Molecular structure and properties at liquid surfaces and interfaces: the continuum solvation approach

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Outline

CTCC

Introduction

The first model: sharp interfaces
   The DPCM approach
   The IEF-PCM model

Diffuse interfaces
   The electrostatic model
   Beyond electrostatics for diffuse interfaces

Final remarks
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Final remarks
Are there polar bears in Tromsø?
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“Every attempt to employ mathematical methods in the study of chemical questions must be considered profoundly irrational. If mathematical analysis should ever hold a prominent place in chemistry – an aberration which is happily impossible – it would occasion a rapid and widespread degradation of that science.”

August Comte, (1798-1857)
Advancing chemistry through computation

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  August Comte, (1798-1857)

- “The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known and the difficulty is only in that the exact application of these laws leads to equations much too complicated to be soluble.”

  P. A. M. Dirac (1902-1984)
Advancing chemistry through computation

- **Mission of CTCC:** The Centre for Theoretical and Computational Chemistry (CTCC) will be a leading international contributor to computational chemistry by carrying out cutting-edge research in the field of theoretical and computational chemistry at the highest international level.
CTCC placement in chemistry

- Delocalized between UiT and UiO (Coordinated from UiT)
- 10 senior scientists: 5 from Oslo, 5 from Tromsø, 3 affiliates (2 UiO + 1 UiT).
Centre leadership: Kenneth Ruud og Trygve Helgaker

- Molecular properties
- Solvent effect
- Multiwavelets
- Relativistic method development
- Vibrational effects

- Accurate calculations
- Molecular properties
- Linear scaling Methods
- Periodic systems
- Optimization methods
Work Packages

- WP1: Large periodic and nonperiodic systems (T. Helgaker)
- WP2: Fragment approach for large systems (I. Roeggen)
- WP3: Multiscale methods with wavelets (T. Flå)
- WP4: Properties and Spectroscopy (L. Frediani)
- WP5: Dynamics and time development (E. Uggerud)
- WP6: Bioinorganic chemistry (A. Ghosh)
- WP7: Catalysis and organometallic chemistry (M. Tilset)
- WP8: Gas-phase reactions and photochemistry (C. J. Nielsen)
- WP9: Clusters, surfaces and solids (K. Fægri jr.)
Open positions

PostDoc positions in Oslo and Tromsø will be announced shortly (one connected to this project).

Project: Molecular properties at surfaces and interfaces
  - Work Package 1: Wavelet implementation
  - Work Package 2: Green’s function formalism
  - Work Package 3: Non-electrostatic solvation
  - Work Package 4: Molecular properties

Positions will be announced on our web site: www.ctcc.no
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Motivations and goals

- Interfaces are ubiquitous in nature
- Miniaturization: larger portion of the system at the surface
- Growth of spectroscopic techniques addressing chromophores at the surface
- Main goal: description of molecular structure and chromophores at surfaces (project recently financed, PostDoc position available).
Modelling solvation with continuum methods

A few thoughts....

- Continuum solvation modelling: solute-solvent electrostatic interaction is generally considered.
- The physical foundation of electrostatic models is simple, well known, has macroscopic counterpart.
- Non-electrostatic interactions are less investigated. What are non-electrostatic interactions? How are they modeled? No macroscopic model!
- Solvation process: cavitation, electrostatics, repulsion, dispersion.
- In bulk solution non-electrostatic interactions can “safely” be ignored: cancellation effect.
- At the interface, the whole solvation process has to be revisited: non-electrostatics terms matter!
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Electrostatics

A BEM approach: molecular cavity and interface.

\[ \sigma^\eta(s) = -\frac{1}{4\pi} \left(1 - \frac{\epsilon_i^\eta}{\epsilon_e^\eta}\right) E_i^\eta(s) \cdot n(s) \] (1)

Problems: interface tessellation, intersection, numerical instability
Non-electrostatic interactions

Cavitation: energy needed to “create” the cavity

\[ G_{cav.} = \sum_i \frac{a_i}{4\pi r_i^2} G_{cav}(R_i) \quad (2) \]

\[ G_{cav.} = \sum_\gamma \sum_i \frac{a_i^\gamma}{4\pi (r_i^\gamma)^2} G_{cav}(R_i^\gamma) \quad \gamma = 1, 2 \quad (3) \]

Simple interface extension: two cavitation energy terms, one for each solvent.
Non-electrostatic interactions

Lennard-Jones interaction between solute and solvent.

\[ V(u) = -\frac{36V_0}{u_0^2}(u - u_0)^2 - V_0 \]

