Influence of varying dielectric backgrounds in colloid simulations

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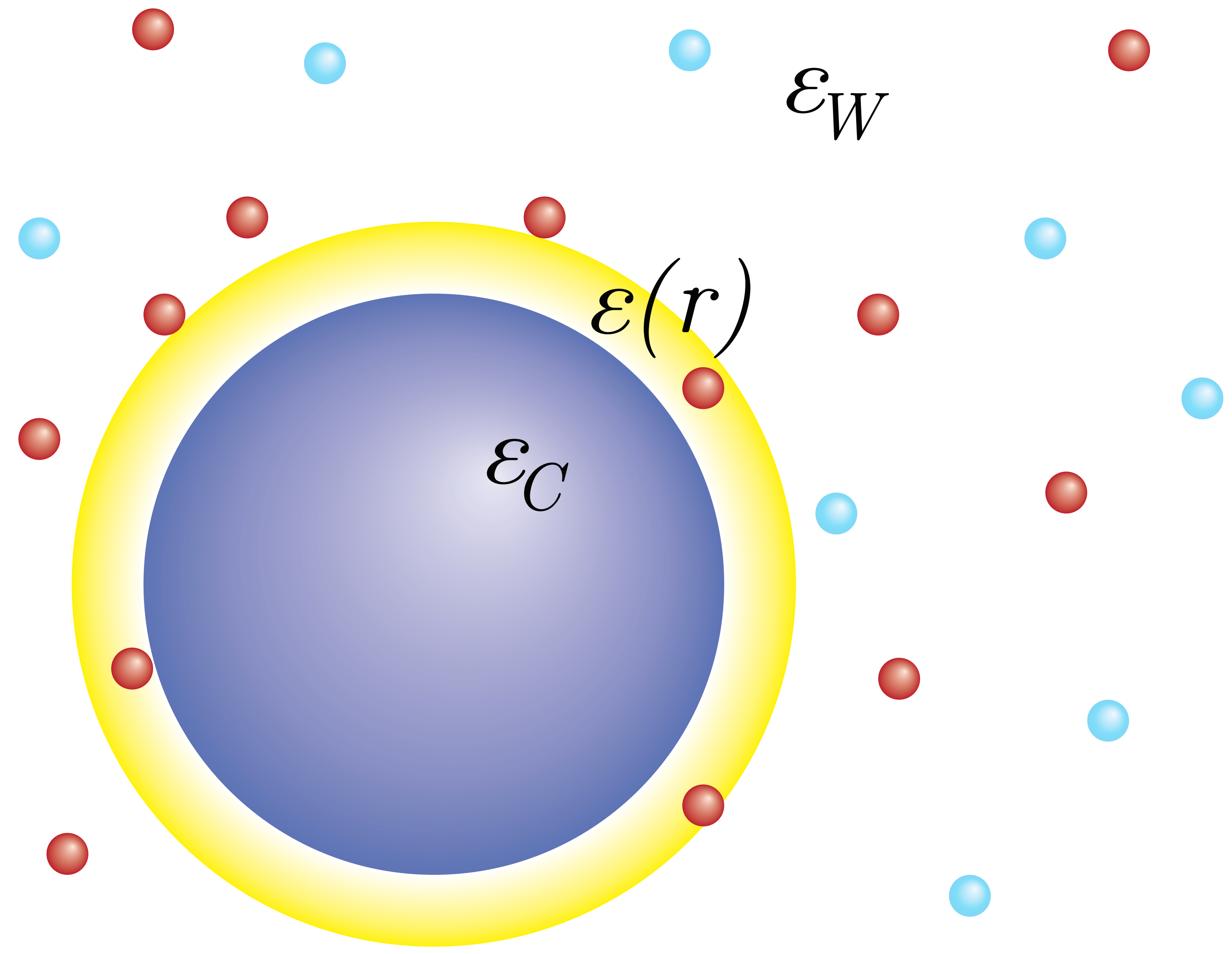
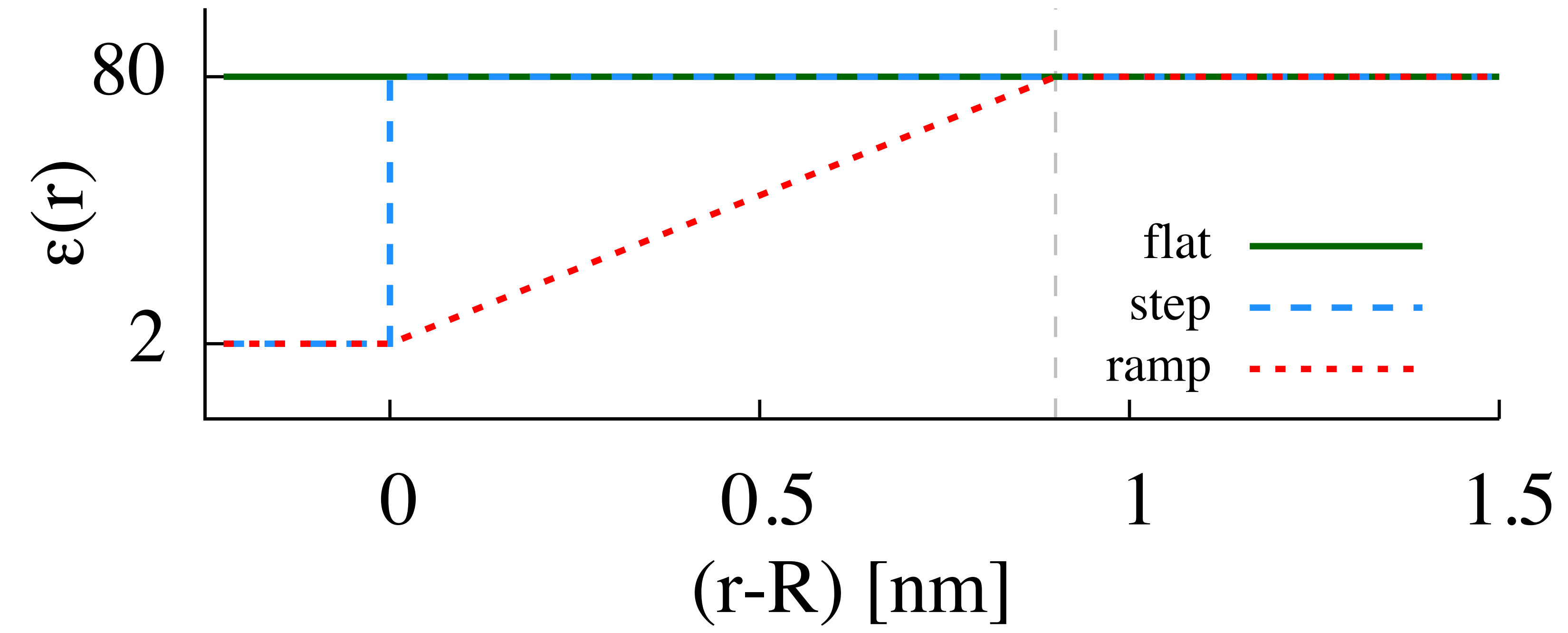
What are colloids? And what‘s their problem?

