CHANNEL Theory vNext: MD → Kernels → Continuum → Device

CHANNEL: CHArge aNd ioN NanoscaLe-to-device Link

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Abstract

This document describes a thermodynamically-auditable continuum framework for OMIEC/electrochemical systems, designed to ingest nanoscale information (MD/CG/experiments) as *profiles/kernels*, produce continuum predictions via Poisson–Nernst–Planck (PNP) with material-specific closure, and optionally map to device observables (e.g., OECT drain current).

vNext introduces a clean separation between the invariant "skeleton" (conservation laws, electrostatic bookkeeping, flux–force structure, boundary control, and audits) and the material-specific *closure* (kernels and free-energy / chemical-potential models). Three closure modes are supported: (A) analytic Ω-based closure, (B) Ω-based closure augmented by an extra energy-density kernel ω_{extra}, and (C) μ-closure via per-species dimensionless excess potentials ϕ_i^{ex}.

Contents

1 Goals and scope

1.1 Primary scientific goal

Given a material class (e.g., OMIECs), device geometry, electrolyte choice, and a nanoscale description (MD/CG/experimental profiles), build a single workflow that:

1. produces continuum predictions of steady and transient electrochemical response (Q–V_G, C^*, hysteresis, ionic profiles, doping profiles), and
2. provides explicit audits for internal consistency (Gauss/Maxwell bookkeeping, conservation, convergence), enabling systematic model refinement.

1.2 What is invariant vs what is material-specific

Invariant skeleton (must stay explicit, not black-boxed).

1. Conservation for each conserved species i:

$$\partial_t c_i + \nabla \cdot \boldsymbol{J}_i = R_i. \tag{1}$$

2. Electrostatic coupling through free charge:

$$\rho_{\text{free}} = \rho_{\text{base}} + \sum_i q_i c_i + \rho_{\text{redox}}. \tag{2}$$

3. Explicit choice of electrical control: Dirichlet (voltage-controlled) vs Neumann (charge-controlled), related by Legendre transforms.

4. Flux–force structure (Onsager/gradient flow template):

$$\boldsymbol{J}_i = -M_i c_i \boldsymbol{\nabla} \mu_i \quad (\text{with } M_i = D_i/(k_{\mathrm{B}}T)). \tag{3}$$

5. Reaction detailed-balance structure: forward/backward rates must reproduce the chosen equilibrium.

6. Audits: Gauss/Maxwell bookkeeping, $d\Omega/dV_G$ relation when Ω exists, numerical convergence and positivity.

Material-specific closure (allowed to be analytic, numerical, or learned). Examples include $\varepsilon_{\mathrm{r}}(\cdot)$, accessible-volume factors $h_i(\cdot)$, insertion free energies $\Delta\mu_i^0(\cdot)$, diffusion $D_i(\cdot)$, and redox energetics/kinetics.

2 Geometry, fields, and notation

We describe a 1D slab of thickness d with coordinate $z \in [0, d]$. The model is written so that extension to 2D/3D is a drop-in replacement of ∂_z by $\boldsymbol{\nabla}$ and of 1D finite-volume by multidimensional discretizations.

2.1 State variables

- $c_i(z,t)$: number density of mobile species i (units: m^{-3}).
- $\psi(z,t)$: electrostatic potential (units: V).
- $\alpha(z,t)$: redox/doping site occupancy fraction (dimensionless), when applicable.

2.2 Kernels / profiles (from MD/CG/experiment)

All kernels can be (i) a 1D profile $f(z)$ or (ii) a smooth field $f(z;\alpha)$ (or more generally $f(z;\boldsymbol{s})$ for an extended state $\boldsymbol{s}$).

