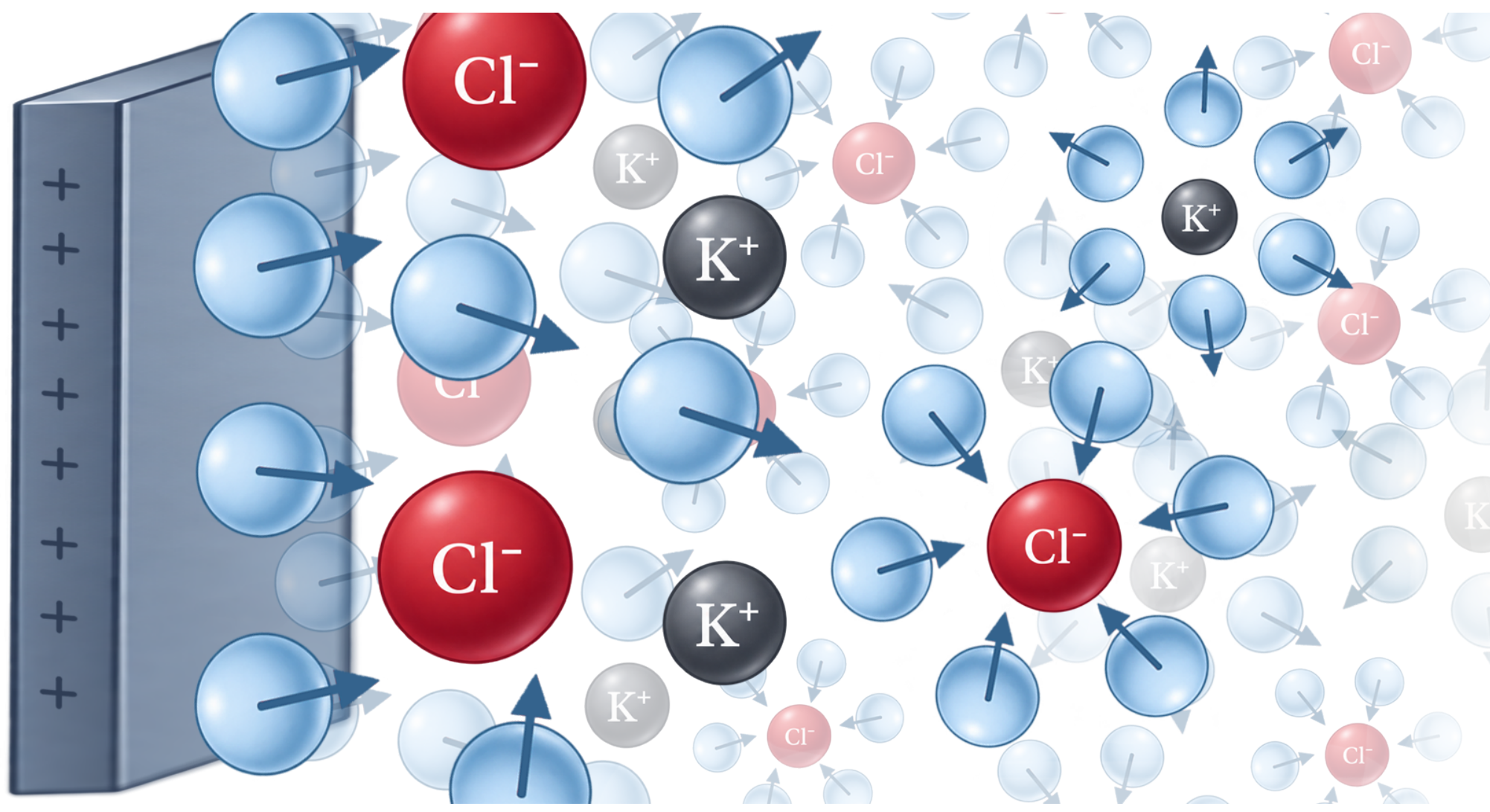


1. Abstract



A charged interface simultaneously redistributes ions, orients molecular dipoles, and reorganizes the local packing of the liquid. These effects are strongly coupled: the ionic atmosphere changes the electric field, the field polarizes the solvent, and excluded volume determines which configurations are locally accessible.

We are constructing a **thermodynamically consistent classical density-functional theory** in which a species-resolved (**civilized**) **electrolyte model** is combined with a **PC-SAFT-based coarse grained molecular description of water**. This poster reports the separately tested building blocks and the numerical protocol being developed for their coupled solution.

