrochemical interfaces, people have developed more and more freeenergy functional forms and carried out a lot of theoretical expansion [19]. The development framework of FDFT is shown in Figure 2. This perspective summarizes the development of FDFT and its combination with other theories, as well as the future development direction.

Figure 2

Fluid Density Functional Theory and Static Interface Properties

Establishment of fluid density functional theory

Density functional theory (DFT) is developed from the description of the quantum state of electrons [20,21]. The most vital principle in DFT is that when the system reaches equilibrium or ground state, the monomer density of the system is determined by the monomer external potential. For classical systems, Helmholtz free energy is a functional of the monomer density. In the grand-canonical ensemble, when the system reaches its equilibrium, its grand potential will be minimized. The microscopic structure and macroscopic thermodynamic properties of the equilibrium state can be obtained by constructing the free energy and calculating the functional variation of the density distribution function. Compared with Monte Carlo, molecular dynamics, and other simulation methods, FDFT has obvious advantages in computing speed, and the difference in accuracy is small [22] (Figure 3a).

For FDFT, its essence is to construct the grand potential functional Ω of the system, or the intrinsic Helmholtz free-energy functional F

$$\Omega[\rho(\mathbf{r})] = F[\rho(\mathbf{r})] - \sum_{i=1}^{M} \int \rho_i(\mathbf{r}) \left[\mu_i - V_i(\mathbf{r}) \right] d\mathbf{r}$$
(1)

where μ_i is chemical potential, V_i is external potential, and F is Helmholtz free-energy functional, which can be divided into ideal term and excess term

$$F[\rho(\mathbf{r})] = F^{\mathrm{id}}[\rho(\mathbf{r})] + F^{\mathrm{ex}}[\rho(\mathbf{r})]$$
(2)



The development framework of FDFT. The theory developed from static to dynamic, and then coupled with reaction, and finally established JDFT.





(a) The accuracy and time advantage of FDFT. (b) Applications of FDFT in the electrolyte screening. The screening features contain the electrode structure, chain length, and the ionophilicity and hydrophilicity of the surface. (c) Competitive adsorption mechanism and polyelectrolyte screening in CEOR

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where F^{id} is ideal free energy and F^{ex} is excess free energy. The calculation of the ideal term is known precisely

$$\beta F^{\mathrm{id}}[\rho(\mathbf{r})] = \sum_{i=1}^{M} \int \rho_i(\mathbf{r}) \left\{ \ln \left[\rho_i(\mathbf{r}) \Lambda_i^3 \right] - 1 \right\} \mathrm{d}\mathbf{r}$$
(3)

where $\beta^{-1} = k_B T$, Λ is the thermal wavelength. The emphasis is on the excess inherent Helmholtz energy based on various forms of mean spherical approximation [23]. By constructing different excess free energy, the theory can be applied to different systems to increase calculation accuracy [24]. Free-energy functionals have evolved from simple mean-field assumptions and various local approximations to more complex methods, such as fundamental measure theory and bridge functionals [25,26]

$$F^{ex}[\rho_{i}(\mathbf{r})] = F^{ex}_{hs}[\rho_{i}(\mathbf{r})] + F^{ex}_{C}[\rho_{i}(\mathbf{r})] + F^{ex}_{el}[\rho_{i}(\mathbf{r})] + F^{ex}_{ch}[\rho_{i}(\mathbf{r})] + F^{ex}_{as}[\rho_{i}(\mathbf{r})]$$
(4)

where F_{hs}^{ex} , F_C^{ex} , F_{el}^{ex} , F_{ch}^{ex} and F_{as}^{ex} represent the excess Helmholtz free-energy functional ascribed to hardsphere repulsion, direct Coulombic energy, electrostatic correlations, chain connectivity, and ion associations, respectively. The Euler–Lagrange equation is obtained by minimizing the grand potential related to density distribution $\delta\Omega[\rho(r)]/\delta\rho(r) = 0$. So far, the relationship between density distribution function $\rho(r)$ driven by chemical potential μ and position r is obtained.

$$\rho_i(\mathbf{r}) = \Lambda_i^{-3} \exp\left\{\beta\mu_i - \beta V_i(\mathbf{r}) - \frac{\delta\beta F^{ex}[\rho(\mathbf{r})]}{\delta\rho_i}\right\}$$
(5)

The steady interface density profile can be explored by iteratively solving the equations.