- $\varepsilon_{\mathrm{r}}(z;\alpha)$: relative dielectric profile.
- $n_s(z)$: density of redox sites (units: m^{-3}).
- $\rho_{\mathrm{base}}(z)$: fixed/background free-charge density (units: $\mathrm{C\,m}^{-3}$).
- $h_i(z;\alpha)$: accessible volume fraction for species i (dimensionless).
- $\Delta\mu_i^0(z;\alpha)$: one-body insertion free energy offset (units: J).
- $\omega_{\mathrm{extra}}(z;\alpha)$: optional extra energy-density term (units: $\mathrm{J\,m}^{-3}$).
- $\phi_i^{\mathrm{ex}}(z;\alpha)$: optional *dimensionless* excess potential for μ-closure.

Reference anchoring. All kernels must be anchored to a reservoir reference so that at a chosen reservoir location z_{res} one has (convention)

$$\psi(z_{\mathrm{res}}) = 0, \quad \varepsilon_{\mathrm{r}}(z_{\mathrm{res}}) = \varepsilon_{\mathrm{r}}^{\mathrm{res}}, \quad h_i(z_{\mathrm{res}}) = 1, \quad \Delta\mu_i^0(z_{\mathrm{res}}) = 0, \quad \phi_i^{\mathrm{ex}}(z_{\mathrm{res}}) = 0. \tag{4}$$

This anchoring is essential for avoiding double counting and for interpreting V_G.

3 Electrostatics: Dirichlet electric enthalpy

We adopt a Dirichlet (voltage-controlled) formulation with boundary conditions

$$\psi(0) = 0, \qquad \psi(d) = V_G. \tag{5}$$

For a local dielectric $\varepsilon_{\mathrm{r}}(z;\alpha)$, Gauss/Poisson reads

$$-\partial_z \left(\varepsilon_0 \varepsilon_{\mathrm{r}}(z;\alpha)\, \partial_z \psi\right) = \rho_{\mathrm{free}}(z). \tag{6}$$

The Dirichlet electric enthalpy density is written as

$$\omega_{\mathrm{field}} = -\frac{1}{2}\varepsilon_0 \varepsilon_{\mathrm{r}} \left|\partial_z \psi\right|^2 + \psi\, \rho_{\mathrm{free}}, \tag{7}$$

which is convenient for consistent variational bookkeeping and avoids electrostatic double counting.

4 Ion thermodynamics: q_0 protocol (double-counting control)

A recurring ambiguity in MD-to-continuum pipelines is whether the "excess" insertion free energy already contains an accessible-volume/sieving factor. CHANNEL treats this as an explicit protocol choice.

4.1 q0_strategy A: explicit h_i + conditional $\Delta\mu_i^0$

In strategy A, h_i is a separate kernel and $\Delta\mu_i^0$ is a conditional insertion free energy *beyond* the accessible-volume effect. Define

$$U_i^{\mathrm{ex}}(z;\alpha) = U_i^{\mathrm{Born}}(z;\alpha) + \Delta\mu_i^0(z;\alpha), \tag{8}$$

with Born contribution

$$U_i^{\mathrm{Born}}(z;\alpha) = \frac{q_i^2}{8\pi\varepsilon_0 r_i^{\mathrm{Born}}} \left(\frac{1}{\varepsilon_{\mathrm{r}}(z;\alpha)} - \frac{1}{\varepsilon_{\mathrm{r}}^{\mathrm{res}}}\right). \tag{9}$$

The ideal entropy uses h_i as an accessible-volume correction:

$$\mu_i = k_{\mathrm{B}}T \ln \frac{c_i}{h_i c_i^{\mathrm{res}}} + U_i^{\mathrm{ex}} + q_i\psi + \cdots \tag{10}$$

where c_i^{res} is the reservoir density.

4.2 q0_strategy B: lumped $\Delta\mu_i^0$ (force $h_i \equiv 1$)

In strategy B, the user provides a single $\Delta\mu_i^0$ that already includes the effect of sieving/accessible volume. CHANNEL enforces $h_i \equiv 1$ and the same definition

$$U_i^{\mathrm{ex}} = U_i^{\mathrm{Born}} + \Delta\mu_i^0. \tag{11}$$

Implementation note (CHANNEL enforcement). CHANNEL always uses the decomposition $U_i^{\mathrm{ex}} = U_i^{\mathrm{Born}} + \Delta\mu_i^0$, and h_i enters only through the ideal term and the drift potential $(-\ln h_i)$. This makes the double-counting protocol auditable.