2. Finite-size electrolyte with explicit dipolar solvent

The model is built as a controlled hierarchy for ions $i \in \{+, -\}$ and orientable (dipolar) solvent density $\rho_d(z, \omega)$:

$$\beta\Omega = \beta F_{id} + \beta F_{WBII} + \beta F_{MF}^{el} + \beta F_{res}^{MSA} + \text{Tr } \rho [\beta V^{\text{ext}}(z) - \beta\mu].$$

The reduced charge and polarization fields via first orientational moment $\eta(z)$ and reduced dipole m are

$$Q(z) = q [\rho_+(z) - \rho_-(z)], \quad P(z) = \sqrt{\frac{4\pi}{3}} m \rho_d(z) \eta(z).$$

Mean-field electrostatic free energy for the slab geometry of Area A and electrostatic potential ϕ in Gaussian units for BC $\phi'(L) = 0$, $P(L) = 0$,

$$\beta F_{MF}^{el}(\phi) = A \int_0^L \left[\frac{[\phi'(z)]^2}{8\pi} - Q(z)\phi(z) - P(z)\phi'(z) \right] dz.$$

White-Bear-II FMT supplies species-resolved excluded volume via a decomposition of particle volume, surface, and curvature overlap weights, $w_\alpha^{(i)}$, around each point [1],

$$n_\alpha(z) = \sum_i \rho_i * w_\alpha^{(i)}, \quad c_i^{(1)}(z) = - \sum_\alpha \frac{\partial \Phi_{WBII}}{\partial n_\alpha} * w_\alpha^{(i), \text{rev}},$$

MSA-derived residue adds short-range ii , id , and dd direct-correlation channels [2],

$$\beta F_{res}^{MSA} = -\frac{1}{2} \int dz [QK_{ii} * Q + 2QK_{id} * P + PK_{dd} * P].$$