Colloids are everywhere:

- big particles in suspension
- interesting topic for simulations
- simulation setup
- long-range interactions not exactly known
- bulk permittivity (if any...)



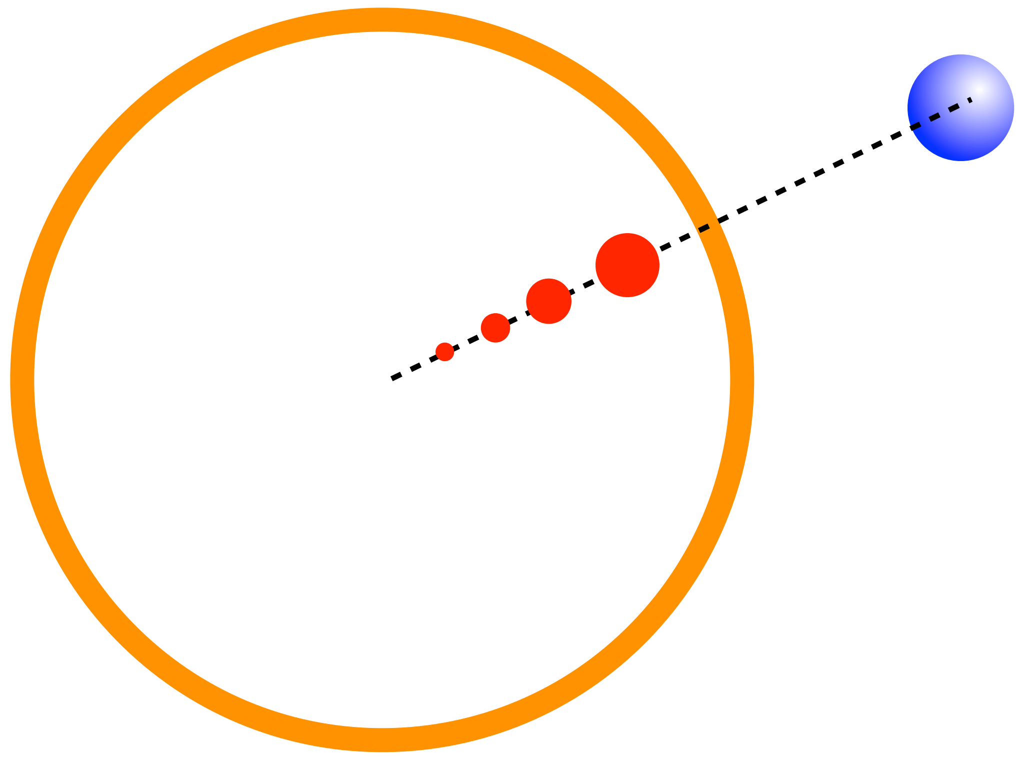


- mirror charges
- repulsion/attraction from interfaces
- moving within the variation?
- self-energy