5 Closure modes A/B/C

The continuum skeleton requires chemical potentials μ_i (or equivalent drift potentials) and, for Ω-based closures, a grand-potential functional.

5.1 Mode A: analytic Ω-based closure (default OMIEC)

A minimal per-volume grand-potential density is

$$\omega = \omega_{\text{field}} + \omega_{\text{ion}} + \omega_{\text{redox}} \;\; (+\,\omega_{\text{extra}} \text{ in Mode B}). \tag{12}$$

The ion part (for q0_strategy A) is

$$\omega_{\text{ion}} = \sum_i \left[k_{\text{B}}T\, c_i \left(\ln \frac{c_i}{h_i c_i^{\text{res}}} - 1 \right) + c_i U_i^{\text{ex}} \right]. \tag{13}$$

Then

$$\mu_i = \frac{\delta \Omega}{\delta c_i} = k_{\text{B}}T \ln \frac{c_i}{h_i c_i^{\text{res}}} + U_i^{\text{ex}} + q_i \psi. \tag{14}$$

5.2 Mode B: Ω-based closure + ω_{extra}

Mode B keeps Mode A but adds an extra energy density kernel $\omega_{\text{extra}}(z;\alpha)$ (units: $\text{J}\,\text{m}^{-3}$):

$$\Omega_{\text{extra}} = \int_0^d \omega_{\text{extra}}(z;\alpha)\, dz. \tag{15}$$

This term modifies $\delta\Omega/\delta\alpha$ through its local derivative $\partial\omega_{\text{extra}}/\partial\alpha$ and therefore affects redox equilibrium and kinetics, while preserving auditability (since Ω remains defined).

5.3 Mode C: μ-closure via ϕ_i^{ex}

Mode C targets "unknown electrochemistry" where a global Ω may not be known. Instead, per species i we provide a dimensionless excess potential kernel $\phi_i^{\text{ex}}(z;\alpha)$ and define

$$\frac{\mu_i}{k_{\text{B}}T} = \ln \frac{c_i}{c_i^{\text{res}}} + \phi_i^{\text{ex}}(z;\alpha) + \beta q_i \psi. \tag{16}$$

The drift potential used by the transport discretization is

$$\Phi_i \equiv \frac{\mu_i^{(\text{no ideal})}}{k_{\text{B}}T} = \phi_i^{\text{ex}} + \beta q_i \psi. \tag{17}$$

Audit implication. Since Ω is not defined by default in Mode C, Maxwell/energy audits involving Ω are not applicable. One should instead (i) run integrability checks in the space of state variables, (ii) optionally reconstruct an effective Ω over the validated domain, and (iii) distill back to Mode B/A when possible.

6 Redox/doping site model

When redox sites are present, we include an occupancy field $\alpha(z,t) \in (0,1)$ and a site density $n_s(z)$. A minimal local redox free-energy density is

$$\omega_{\text{redox}} = n_s \left[k_{\text{B}}T \left(\alpha \ln \alpha + (1-\alpha) \ln(1-\alpha) \right) + \alpha \Delta G^0 - k_{\text{B}}T\, \alpha \ln(K_X c_X) \right], \tag{18}$$

where c_X is the counterion density and K_X is an equilibrium constant (units chosen so that $K_X c_X$ is dimensionless).

6.1 Equilibrium condition

In the absence of additional feedback terms, local equilibrium implies

$$\ln \frac{\alpha}{1-\alpha} = \ln(K_X c_X) - \beta \left(\Delta G^0 + \sigma_P e \, \psi \right), \tag{19}$$

where σ_P is the signed number of elementary charges per occupied site.

