

Estimation of Evaporation/Condensation Coefficients by Quantum Statistical Mechanics Theory (QSMT)

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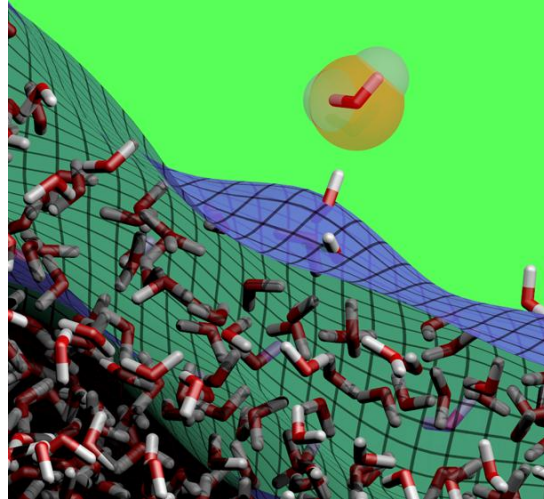


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Outline

- Evaporation/Condensation Coefficient
- Quantum Mechanics Effects During the Evaporation/Condensation
 - Classical Force Fields against to Quantum Chemical Potentials
- Quantum Statistical Mechanics Theory (QSMT)
 - How and Why?
- Alternative Methodology for Observing of these Effects
 - Ab initio MD (AIMD) Simulation
- Advantages and Drawbacks

- probability of the crossing of the interface by a molecule

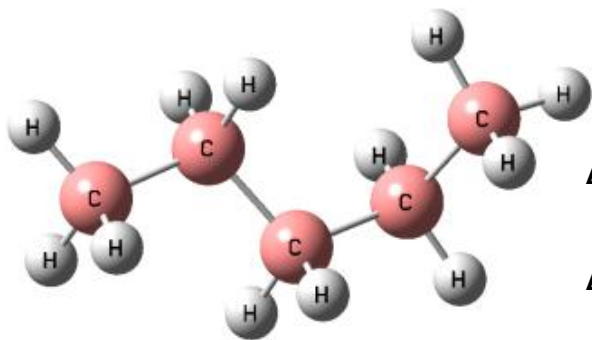


Ref: J. Phys. Chem. B 2013, 117, 1419–1428

Although conceptually seems to be simple, BUT

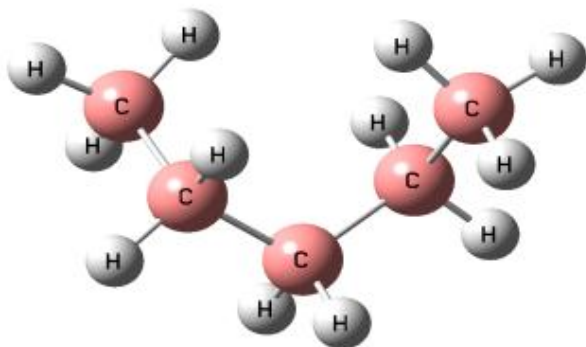
- This coefficient are quite difficult to measure
- This coefficient for water has been varied in the range **0.01–1**.
Why?

Quantum Mechanics Effects During the Evaporation



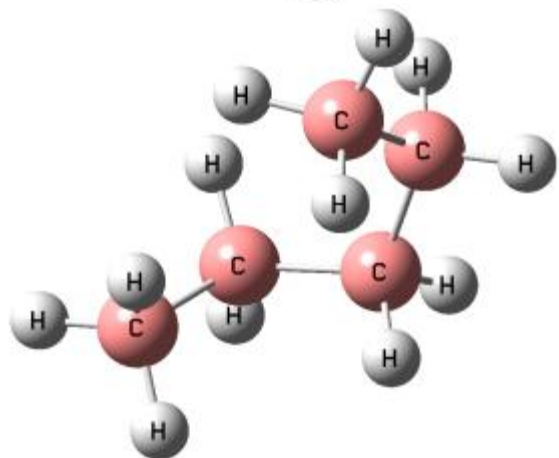
$\Delta E = 0.58$ Kcal/mol \rightarrow QC calculations; *Ref: J. Phys. Chem. A. 117:3118-32 (2013).*