Dispersion

\[ G_{\text{dis.}}^S(M) = -\sum_{n=6,8,10} \sum_{s \in S} \sum_{m \in M} d_{ms}^{(n)} N_s \rho_S \int_{\Omega_s} \frac{g_{ms}(r_{ms})}{r_{ms}^n} \, dr^3 \]  

\[ G_{\text{dis.}}^{S_1}(M) = \sum_{n=6,8,10} \sum_{s \in S_1} \sum_{m \in M} d_{ms}^{(n)} N_s \rho_{S_1} \times \]

\[ \times \left[ \sum_{t_s} A_{ms}(r_{nts}) \cdot n_{ts} a_{ts} + \sum_{t_p} A_{ms}(r_{mnt}) \cdot n_{p} a_{tp} \right] \]
Non-electrostatic interactions

Lennard-Jones interaction between solute and solvent.

\[ V(u) \]

Repulsion

\[ G_{rep.}(M) = \sum_{s \in S} \sum_{m \in M} c_{ms} N_s \rho S \int_{\Omega_s} g_{ms}(r_{ms}) e^{-\gamma_{ms} r_{ms}} \, dr^3 \quad (2) \]

\[ A_{ms}(r_{ms}) = c_{ms} \left[ \frac{1}{\gamma_{ms} r_{ms}} + \frac{2}{\gamma_{ms}^2 r_{ms}^2} + \frac{2}{\gamma_{ms}^3 r_{ms}^3} \right] e^{-\gamma_{ms} r_{ms}} \cdot r_{ms} \quad (3) \]
Aliphatic alcohols at the gas-water surface

Experiment (kinetics of the phase transfer), Nathanson et. al., J. Phys. Chem. 100, 13007, 1996
Aliphatic alcohols at the gas-water surface

Aliphatic alcohols at the gas-water surface

Continuum Model results
Cavitation, Repulsion, Electrostatic, Dispersion

Distance, (Å)

Energy, Kcal/mol
Aliphatic alcohols at the gas-water surface

Continuum Model results

Non-electrost. Total

![Graph showing energy vs distance for aliphatic alcohols at the gas-water surface, with energy in Kcal/mol on the y-axis and distance in Å on the x-axis. The graph displays smooth curves for different states of interaction.]
Aliphatic alcohols at the gas-water surface

Continuum Model results
From methanol to octanol
The Green’s function approach

Operative definition: Potential generated by a unit point charge.

\[ \nabla_r \cdot \epsilon(r) \nabla G(r, r') = -4\pi \delta(r - r') \]  

(4)

The solvent details are “hidden” in the Green’s function.

\[ \int_{\Gamma} A(G_i, G_e) V(s) \, ds = \int_{\Gamma} B(G_i, G_e) \sigma(s) \]  

(5)
The Green’s function challenge

Green’s functions are known for the following environments:

- Homogeneous dielectric: $\epsilon(r) = \epsilon$
- Liquid crystal: $\epsilon(r) = \epsilon_{ij}$ ($i, j = x, y, z$)
- Ionic solution: $\epsilon \Delta V + \kappa^2 V = -4\pi \rho$
- Sharp planar interface:
  
  $$
  \epsilon(r) = \begin{cases} 
  \epsilon_1 & \text{if } z \geq 0 \\
  \epsilon_1 & \text{if } z < 0
  \end{cases}
  $$

- Diffuse planar interface: $\epsilon(r) = \epsilon(z)$

General case $\epsilon(r)$ is a complex problem we would like to address!
Integral Equation Formalism

\[ \rho(r) \]

\[ V(\rho) = D(G^I, G^O) \cdot \sigma(s) \]

\[ D^{-1}(G^I, G^O) \cdot V(\rho) = \sigma(s) \]

\( G^I \) and \( G^O \): electrostatic Green’s functions inside and outside the cavity.
QM calculations require operators on a basis of orbitals:

$$F_{\mu\nu} = \langle \chi_{\mu} \mid \hat{F} \mid \chi_{\nu} \rangle$$  \hspace{1cm} (6)

Solvent operators have an additional index over the sampling points of the cavity:

$$F_{\mu\nu} = \sum_i F^i_{\mu\nu}$$  \hspace{1cm} (7)

A medium size system: $10^3$ basis functions, $10^4$ sampling points on the cavity. $N = 10^3 \cdot 10^3 \cdot 10^4 = 10^{10}$ elements!!.
PNF at the water surface

B3LYP/6-311+G(d,p)

<table>
<thead>
<tr>
<th>Environment</th>
<th>$\lambda_{\text{max}}$ (nm, calc)</th>
<th>$\lambda_{\text{max}}$ (nm, exp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum</td>
<td>295</td>
<td>—</td>
</tr>
<tr>
<td>Hexane</td>
<td>—</td>
<td>284</td>
</tr>
<tr>
<td>Water surface (z = -2Å)</td>
<td>312</td>
<td></td>
</tr>
<tr>
<td>Water surface (z = 0Å)</td>
<td>314</td>
<td>310</td>
</tr>
<tr>
<td>Water surface (z = 2Å)</td>
<td>320</td>
<td></td>
</tr>
<tr>
<td>Bulk water</td>
<td>325</td>
<td>322</td>
</tr>
</tbody>
</table>
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Diffuse interfaces