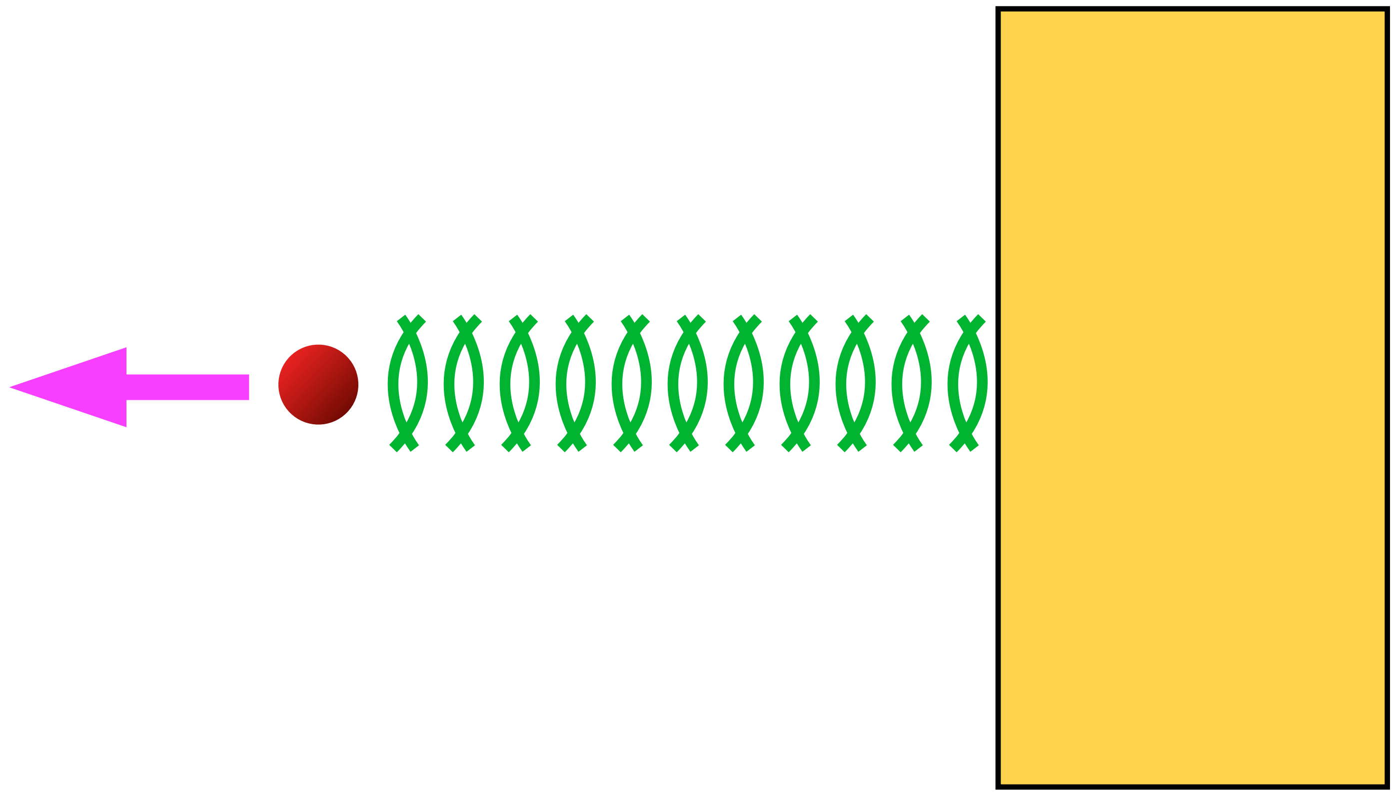
$$-\nabla \cdot \varepsilon(r) \nabla G(\mathbf{r}, \mathbf{r}_s) = 4\pi\delta(\mathbf{r} - \mathbf{r}_s),$$

$$U_i^{\text{self}} = \frac{Z_i^2 e^2}{4\pi\varepsilon_0}\left[\frac{G_{\text{pol}}(\mathbf{r}_i, \mathbf{r}_i)}{2} + \frac{1}{2\varepsilon(r_i)a_i}\right]$$

Two algorithms: MEMD and HIM



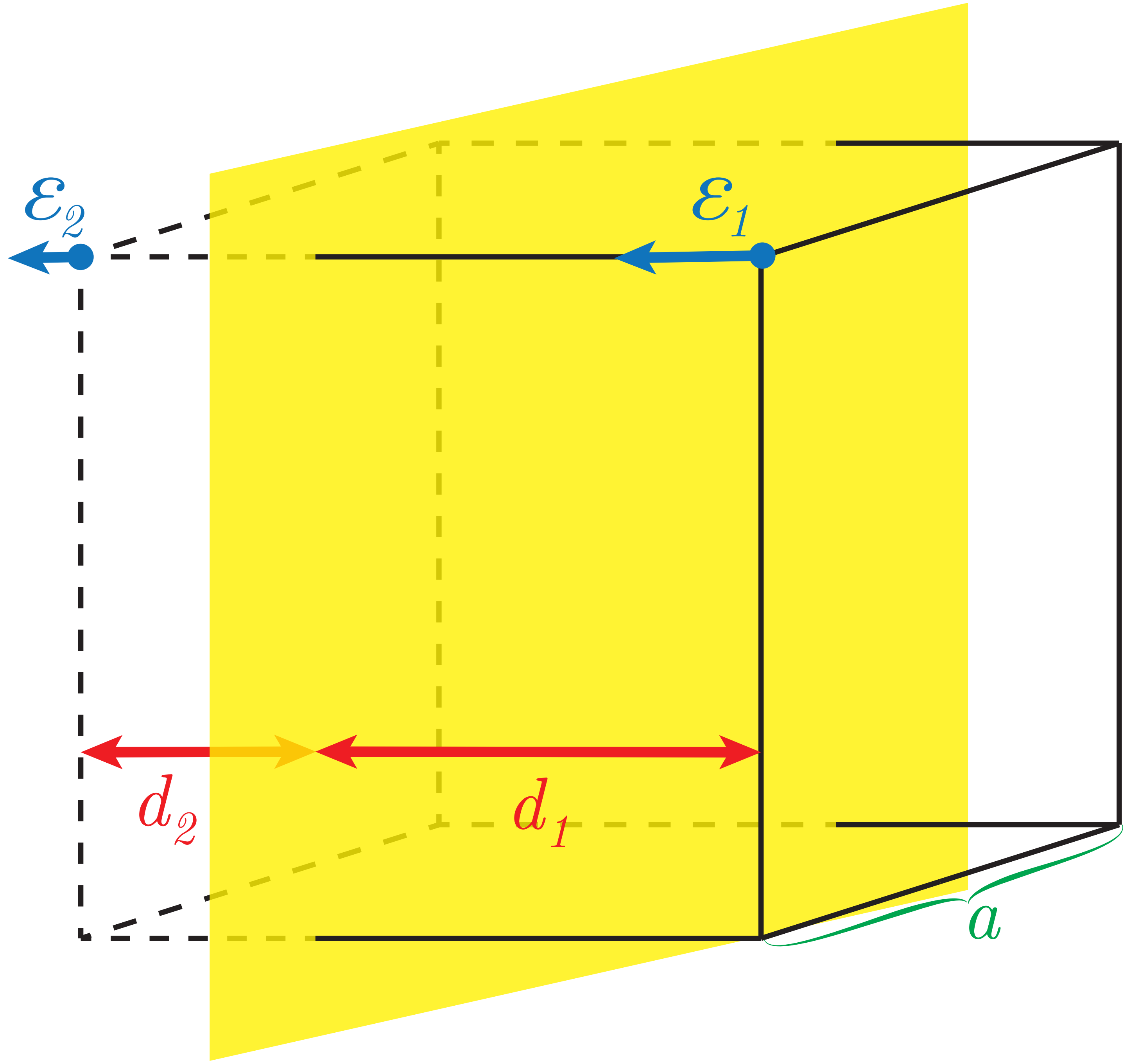
- MC-simulation: energy
- series of mirror charges
- mathematical trick
- able to deal with harmonic functions, piecewise