$\Delta E = 0.94$ Kcal/mol \rightarrow OPLS-FF results; *Ref: J. Phys. Chem. B. 110, 21198 (2006).*



$\Delta E = 0.91$ Kcal/mol

$\Delta E = 1.89$ Kcal/mol



$\Delta E = 2.76$ Kcal/mol

$\Delta E = 3.29$ Kcal/mol

Relative errors of OPLS
FF are in the range

20 to 100%

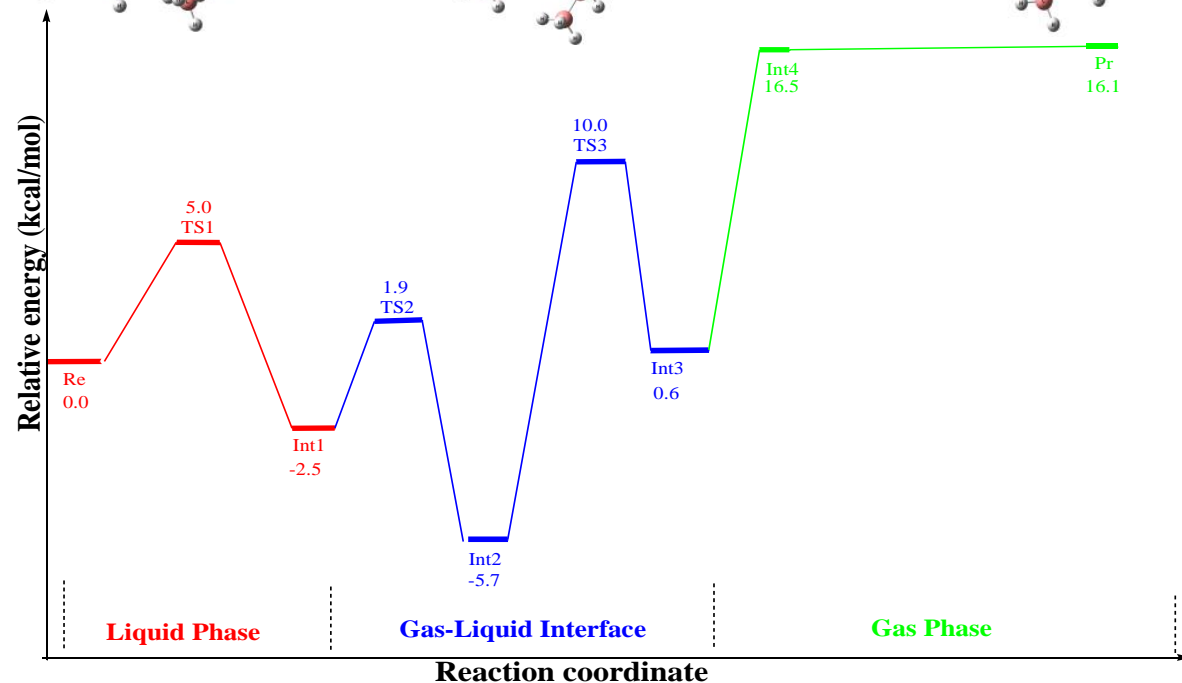
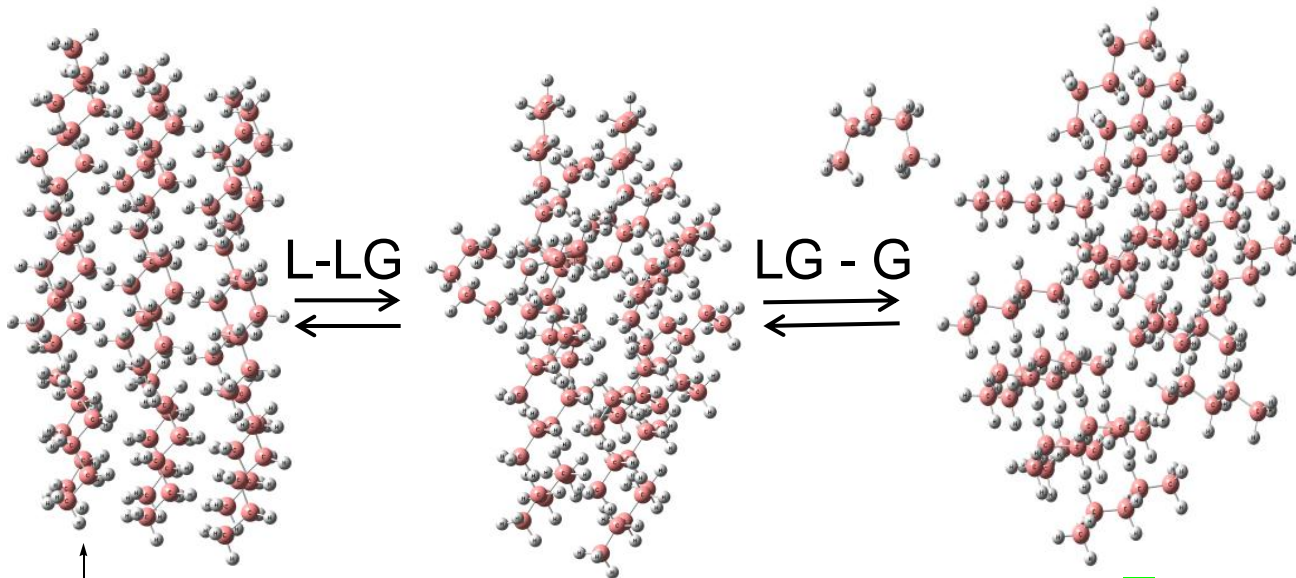