Static properties of novel electrochemical interfaces

Compared with PB equation, which is a traditional theory to describe electric double layer (EDL), FDFT can describe high-concentration electrolytes such as ionic liquids and organic solvents and special electrode materials since more complex intermolecular interactions, that is, van der Waals force and electrostatic force are considered. Lian et al. studied how to improve the capacitance performance of EDL capacitors using ionic liquid mixtures [27] as shown in Figure 3b. Their subsequent studies revealed that the composition of electrolyte has a significant impact on EDL structure and

zero-charge potential [28]. In FDFT, species are treated by the hard spherical coarse-graining model, nevertheless, with the emergence of many chain-shaped electrolytes, it is difficult to accurately predict the interface structure by the previous model. Therefore, the polymer density functional theory (PDFT) has been proposed to investigate the impact of electrolyte chain length [29] on species distribution. The microstructure, charging behavior, and EDL capacitance of ionic liquids with different tail chain lengths can be investigated by PDFT [30]. FDFT also exhibits satisfactory speed and accuracy in polymer solutions. In order to efficiently screen out suitable electrolytes, based on long-rangecorrected hybrid density functional theory, the electrochemical potential window of cation-anion pairs can be theoretically predicted by FDFT [31].

FDFT can also accurately describe the electrode properties, assisting in the screening of efficient electrode materials. As shown in Figure 3b, the developed FDFT is used to optimize the design of electrode materials. Considering the pore diameter and curvature effect of amorphous porous materials, the influence of electrode pore structure on capacitance performance was explored [32]. In addition, the effect of the hydrophobicity of the pore wall was also investigated. When the pore hydrophobicity increased, the capacitance voltage curve changed from a bell shape to a double-hump shape [33,34].

In addition to the study of the electrode–electrolyte interface, Cheng et al. explored the electrochemical interface problem in the petrochemical field by using PDFT [35] (Figure 3c). The competitive adsorption problem in oil reservoirs was studied. It is helpful to further understand the competitive adsorption in chemical-enhanced oil recovery (CEOR). FDFT is gradually being used to solve more industrial problems and is being introduced into more energy storage materials and equipment, including modified electrodes and solidstate electrolytes.

Time-dependent Fluid Density Functional Theory and Dynamic Interface Properties Dynamic extension of fluid density functional theory

The steady-state structure determines many properties such as adsorption, capacitance, and resistance in the electrode–electrolyte interface. However, the dynamic relaxation process of the interface structure is equally important, which involves the charge and discharge





(a) Development of FDFT from a steady state to a dynamic state: combination with transfer equation. (b) TD-FDFT explored the charging dynamics of the ionic liquid at room temperature. (c) The numerical simulation of the pore-filling process (d) and the timescale of capacitor charging.
(b) Reprinted from Ref. [40] with permission from the AIP Publication Group. (c) Reprinted from Ref. [41] with permission from the AIP Publication Group.

dynamic characteristics of electrochemical devices [36,37]. TD-FDFT is an extension of FDFT, which is based on the assumption of local thermodynamic equilibrium and can be used to describe dynamic processes [16]. The basic idea of TD-FDFT is to combine the transport equation with FDFT, take the chemical potential corresponding to each free-energy functional in FDFT as the driving term [38], and then obtain the dependence of species density and time under complex intermolecular interactions (Figure 4a). The transport equation is

$$\frac{\partial \rho_i}{\partial t} = -\nabla \left(J_i + u \rho_i \right) - R_i \tag{6}$$

where $J_i = -D_i \rho_i \nabla \mu_i$, *J* is the flux, *u* is the flow rate of species, μ_i is the local electrochemical potential, and R_i is the source term. In TD-FDFT, the time evolution of the local density distribution of ion species is controlled by the diffusion equation, and is expressed as the relationship between $\rho_i(r, t)$ and the gradient of chemical and external potential [39]

$$\frac{\partial \rho_i(r, t)}{\partial t} = \nabla \cdot \{ D_i \rho_i(r, t) \nabla [\beta \mu_i(r, t) + \beta V_i^0(r)] \}$$
(7)

where D_i is the diffusion constant, V^0 is the external potential. The diffusion equation is driven by chemical potential, which consists of the ideal term, electric potential term, and excess term

$$\mu_i(r, t) = k_B T \ln[\rho_i(r, t)\Lambda_i^3 r] + eZ_i \Psi(r, t) + \mu_i^{ex}(r, t)$$
(8)