6.2 Including α-feedback from kernels (Mode A/B)

When kernels depend on α (e.g., $\varepsilon_{\mathrm{r}}(z;\alpha)$, $h_i(z;\alpha)$, $U_i^{\mathrm{ex}}(z;\alpha)$), the stationarity condition becomes

$$k_{\mathrm{B}}T \ln \frac{\alpha}{1-\alpha} + \Delta G^0 - k_{\mathrm{B}}T \ln(K_X c_X) + \sigma_P e \, \psi + F(z) = 0, \tag{20}$$

where the feedback term per site (units: J) is

$$F(z) = \frac{1}{n_s} \sum_i \left[c_i \, \frac{\partial U_i^{\mathrm{ex}}}{\partial \alpha} - k_{\mathrm{B}}T \, c_i \, \frac{\partial}{\partial \alpha} \ln h_i \right] - \frac{\varepsilon_0}{2 n_s} \frac{\partial \varepsilon_{\mathrm{r}}}{\partial \alpha} \, |\partial_z \psi|^2 + \frac{1}{n_s} \frac{\partial \omega_{\mathrm{extra}}}{\partial \alpha} \quad \text{(Mode B)}. \tag{21}$$

6.3 Kinetics with detailed balance

A simple two-state kinetic model is

$$\partial_t \alpha = k_{\mathrm{on}} \, c_X \, (1-\alpha) - k_{\mathrm{off}} \, \alpha. \tag{22}$$

Detailed balance requires

$$\frac{k_{\mathrm{on}}}{k_{\mathrm{off}}} = K_X \exp\left[-\beta \left(\Delta G^0 + \sigma_P e \psi + F \right) \right], \tag{23}$$

so that the kinetic steady state matches the equilibrium condition.

7 Continuum dynamics: transport + Poisson

7.1 Transport (gradient-flow / Nernst–Planck)

Using $\boldsymbol{J}_i = -M_i c_i \boldsymbol{\nabla} \mu_i$ with $M_i = D_i/(k_{\mathrm{B}}T)$ yields the familiar Nernst–Planck form

$$\boldsymbol{J}_i = -D_i \left(\boldsymbol{\nabla} c_i + c_i \boldsymbol{\nabla} \Phi_i \right), \tag{24}$$

where Φ_i is the dimensionless drift potential:

$$\Phi_i = \beta \left(U_i^{\mathrm{ex}} + q_i \psi \right) - \ln h_i \quad \text{(Mode A/B)}, \qquad \Phi_i = \phi_i^{\mathrm{ex}} + \beta q_i \psi \quad \text{(Mode C)}. \tag{25}$$

7.2 Boundary conditions (default)

CHANNEL's default 1D implementation uses:

- Left boundary ($z = 0$): Dirichlet reservoir for mobile ions $c_i(0) = c_i^{\mathrm{res}}$ and electric potential $\psi(0) = 0$.
- Right boundary ($z = d$): no-flux for ions and Dirichlet potential $\psi(d) = V_G$.

Other boundary types (blocking, Butler–Volmer, surface capacitance) are intended as plugins in the broader framework.

8 Numerical algorithms (1D reference solvers)

8.1 Algorithm 1: MD/CG/experiment → profiles/kernels

(Implemented outside CHANNEL, typically in PILOTS.)

1. Define geometry and binning along z; gather MD samples (possibly conditioned on α or other slow variables).
2. Estimate $\varepsilon_{\mathrm{r}}(z;\alpha)$ (e.g., from polarization response / fluctuation estimators), $h_i(z;\alpha)$ (accessible volume), and insertion kernels $\Delta\mu_i^0(z;\alpha)$.
3. Enforce anchors and domain constraints: $\varepsilon_{\mathrm{r}} > 0$, $0 < h_i \leq 1$, reference values at z_{res}.
4. Smooth/interpolate to continuous profiles or z–α fields.