ΔE is about **1-3 kcal/mol**,
Sampling by OPLS FF
would be challenging



Classical FF cannot be
reliable for modelling of
hydrocarbons

Quantum Mechanics Effects During the Evaporation



*New insight
In evaporation of fuel
droplet using QC
calculations*

Ref:

Quantum mechanical effects in *n*-alkane droplets. Nasiri, R. et. al., It's to be presented in ILASS, 1-5 September 2013.

- 1- Phase transformations between L and L-G \rightarrow Activation processes
- 2- Transition between L-G and G \rightarrow No energy barrier
- 3- Multi-step process \rightarrow Evaporation coefficient cannot be limited by only one value even under constant thermodynamic conditions

In Classical MD, No Electronic Effects :
Electrostatic and Dispersion, Polarization

Those can be Significant in the Fuel Droplet System
Due to High Temperature and Nature of Structure

Uncertainty in Estimation of the Properties,
Then Need for Improved Method

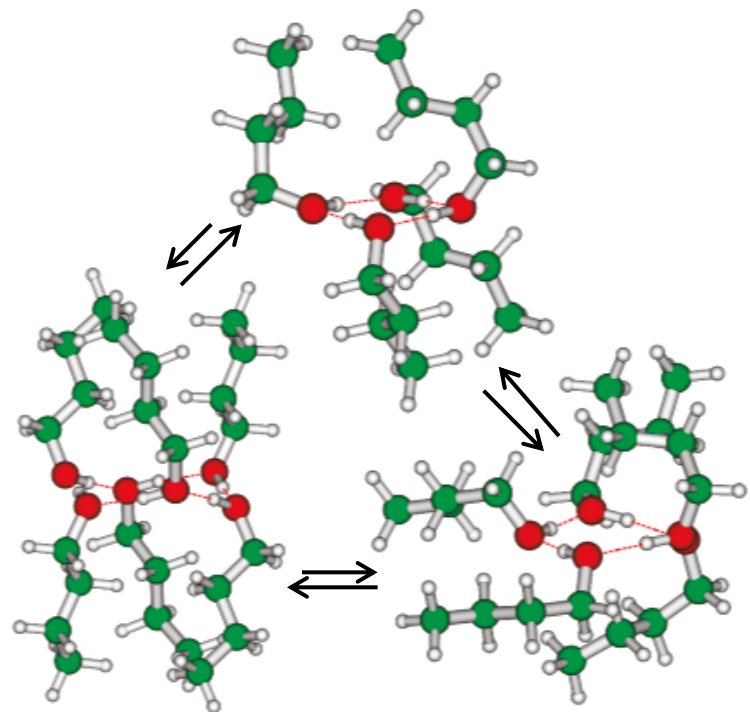
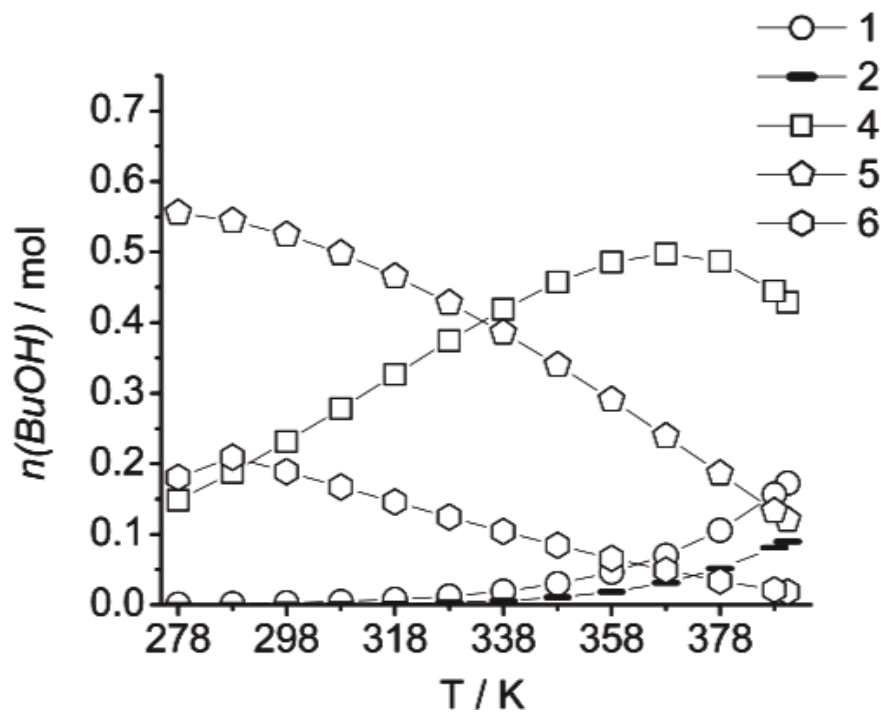
Mathematical Basis

$$\langle E^{\text{tot}} \rangle = \sum_{\varphi=1}^N N_{\varphi} (\langle E_{\varphi} \rangle + \langle u_{\varphi}^{\text{int}} \rangle)$$

$$E^{\text{tot}} = \sum_{\varphi=1}^N N_{\varphi} (\mathcal{E}_{\varphi}^{\text{tr}} + \mathcal{E}_{\varphi}^{\text{vib}} + \mathcal{E}_{\varphi}^{\text{rot}} + \mathcal{E}_{\varphi}^{\text{el}} + u_{\varphi}^{\text{int}}).$$