The dynamic calculation can be realized by matching the Poisson equation

$$\nabla^2 \psi = -\frac{e}{\varepsilon_0 \varepsilon_r} \sum_i z_i \rho_i \tag{9}$$

Compared with FDFT, TD-FDFT realizes the leap from $\rho_i(r)$ to $\rho_i(r, t)$, adds the evolution of density distribution with time, and obtains the relationship between the density distribution function $\rho_i(r, t)$ and the position r and time t.

Dynamic properties of novel electrochemical interfaces Exploring the dynamic relaxation process of the novel electrochemical interface is helpful to reveal the mechanism of the charge–discharge process [9]. TD-FDFT can be used to study the charging dynamics of EDL containing room temperature ionic liquid and additionally considers electrostatic correlations and ion-size effects [40] (Figure 4b). In addition, a comprehensive numerical simulation of the pore-charging process was conducted, exploring how electrolytes in porous electrodes respond to potential, and discussing the main timescales of pore charging [41] (Figure 4c). TD-FDFT also predicted the timescale of artificial capacitor charging and found that electrode charges formed exponentially in two timescales [42] (Figure 4d). The dynamic advantages of FDFT gradually emerge in the charging and discharging research of energy storage equipment, and are coupled with more physical fields, including heat, flow, reaction, and so on.

Exploration of Reaction Interface and Joint DFT

Coupling of fluid density functional theory and reaction model

In many novel electrochemical interfaces, surface chemical reactions are often accompanied by substance transportation [43]. At the microscale, it is difficult to measure the relevant interface properties that play a crucial role in the performance and function of electrochemical equipment, so it is necessary to develop the corresponding interface theory coupled with reactions (Figure 5a).

For a slit-pore system, according to the FDFT results, we can derive the surface charge density

$$Q = -\sum_{i} Z_{i}e \int_{0}^{H/2} dz \rho_{i}(z)$$
(10)

where Z_i is valence, *e* is elementary charge, and $\rho_i(z)$ is ion density at position *z*. There is a chemical reaction on the surface with a certain reaction equilibrium constant *K*. For interfacial protonation/deprotonation reactions, the surface proton density can be predicted from the Boltzmann equation

$$[H^{+}]_{s} = C_{H^{+}}(z)|_{z=s} = C_{1} \exp\left(-\frac{z_{i}F\psi_{0}}{RT}\right)$$
(11)

where ψ_0 is the surface electrical potential, C_1 is the bulk concentration of H⁺ ions, and pH = $-\log(C_{\text{H}^+})$. At a certain pH value, the surface charge density can be obtained. By solving the EDL and surface-reaction models simultaneously, the interface properties with stable surface reactions can be obtained [44].

The surface reaction-coupled FDFT method has been applied to explore the charge regulation in silica nanopores. Charge regulation is carried out on the silicon dioxide surface through the protonation/deprotonation reaction of dissociated functional groups [44] (Figure 5b). In addition, oxygen-containing functional groups have a significant influence on electrochemical capacitance behavior of carbon electrodes. Su et al. proposed a coarse-grained model based on FDFT to describe the electrochemical capacitor with the Faraday reaction, which provides a theoretical routine for studying pseudocapacitors [45] (Figure 5c).





(a) The reaction model was combined with FDFT to explore the electrochemical interface properties with reaction, which is used to (b) explore the surface properties of silica nanopores, (c) the influence of graphene oxide surface functional groups on energy storage performance, (d) and describe the interface phenomena and charging dynamics of associated ionic liquids.