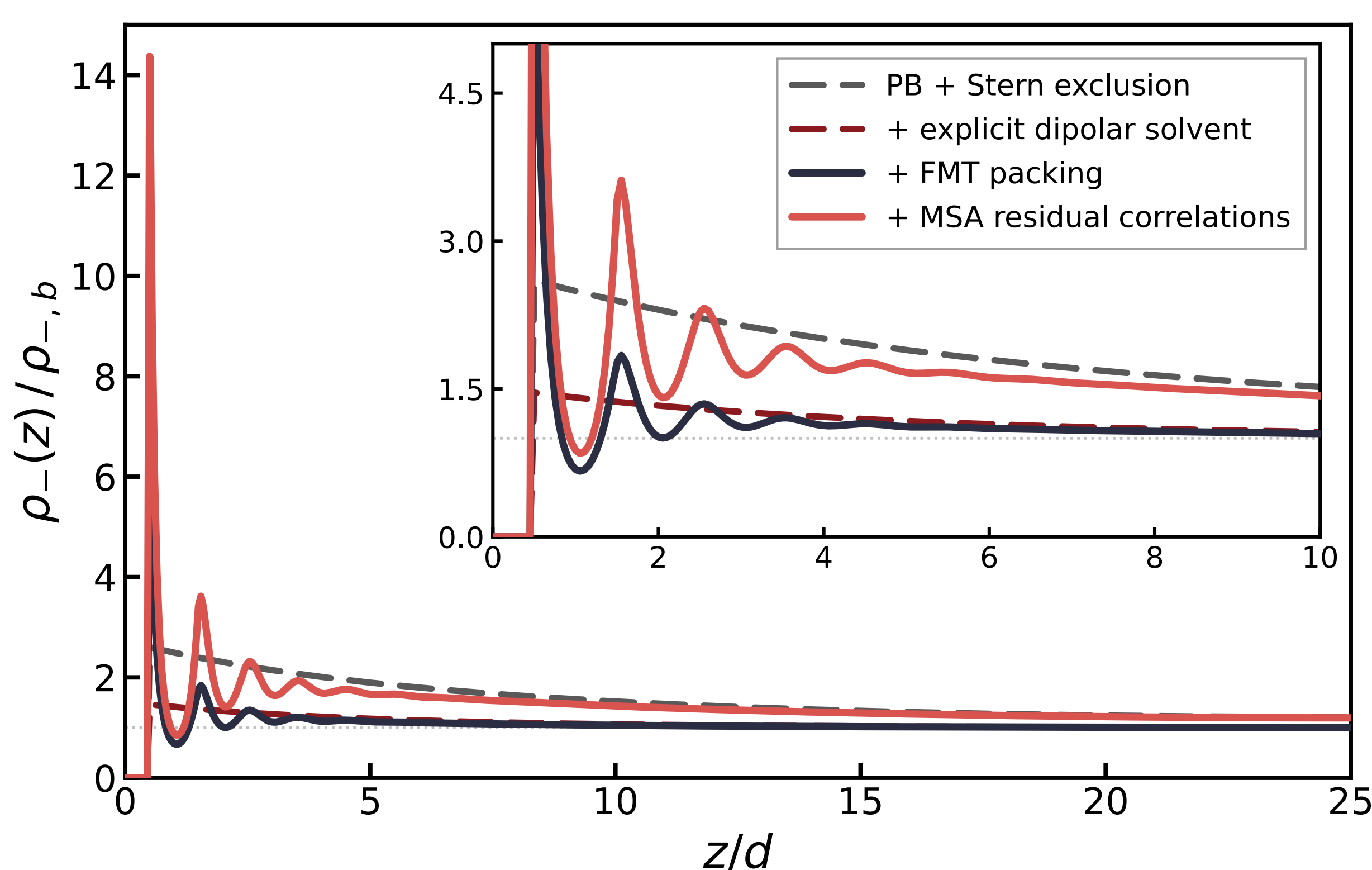


Fig. 1: **Model hierarchy at one fixed wall potential.** Stern–PB uses a bulk dielectric background ($\epsilon_w = 79.7$); the dipolar models carry polarization (2.33 D) explicitly [3]. Wall Potential is 25.7 mV

4. Numerical solution and validation protocol

Equilibrium is the fixed point of the bulk-subtracted Euler–Lagrange map,

$$\rho_i^{\text{new}}(z) = \rho_i^b \exp \left[-\beta V_i^{\text{ext}}(z) - \sum_x (\mu_i^x(z) - \mu_{i,b}^x) \right].$$

- Discretization:** Planar FMT weights are cell-integrated and normalized to their exact moments; non-local derivatives are evaluated by adjoint convolutions with reversed kernels.
- Continue in wall potential and resolution.** A converged, lower-potential state seeds the next target; accepted states are then transferred to finer grids.
- Globalize the nonlinear solve:** Safeguarded Anderson warm-up is followed by Newton–Krylov iterations [4] with finite-difference Jacobian–vector products, GMRES, preconditioning, and an Armijo line search.
- Acceptance:** Solver status is diagnostic. A state is accepted only when the recomputed map defect, profile domain, bulk recovery, wall masks, WBII packing bound, active association mass action, and MSA acceptance all pass.

Acceptance rule: numerical convergence $\wedge$ physical admissibility $\wedge$ closure consistency.

3. Non-local water free-energy extension

Add these contributions to WBII-FMT hard-core reference: Yu–Wu-type [5] **chain connectivity**, four-site Wertheim TPT1 **association**, and Gross–Sadowski PC-SAFT **dispersion** [6],

$$\beta F_{\text{water}} = \beta F_{id} + \beta F_{WBII} + \beta F_{\text{chain}} + \beta F_{\text{assoc}} + \beta F_{\text{disp}} + \int dz \beta \rho_w V_w^{\text{wall}}.$$

The local chain and association densities use the total FMT contact field,

$$\Phi_{\text{chain}} = \frac{1-m}{m} n_0^{(w)} \zeta \ln y_{ww}^{\text{hs}}, \quad \Phi_{\text{assoc}} = 4b \left(\ln X - \frac{X}{2} + \frac{1}{2} \right),$$

where $b = n_0^{(w)} \zeta$, $\Delta = D_0 y_{ww}^{\text{hs}}$, $a = 2b\Delta$, and mass action $aX^2 + X - 1 = 0$, with unbonded association site fraction, X ; effective segment number, m ; water scalar weighted density, $n_0^{(w)}$; local FMT contact-anisotropy correction, ζ ; and FMT hard-sphere contact value, y_{ww}^{hs} . Dispersion is evaluated from a normalized smoothed water density $\bar{\rho}_w = w_{\text{disp}} * \rho_w$.

