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Surface Phenomenon at the liquid/vapor interface of water and methanol from first principles simulation

I-F. W. Kuo, C. Mundy, M. McGrath, J. I. Siepmann

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SURFACE PHENOMENON AT THE LIQUID/VAPOR INTERFACE OF WATER AND METHANOL FROM FIRST PRINCIPLES SIMULATION

I-Feng W. Kuo and Christopher J. Mundy
Lawrence Livermore National Laboratory

Matthew J. McGrath and J. Ilja Siepmann
University of Minnesota

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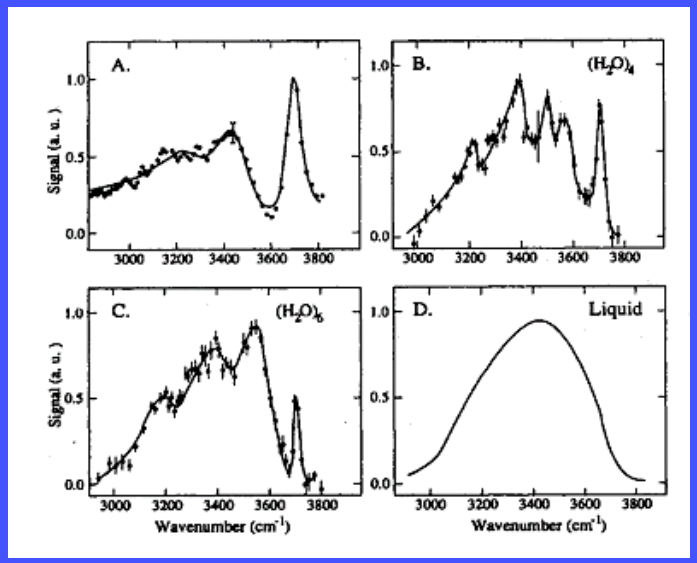
Experiments offer new insights into the liquid-vapor interface of hydrogen bonded systems

Sum Frequency Generation (SFG)

Du et. al., *Phys. Rev. Lett.* 70, 2313 (1993)
Raymond *et. al. J. Phys. Chem. B* 107, 546 (2003)

single donor

Free OH-stretch



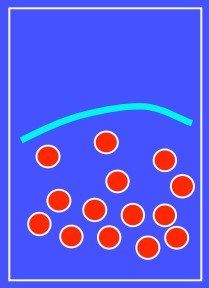
NEXAFS and EXAFS

Wilson *et. al., J. Phys. Chem. B* 105, 3346 (2001)
Wilson *et. al., J. Chem. Phys.* 117, 7738 (2002)
Wilson *et. al., J.Phys. Cond. Matt.* 14, L221 (2002)

Water

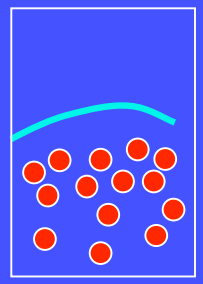
"acceptor only"

increase of O-O distance



Methanol

decrease of O-O distance



Are polarizable force fields necessary for the determination of interfacial properties?

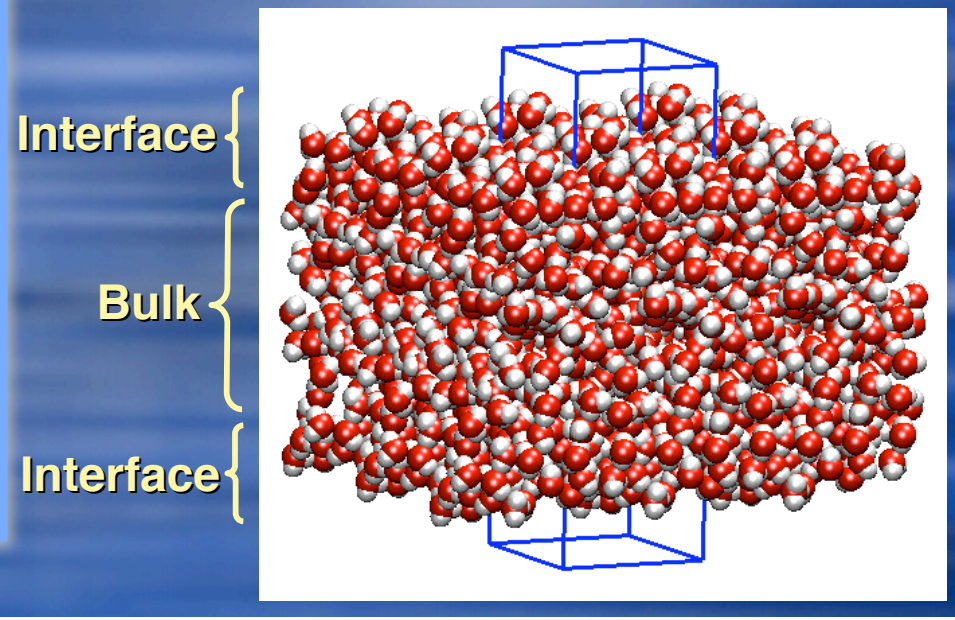
Simulating the liquid-vapor interface with ab initio methods is a computational challenge