- MD-simulation: force
- electric and magnetic fields
- field propagation
- arbitrary permittivity on a lattice

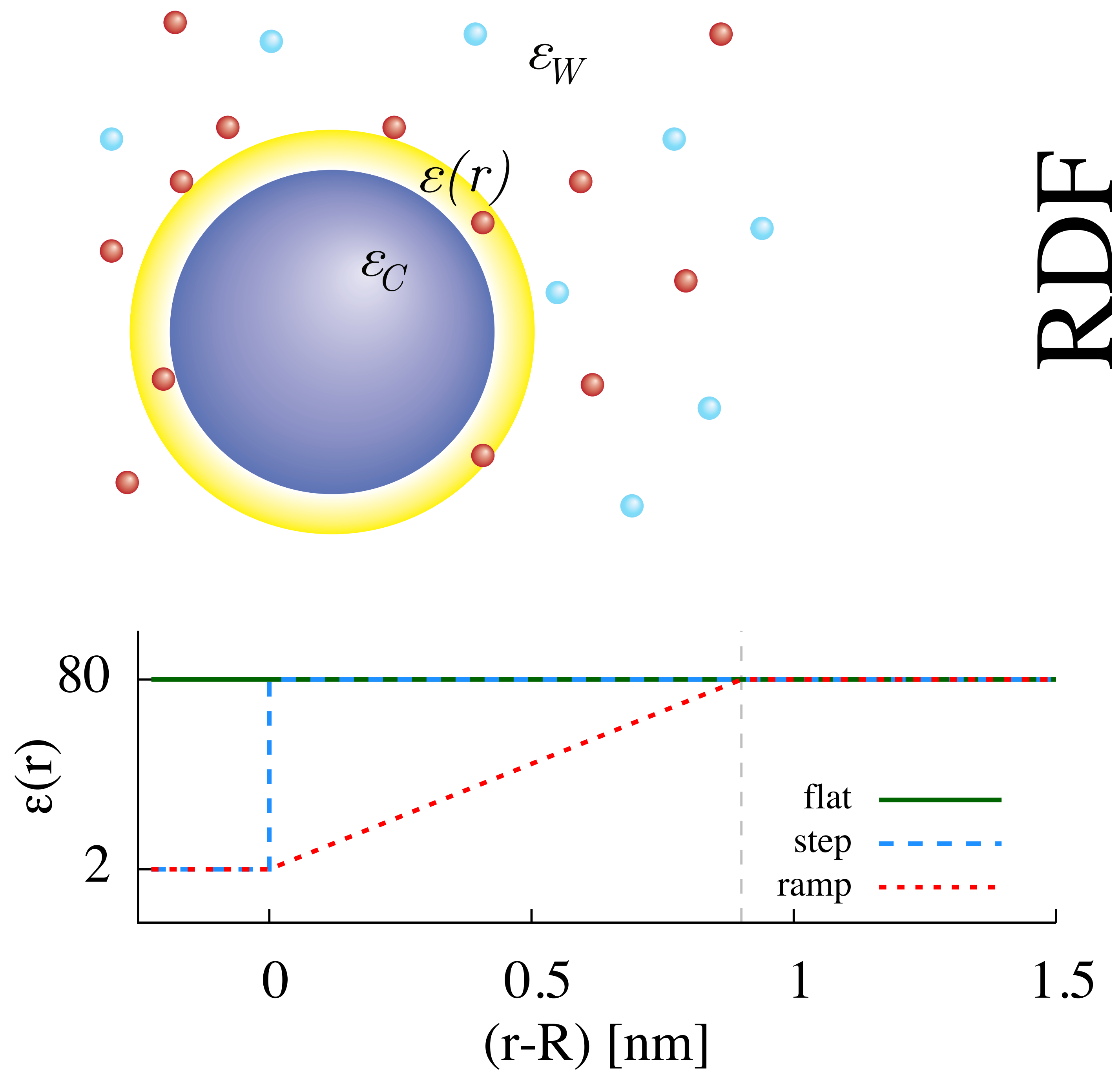
Discretization of MEMD

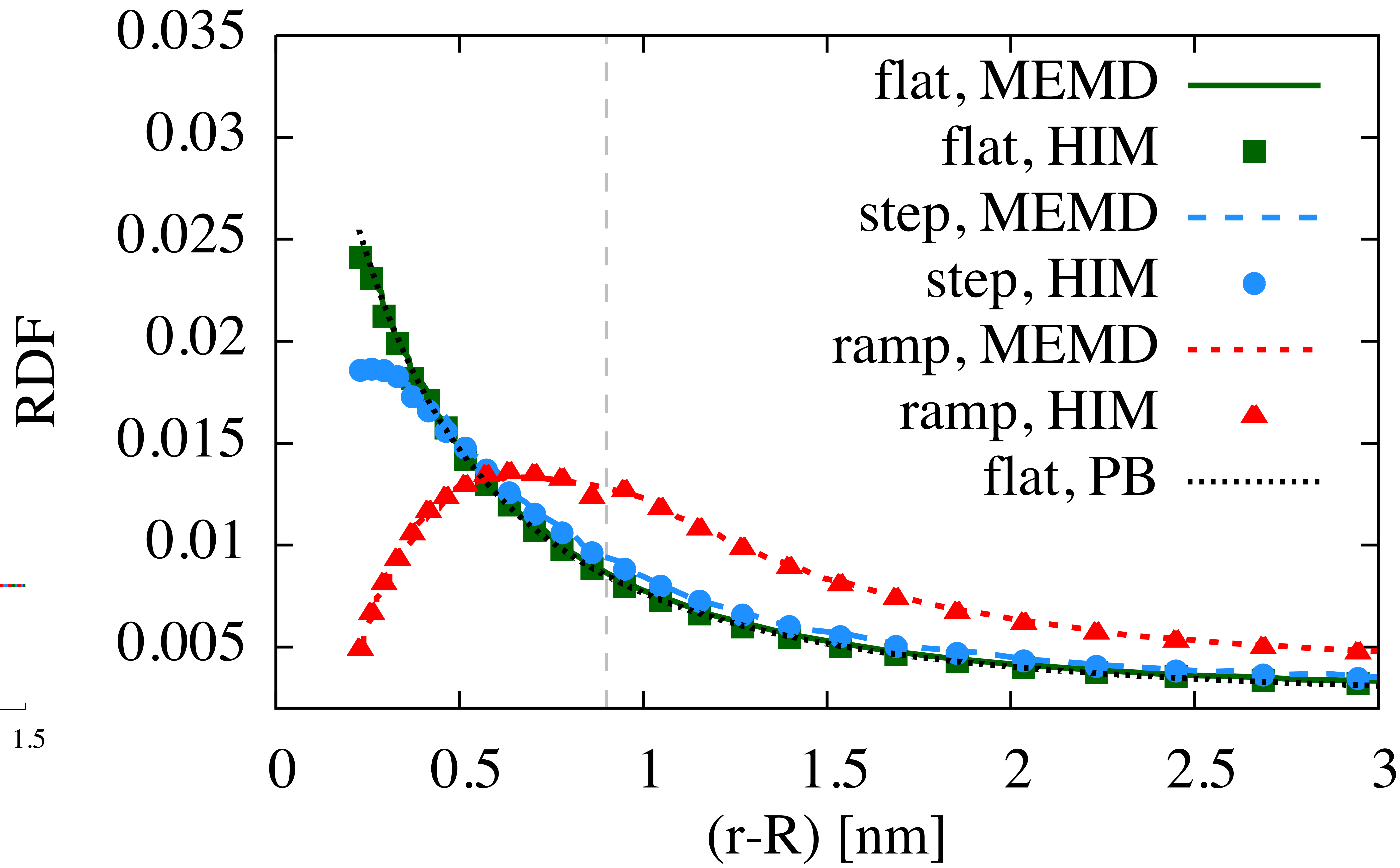
- permittivity as a vector (differential 1-form)
- permittivity difference between adjacent lattice points
- if gradient too steep: marked as interface link
- linearly interpolated