Green’s function: (numerical integration required)

\[ G^E(r, r') = \frac{1}{D(\epsilon(z))|r - r'|} + G_{im}^E(r, r') \]  

(8)
Beyond sharp interfaces

Energetics: Chloride anion
Interface thickness: 7Å

![Graph showing energetic changes with distance for 7Å interface thickness](image1)

Interface thickness: 20Å

![Graph showing energetic changes with distance for 20Å interface thickness](image2)
Beyond sharp interfaces

Spectroscopy: Charge Transfer transition in DEPNA (diethylparanitroanilinle)

\[ \text{N} \text{N} \text{O} \text{O} \text{CH}_2 \text{CH}_3 \quad \text{N} \text{N} \text{O} \text{O} \text{CH}_2 \text{CH}_3 \quad \hbar \omega \]

1. Steep-profile

2. Density-derived profile

\[ \text{Energy} \quad \epsilon(z) \quad \text{Distance Å} \]

\[ \text{Energy} \quad \epsilon(z) \quad \text{Distance Å} \]
Quantistic repulsion

Pauli repulsion between solute and solvent proportional to the electron density outside the cavity.

\[ G_{\text{rep}} = \alpha \int_{r \notin C} \, d\mathbf{r} P_A(\mathbf{r}) \]  

(9)

For interfaces the position dependent density \( \rho(\mathbf{r}) \) is introduced.

\[ G_{\text{rep}} = \alpha' \int_{r \notin C} \, d\mathbf{r} P_A \rho(\mathbf{r})(\mathbf{r}) \]  

(10)
Iodide and nitrile as surfactants

- Surfactant behavior for halides was excluded by conventional wisdom.
- X-ray and PS spectroscopy of medium-size water cluster containing halides gave evidence of the contrary
- Simulations with polarizable (many body) potentials confirmed the picture
- Continuum solvation gave the same qualitative picture when dispersion was introduced
Iodide and nitrile as surfactants

1. Halides

2. $\text{N}_3^-$
Quantistic dispersion

Mutual polarization of two molecules (solute and solvent)

\[ G_{disp} = -\frac{1}{4} \sum_{rstu} \beta [rs|tu] P_{ru} \left\{ (S^{-1})_{st} - \frac{P_{st}}{2} \right\} \] (11)

\( \beta \) depends on the solvent and it becomes position-dependent at the interface:

\[ \beta(z) = \frac{\eta^2(z) - 1}{\eta(z) \left( \eta(z) + \frac{\omega_A}{I_B(z)} \right)} \] (12)

Problem: Solute-solvent dispersion is computationally expensive
Cavitation for diffuse interfaces

\[ G_{\text{cav}} = \sum_i a_i \frac{4\pi R_i^2}{4\pi R_i^2} G(R_i) \]  

(13)

\[ G_{\text{cav}} = \sum_i \frac{[1 - w(z_i)] a_i}{4\pi R_i^2} G_1(R_i) + \sum_i \frac{w(z_i)a_i}{4\pi R_i^2} G_2(R_i) \]  

(14)

\[ G_{\text{inter}} = -\gamma S = -\gamma \int_{\Gamma_C} \frac{\arctan(z/D)}{\pi} n_z \, ds \]  

(15)
Full model: preliminary results

Formaldehyde CH$_2$O

![Graph showing energy and distance relationships for various forces (total, cavitation, repulsion, dispersion, electrostatics).]
Full model: preliminary results

Methanol CH$_3$OH

Energy, Kcal/mol vs Distance, (Å)

- Total
- Cavitation
- Repulsion
- Dispersion
- Electrostatics
Full model: preliminary results

Ethanol $\text{CH}_3\text{CH}_2\text{OH}$

![Graph showing energy vs distance for Ethanol with different components: total, cavitation, repulsion, dispersion, electrostatics.](image)
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- The role of non-electrostatic interactions is crucial. Their effect on properties should be investigated in more detail, not only for interfaces.
Conclusions

- Continuum models can be applied successfully to surfaces and interfaces.
- One of the main challenges (theoretical AND computational) is an effective description of electrostatics in complex environments.
- The role of non-electrostatic interactions is crucial. Their effect on properties should be investigated in more detail, not only for interfaces.
- The classic objection: what about specific interactions? MD for structure and layered models QM/MM/PCM could/should be employed.
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