$$\begin{aligned} Q^{\text{tot}}(\{N_{\varphi}\}, V, T) &= \prod_{\varphi=1}^N (N_{\varphi}!)^{-1} \left(\sum_{\substack{n_x, n_y, n_z, \\ n^{\text{vib}}, J}} \exp\left\{-\frac{E_{\varphi}(n_x, n_y, n_z, n^{\text{vib}}, J)}{k_B T}\right\} \exp\left\{-\frac{u_{\varphi}^{\text{int}}}{k_B T}\right\} \right)^{N_{\varphi}} \\ &= \prod_{\varphi=1}^N (N_{\varphi}!)^{-1} \left[\sum_{n_x, n_y, n_z} \exp\left\{-\frac{\mathcal{E}_{\varphi}^{\text{tr}}(n_x, n_y, n_z)}{k_B T}\right\} \sum_J \exp\left\{-\frac{\mathcal{E}_{\varphi}^{\text{rot}}(J)}{k_B T}\right\} \right. \\ &\quad \left. \times \left(\prod_{m=1}^{3K-x} \sum_{n^{\text{vib}}} \exp\left\{-\frac{\mathcal{E}_{\varphi}^{\text{vib}}(n^{\text{vib}}, \nu_{m\varphi})}{k_B T}\right\} \right) \exp\left\{-\frac{\mathcal{E}_{\varphi}^{\text{el}}}{k_B T}\right\} \exp\left\{-\frac{u_{\varphi}^{\text{int}}}{k_B T}\right\} \right]^{N_{\varphi}}. \end{aligned}$$

Application



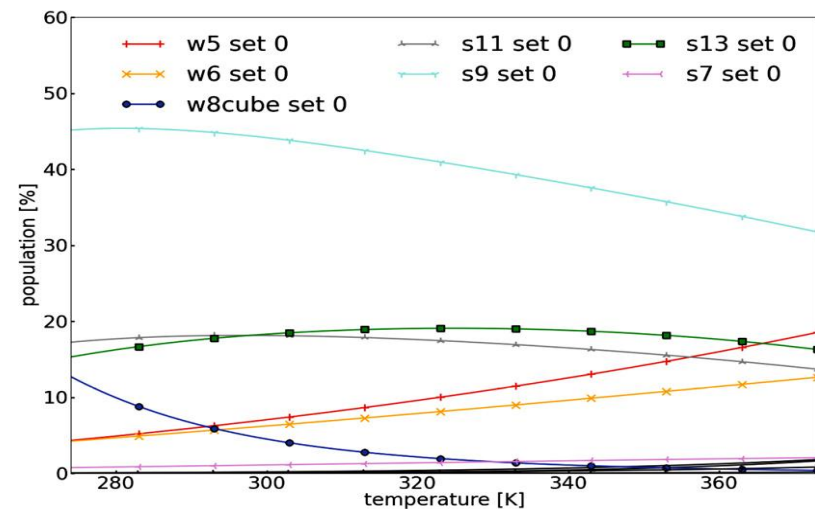
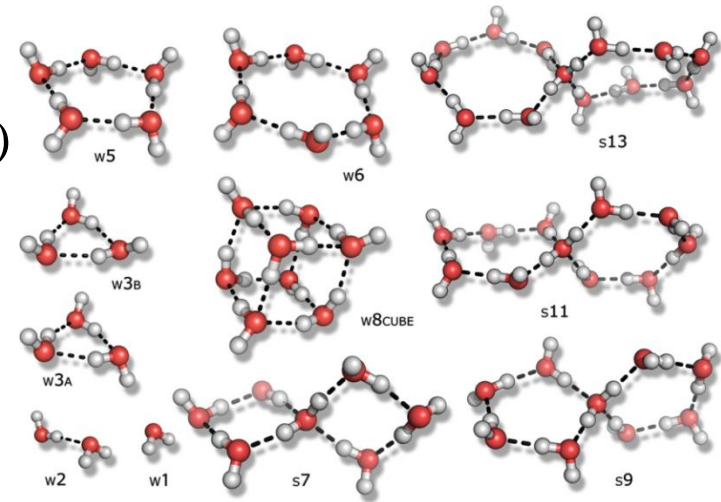
Reference : J. Phys. Chem. B 2011, 115, 3936–3941

1- Calculation of intra-molecular interactions
(Electronic, Vibrational, Rotational, Translational)
energies by quantum chemistry tools,