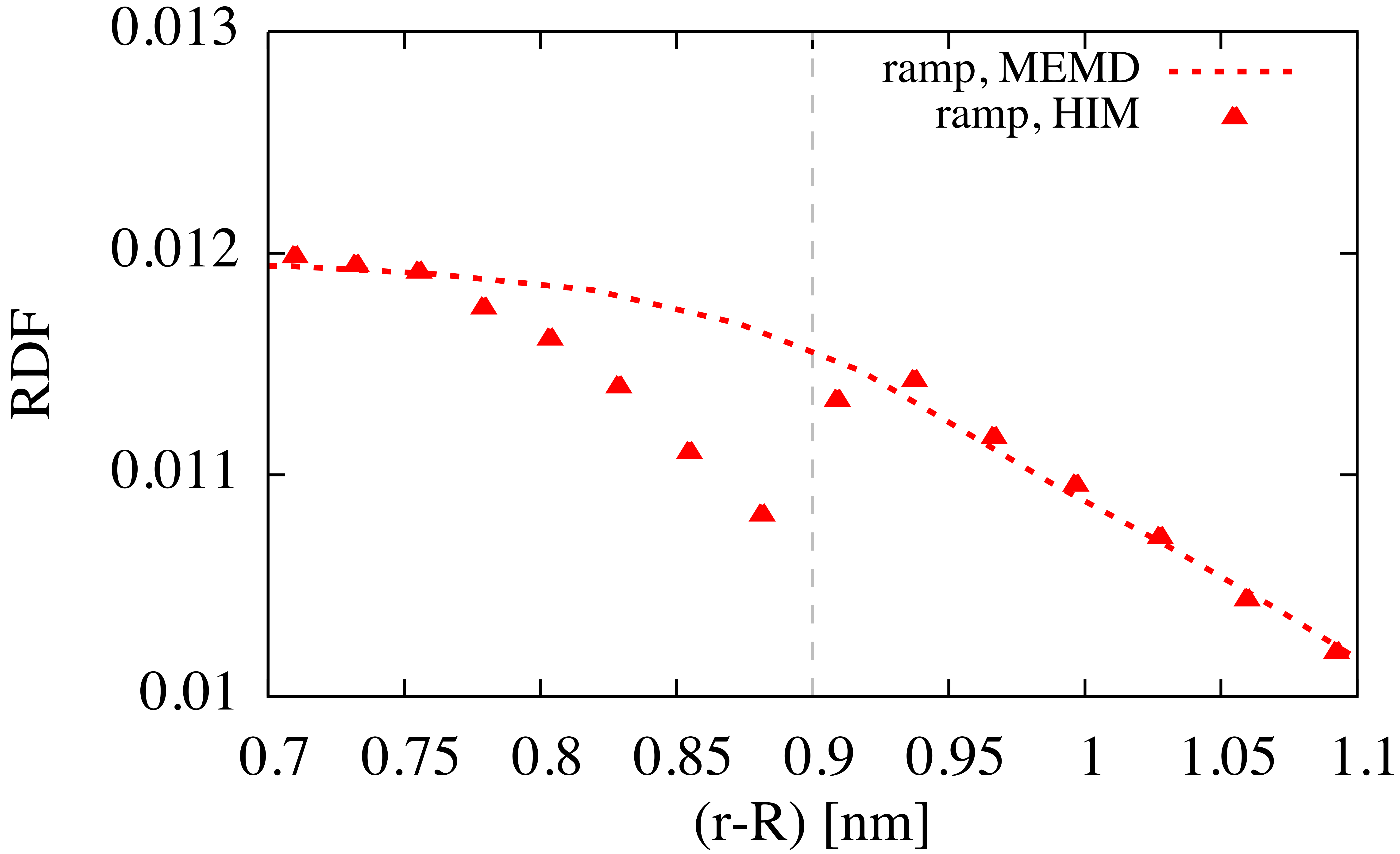
$$\varepsilon_{\mathrm{link}} = \varepsilon_1 \cdot \frac{d_2}{a} + \varepsilon_2 \cdot \frac{d_1}{a},$$

