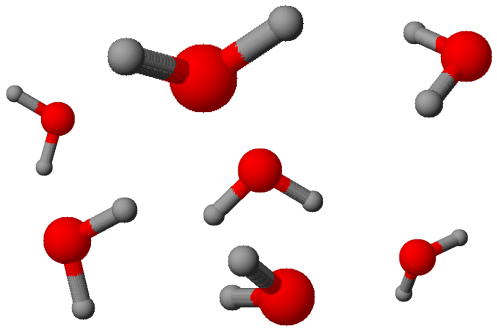
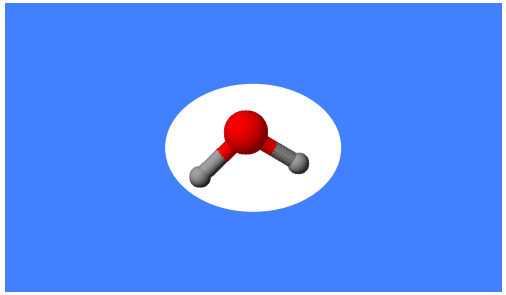
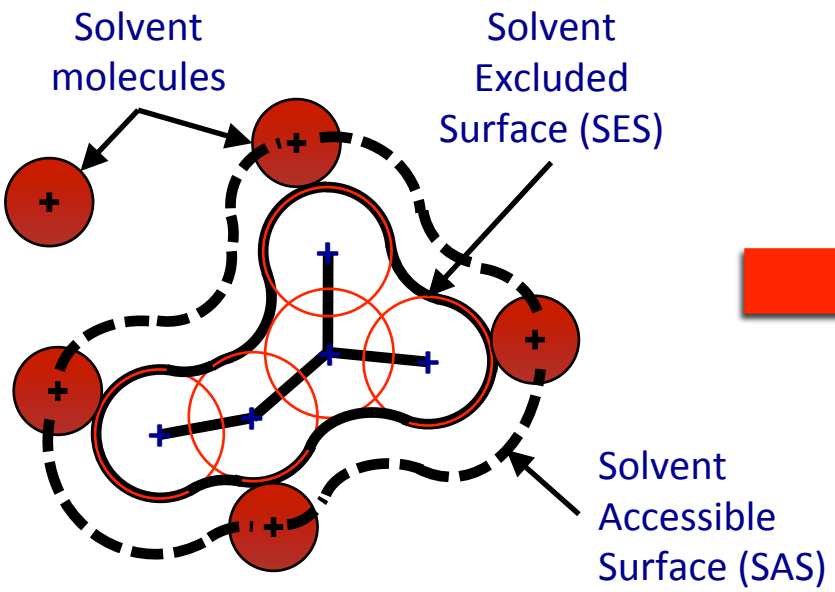
Simulation of solvent effects

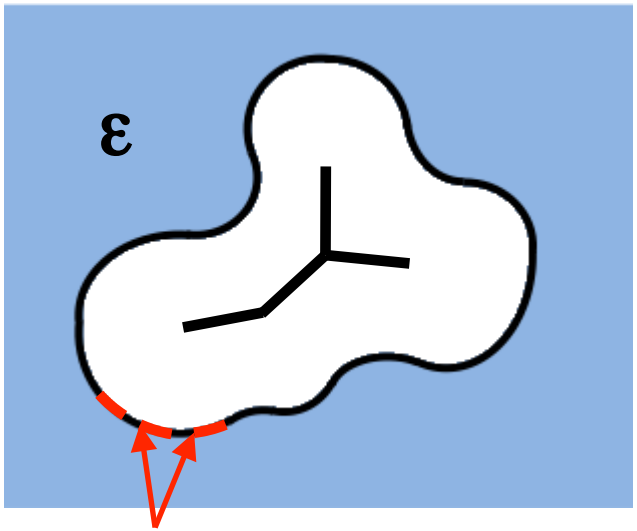
Solvation models

Models	Explicit solvent models	Continuum solvation models
Features	All solvent molecules are explicitly represented. 	Represent solvent as a continuous medium. 
Merits	Detail information is provided. Generally more accurate.	Simple, inexpensive to calculate
Disadvantages	Expensive for computation	Ignore specific short-range effects. Less accurate.

Polarizable Solvation models

Tomasi et al. *Chem. Rev.* **2005**, 105, 2999.





Tessera *k* of surface *a* with Apparent Surface Charge (ASC):

$$\sigma(k) = q(k)/a$$

ASC computed self-consistently:

$$\left(\frac{\varepsilon+1}{\varepsilon-1} - \frac{1}{2\pi}D\right)\sigma(k) = -\frac{1}{2\pi}E(k)$$

E(k): normal component of the electric field generated by the solute on the tessera k