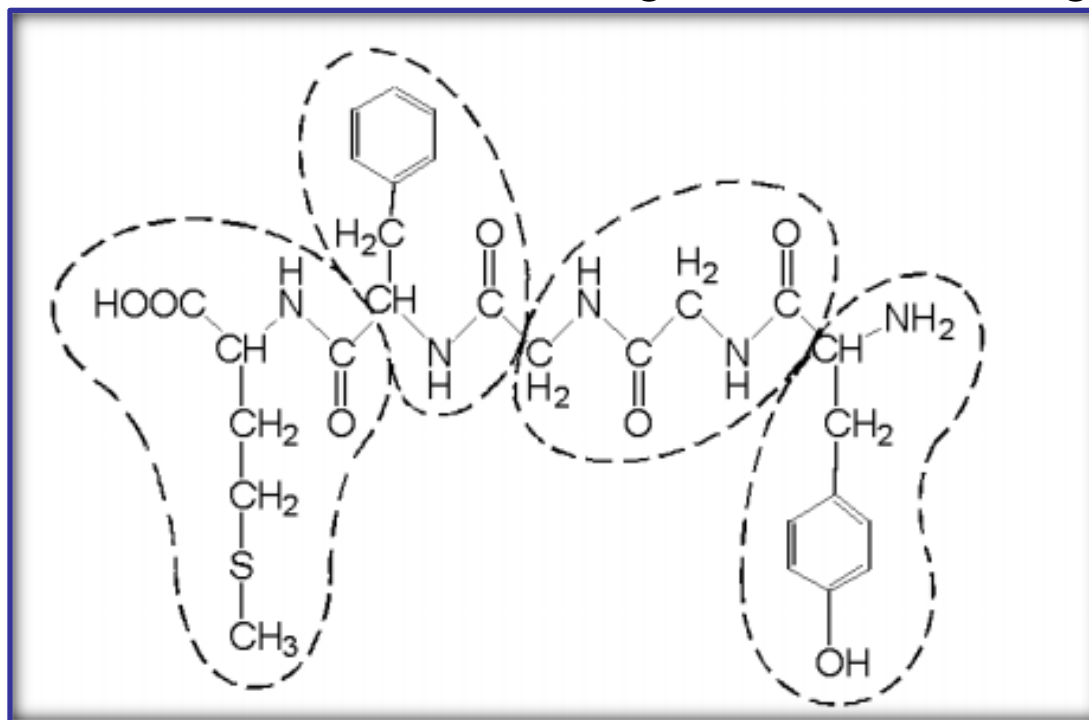
2- Calculation of the inter-molecular interactions
using different types of clusters,

3- Calculation of energy barrier for removal of one
molecule in the wide range of thermodynamic
conditions,

4- Estimation evaporation/condensation
coefficients.



Ab initio MD simulation using FMO methodology



- ✓ Divide the system into fragments
- ✓ Calculate Coulomb interactions of each fragment with the rest of the system
- ✓ Do *ab initio* calculations on fragments and their *n*-mers

Advantages:

- ✓ Reduce of Computational Costs
- ✓ Similarity in both Methods:
Local Density of Electronic States (LDES) but with Different Strategies
- ✓ FMO-MD:
LDES is extended up to $\sim 10^5$ atoms
- ✓ QSMT
High accuracy with high level ab initio potentials

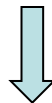
Disadvantages:

- ❖ FMO-MD:
Required time of Supercomputer machine.
- ❖ QSMT
Effects of anharmonicity should be considered in high temperatures

First strategy:

Quantum Statistical Mechanics Theory (QSMT)

Specification of cluster set from quantum chemical calculations



Determination of interaction energies



Set pressure and temperature range to calculate



Determination of transition species between clusters as local minima



Estimation of barrier energies and evaporation/condensation coefficients

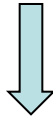
Second strategy:

AIMD simulation using FMO technique

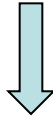
Performing MD simulation with QC potential to bring the system to equilibrium in a desired temperature (vapor-liquid Equilibria)



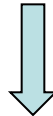
Doing a constraint MD simulation in NVT ensemble



Determination of profile free energy for removal a molecule from nanodrop



Estimation of a set of free energy barriers



Evaporation/Condensation Coefficients

Thanks for Your
Attention

Suggestion and
Question?