Results: counterion concentration

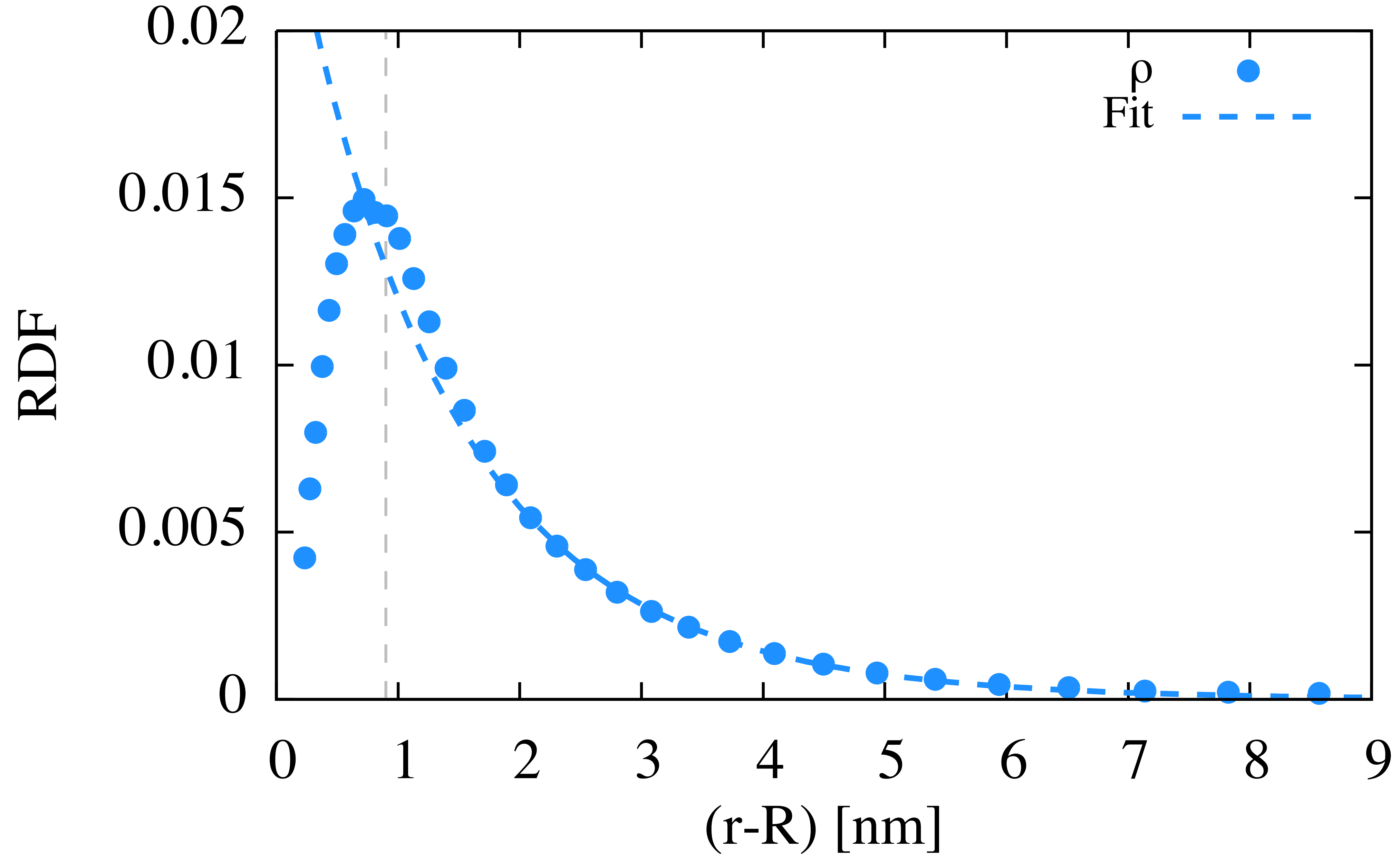




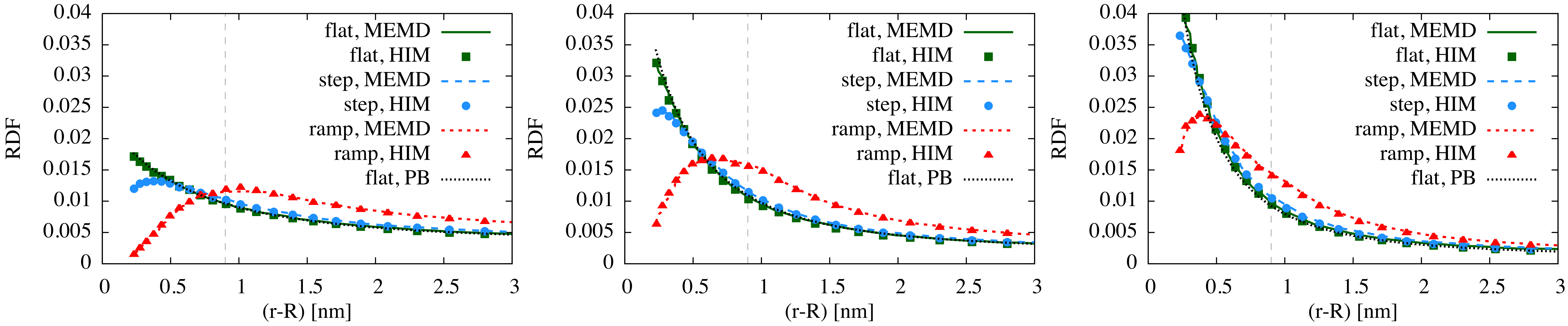
- high salt concentration, close to the surface
- funny kink:



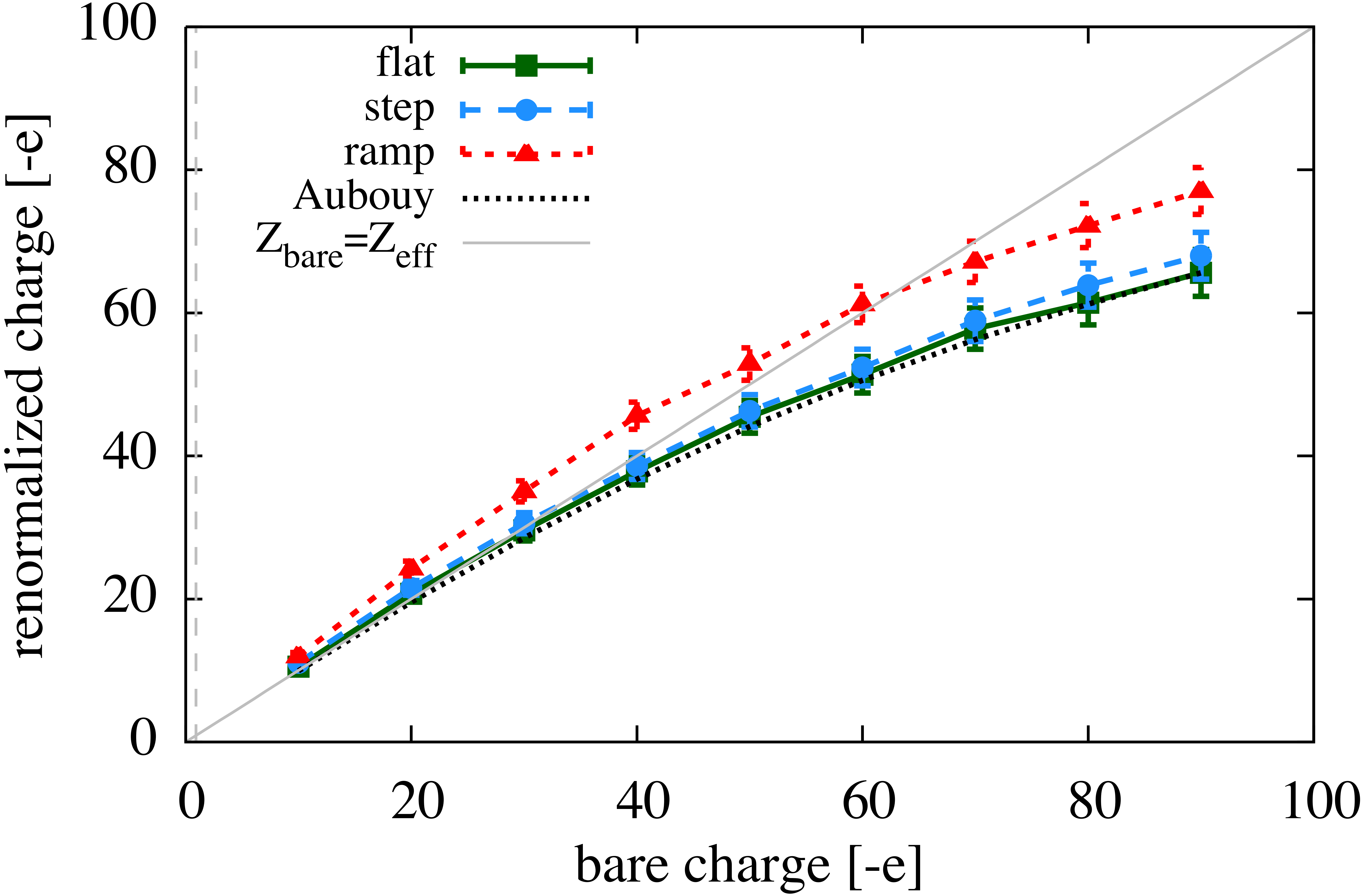
Charge renormalization



$$Z(r) = Z_{\mathrm{eff}} \cdot \frac{1+\kappa r}{1+\kappa R} e^{-\kappa(r-R)}$$

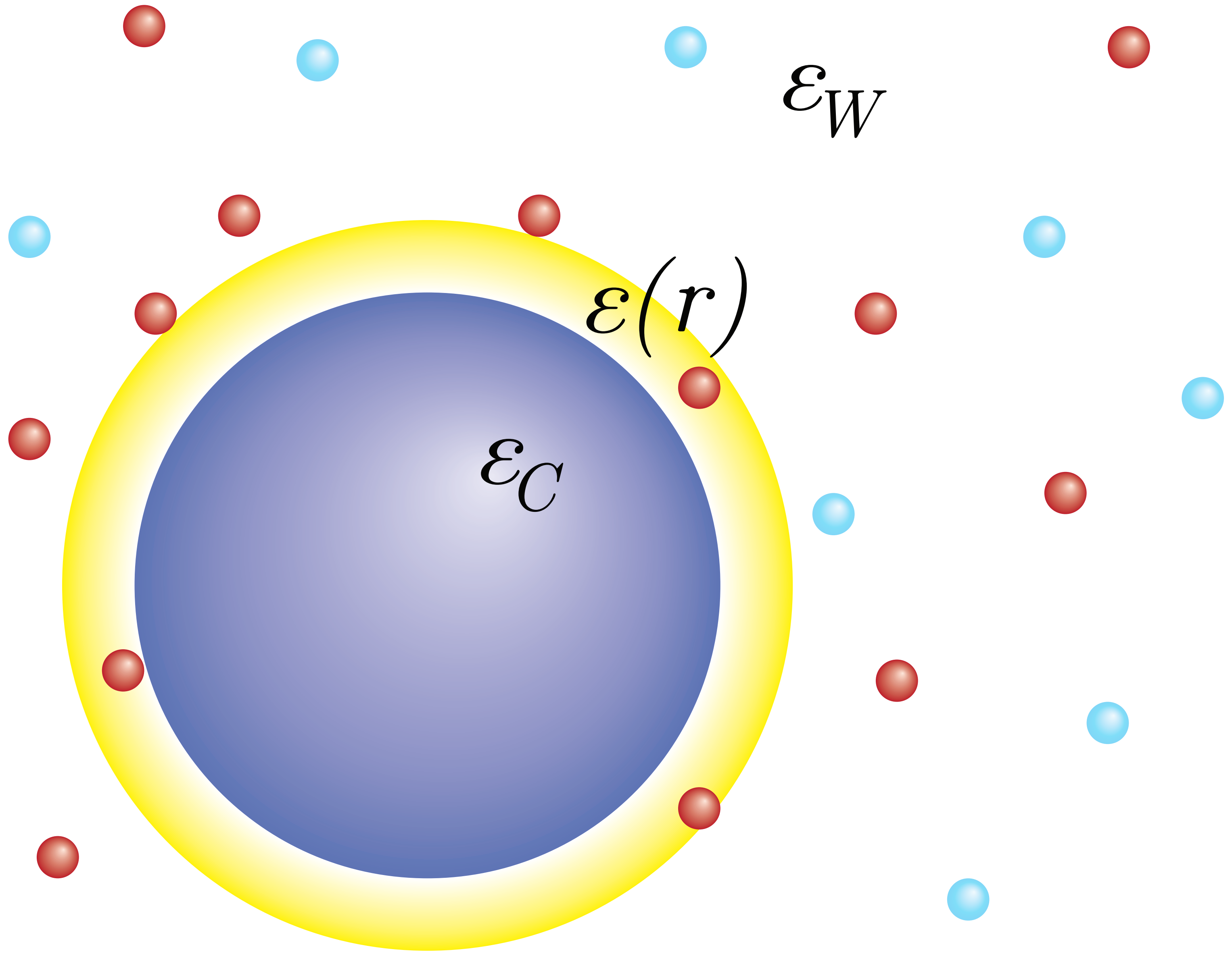


Renormalized charges



Summary

- The two methods agree very well
- Born radius self energy term can get very big
- Dielectric properties around colloids matter, even in the far field



Thank you.