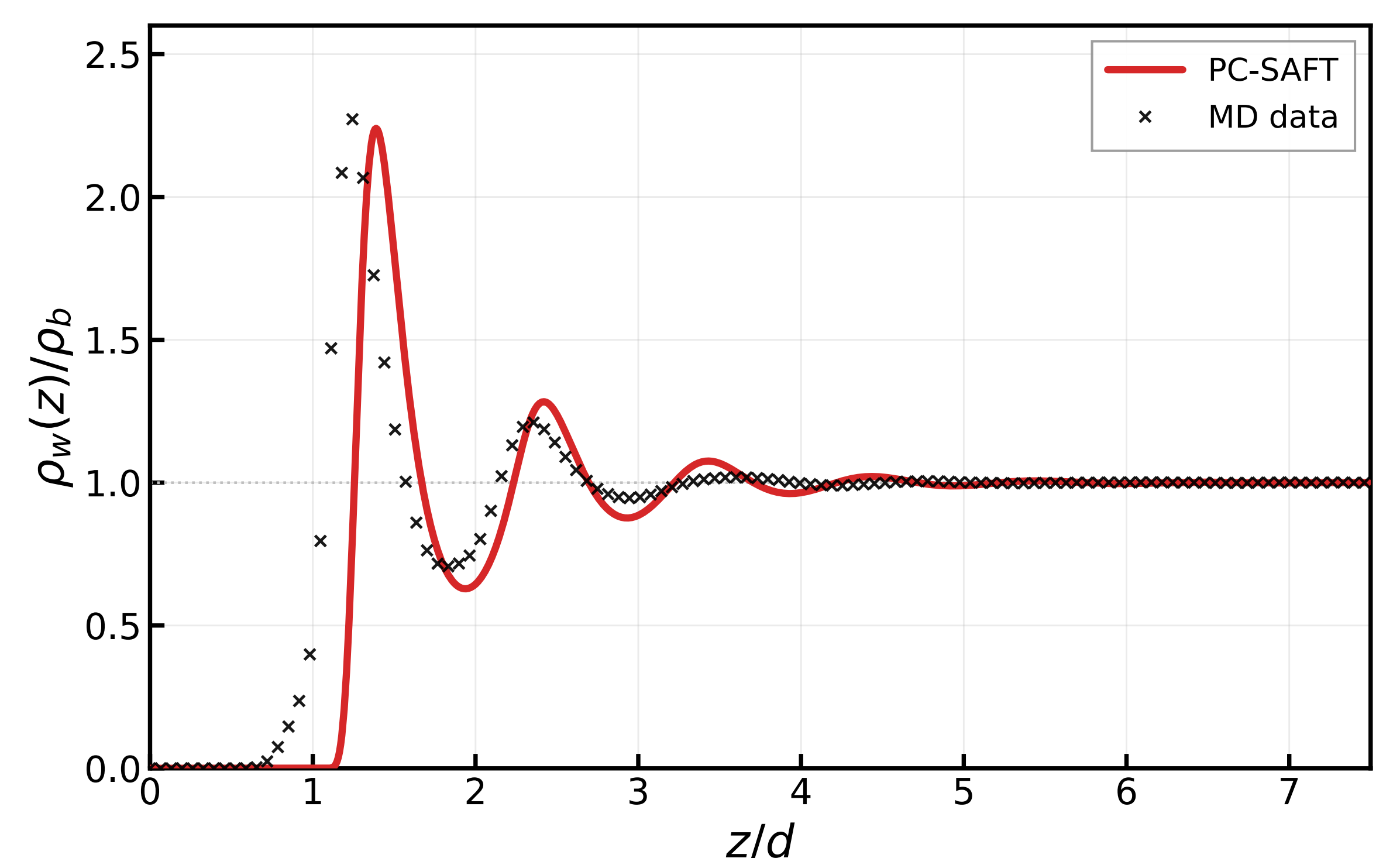


Fig. 2: **Thermodynamic Water Model** The non local profile with r^{-12} external potential is plotted against Gromacs simulation of pure TIP3P water in slab geometry with Yeh–Berkowitz (3dc) correction [7] and folded across the slit.

5. Conclusion

- Decomposition:** Long-range electrostatics is treated at mean-field level, while MSA-derived residual kernels represent the short-range avoiding double counting by construction.
- Volume Exclusion:** WBII-FMT creates contact exclusion and molecular layering.
- Polarization:** MSA residue ii , id , and dd channels restore missing short-range correlations leading to emergence of bulk permittivity [8] and charge screening.
- Wertheim Thermodynamic Perturbation** leads the short-range interaction with **chain** - connectivity of coarse-grained water segments; **association** - mimicking H-bonding, and **dispersion** for non-local attractive cohesion.

Outlook Extend the coarse grained civilized MF model (Sec. 2) to unequal species size (unrestricted case) and combine with the thermodynamic water model (Sec. 3).

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