8.2 Algorithm 2: stationary (equilibrium) solver

Given V_G, iterate to a self-consistent fixed point:

1. (Kernels) Evaluate kernels at current $\alpha(z)$.
2. (Ions) Update c_i from local equilibrium:
   - Mode A/B: $c_i = h_i c_i^{\mathrm{res}} \exp[-\beta(U_i^{\mathrm{ex}} + q_i\psi)]$.
   - Mode C: $c_i = c_i^{\mathrm{res}} \exp[-(\phi_i^{\mathrm{ex}} + \beta q_i\psi)]$.

   If explicit counterion coupling is enabled (Mode A/B), solve the local nonlinear condition induced by ω_{redox}.
3. (Poisson) Solve Poisson with Dirichlet BC to update ψ.
4. (Redox) If redox is enabled, update α either
   - without feedback (closed-form logistic update), or
   - with feedback by solving the nonlinear stationarity condition including $F(z)$.
5. Apply damping/mixing to stabilize convergence.

8.3 Algorithm 3: transient solver (operator splitting + SG flux)

For each timestep $t_n \to t_{n+1}$:

1. Update boundary voltage $V_G(t_{n+1})$ and solve Poisson for ψ using the old charges (quasi-static field update).
2. Reaction step: update α using kinetics with detailed balance. If enabled (Mode A/B), include $F(z)$.
3. Transport step: update mobile c_i using finite-volume discretization with Scharfetter–Gummel fluxes (guarantees positivity under mild conditions).
4. Solve Poisson self-consistently with updated charges.
5. Record observables.

9 Observables and device mapping

9.1 Charge and capacitance

Two consistent calculations of gate charge per area are used:

$$Q_{\mathrm{gate}} = -\varepsilon_0 \varepsilon_{\mathrm{r}}(d)\, \partial_z \psi\big|_{z=d}, \qquad Q_{\mathrm{vol}} = \int_0^d \rho_{\mathrm{free}}(z)\, dz. \tag{26}$$

Their mismatch is an audit of Poisson/discretization consistency.

An equilibrium differential capacitance can be estimated by finite differences:

$$C^*_{\mathrm{eq}} \approx \frac{Q_{\mathrm{gate}}(V_G + \delta V) - Q_{\mathrm{gate}}(V_G - \delta V)}{2\delta V}. \tag{27}$$

9.2 OECT drain current (optional mapping)

A minimal mapping (placeholder) relates the integrated doping fraction $\bar{\alpha}$ and gate charge to a channel conductance model $I_D(V_G)$. This module is intentionally pluggable.

10 Audits and verification

10.1 Always applicable

- Poisson bookkeeping: Q_{gate} vs Q_{vol}.
- Positivity: $c_i \geq 0$, $\alpha \in [0, 1]$.
- Grid/time-step convergence of Q–V_G, C^*, hysteresis metrics.

10.2 Ω-based audits (Modes A/B)

When Ω exists, a Dirichlet Maxwell relation holds (sign convention depends on the chosen electric enthalpy):

$$\frac{d\Omega_{\mathrm{eq}}}{dV_G} = Q_{\mathrm{gate}}. \tag{28}$$

CHANNEL verifies this numerically by symmetric finite difference.

10.3 Mode C audits (recommended)

For Mode C, implement integrability / path-independence checks for μ-closures on a validated domain, and when possible reconstruct an effective Ω and distill it to an analytic or energy-based form (Mode B/A).

11 Extension roadmap (Level-0/1/2)

- **Level-0 (geometry upgrade):** 2D/3D device geometry while using 1D kernels along thickness.
- **Level-1 (state-function libraries):** kernels as functions of local state $(\phi, \alpha, \lambda, \dots)$ evaluated on 2D/3D grids.
- **Level-2 (explicit microstructure):** full spatially varying $n_s(\boldsymbol{r})$, $\rho_{\mathrm{base}}(\boldsymbol{r})$ and anisotropic transport.

Provenance

This vNext LaTeX is aligned with the current CHANNEL C++ implementation (closure modes A/B/C, q0_strategy A/B, Poisson + SG PNP, optional redox feedback, optional ω_{extra} and ϕ^{ex} kernels).