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Based on the study of steady-state surface reaction, Cheng et al. also extended the kinetic theory. Based on modified PNP (MPNP) theory, they theoretically coupled the bulk chemical reaction. In the anion and cation association reaction of the ionic liquids $A^+ + B^- \stackrel{k_a}{\underset{k_d}{\leftarrow}} C$, the kinetic equation is added to the source term R in Equation (6), where the association constant is related to the kinetic parameters for the forward and backward reactions, $K = k_a/k_d$. This method established a new reaction-coupled MPNP theory, which is used to describe the interface phenomena and charging dynamics of associated ionic liquids [46] (Figure 5d).

Development of joint DFT

Based on the above research, many scholars have developed the theory from simple reaction coupling to

Figure 6



$$A_{JDFT}[n, \{N_{\alpha}\}, V(r)] = A_{HK}[n] + A_{lq}[\{N_{\alpha}\}] + \Delta A[n, \{N_{\alpha}\}, V(r)]$$
(12)

where A_{HK} is the electronic energy proposed by Hohenberg–Kohn theorems, A_{lq} is the free energy of liquid expressed by FDFT, ΔA is the coupling energy from the interaction between solute and solvent [48], which is



(a) The idea of JDFT and its applications: (b) the capacitive properties of graphene materials with different surface structures and (c) the electrocatalytic reduction route of CO₂.

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divided into two parts: long-range dielectric screening $\Delta A_{sc}[n, V(r)]$ capturing the tendency of the molecules in the liquid to be found in orientations and polarization states that tend to screen long-range electric fields, and a short-range electron-overlap interaction $\Delta A_{el}[n, \{N_{\alpha}\}]$.

JDFT has been used to study the capacitive properties of graphene materials with different surface structures. The results show that the total capacitance of the material in the low-voltage range is increased by the hole defect, and the total capacitance of the material in the high-voltage range is increased by boron nitrogen doping [49] (Figure 6b). By the helping hand of JDFT, it was discovered that the cation (K⁺) at the electrode/electrolyte interface can stabilize the key intermediate *OCHO for electrocatalytic reduction of CO₂ to HCOOH, and can regulate the concentration of H⁺ at the interface, inhibiting the occurrence of hydrogen evolution reaction, thus improving the CO₂ electroreduction performance of catalysts [50] (Figure 6c).

Conclusion and Perspective

In the exploration of novel electrochemical interfaces, FDFT has been systematically developed and applied, and carried out a series of expansions to address different challenges. From the accurate calculation of steady-state structure to the simulation of interface relaxation dynamic process, and finally to the complex situation of reaction coupling, FDFT has been an important method of interface mesoscale simulation. In this article, we review the development of FDFT, as well as its successful solutions to a series of problems in various industries. FDFT will continue to play a leading role in this field and gradually expand to more electrochemical interface fields, including popular directions such as lithium batteries and solid-state electrolytes.

Currently, employing ODFT to calculate the interfacial reaction properties and FDFT to estimate the solvent effects, that is, JDFT, has attracted more and more attention from researchers. JDFT can directly calculate the equilibrium properties of quantum-mechanically described solutes in diverse solvent environments. To achieve this method, it is necessary to simultaneously develop physical models (free-energy functional) of liquids and their interactions with electrons, perform algorithms for minimizing variational free energy, and tightly and effectively couple these new models with quantum DFT. However, JDFT is still in its infancy and lacks mature modular software. And the part of FDFT only uses a simple free-energy functional. One of the development directions is to establish a stable, accurate, and universal JDFT program. Cross-disciplinary cooperation is needed to promote the development of FDFT with more vitality. In the future, FDFT/IDFT will also shine in the fields of interface structure and dendrite formation in lithium-ion batteries, surface structure and reaction mechanism of various energy conversion catalysts, new electrode materials, prediction of electrochemical pseudocapacitance, and band arrangement at solid–liquid interfaces.

CRediT authorship contribution statement

Jin Cheng: Investigation, Methodology, Formal analysis, Visualization, Writing – original draft. **Jia-Hui Li**: Formal analysis, Visualization, Writing – review & editing. **Cheng Lian:** Conceptualization, Resources, Funding acquisition, Writing – review & editing, Supervision. **Honglai Liu:** Funding acquisition, Resources.

Data Availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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