D: operator accounting for the electrical field generated by σ itself

Polarizable Solvation models

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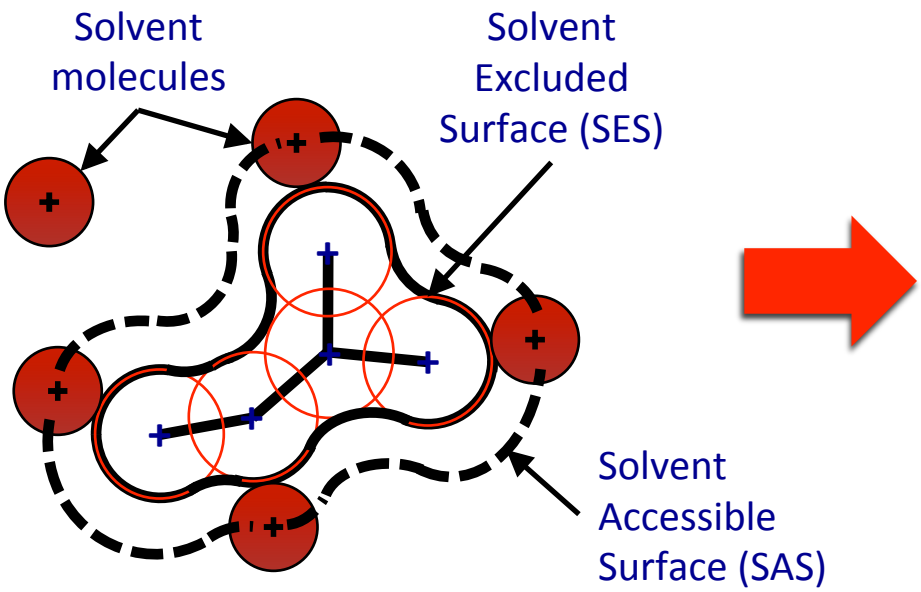
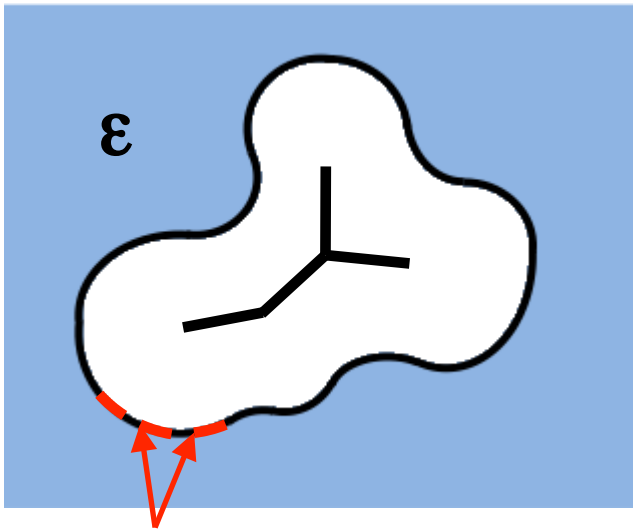




Tessera *k* of surface *a* with Apparent Surface Charge (ASC):

Hamiltonian operator for a solvated molecule

$$\hat{H} = \hat{H}_0 + \hat{V}_{MS}$$

$$\hat{V}_{MS} = \sum_k \sum_i \hat{V}(i,k) q(k)$$

V(i,k): *electronic potential operator at tessera k*

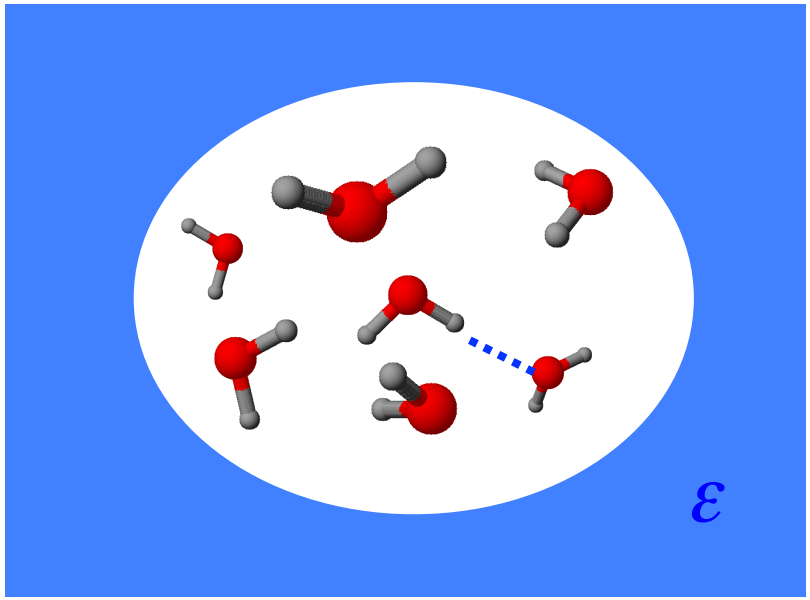
Solvation models

- The first solvation sphere is explicitly described by a number of solvent molecules.
- The remaining solvent molecules are described by an uniform continuum medium with a dielectric constant.

- Advantage:
  Account for specific short-range effects (e.g., H-bonding).

- Disadvantage:
  Increase computational cost.

- Generally give substantial better results than pure continuum models.



Which solvation model should be used?

- A compromise between accuracy and cost.
- Start with gas-phase model (without solvent) before you go for solvation models. Gas-phase calculations usually help to understand the quantum nature of the problem under study. Yet sometimes gas-phase models can be qualitatively wrong.
- Try continuum models before you go for explicit models. Continuum model calculations are unlikely to give you very accurate results, but they are informative in suggesting whether or not long-range solvation effects are important.
- Try mixed models before you go for explicit models. Mixed models are relatively easy to handle and less expensive, with possibly reasonably good results.