- Empirical force fields
  - Parameterized to reproduce bulk properties
  - No Chemistry
- *Ab initio* methods provide a direct link to spectroscopy and reactivity at a large computational expense

Wilson *et. al.*, JCP 91, 4973 (1987)
342 water molecules
21.71Å x 21.71Å x 65.1 Å
Slab thickness = 21.71 Å
TIP4P

We need a criteria for simulating a stable interface via *ab initio*

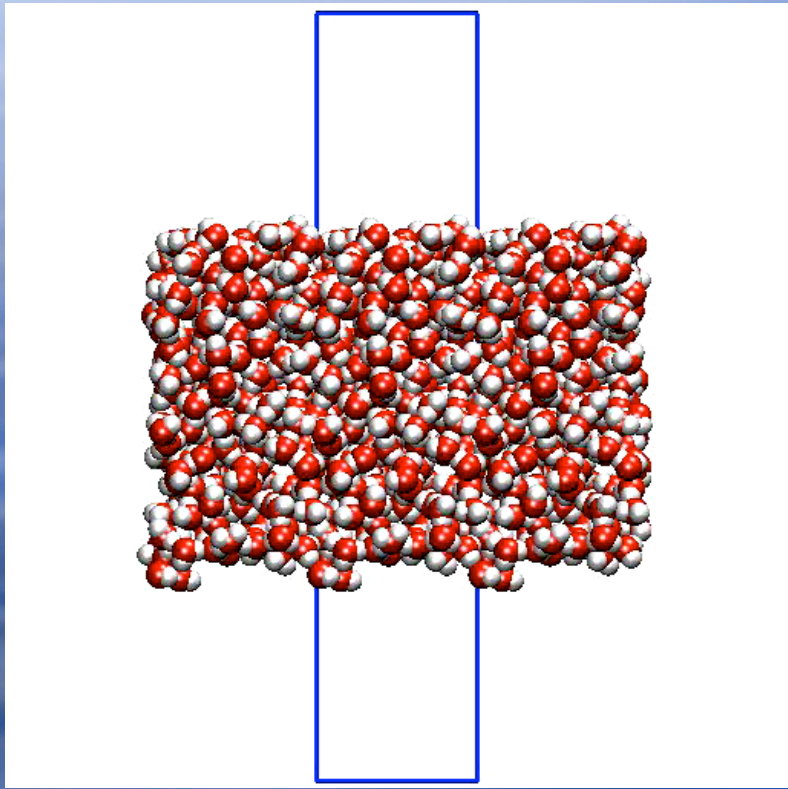
Thick enough to obtain adequate amount of bulk
Vacuum to prevent coupling of free interfaces



LLNL's tera-scale resources are enabling ab initio investigations of heterogeneous systems

- LLNL's MCR Linux cluster (www.top500.org)
  - Intel 2.4 GHz Xeon processor with Quadrics
  - 1440 CPU's (720 nodes)
  - CPMD (60% parallel efficiency)
  - 0.7 million CPU hours (21 days)

- **Kuo and Mundy, *Science* 303, 658 (2004)**
  - 6.5 ps production trajectory
  - 400 a.u. fictitious electronic mass
  - NVT
    - Thermostats on every degree of freedom
    - 300K
  - BLYP with 70 Ryd cut-off (orbitals)
  - 15Å x 15Å x 71.44 Å
  - Slab thickness ~ 35Å
  - 216 water molecules

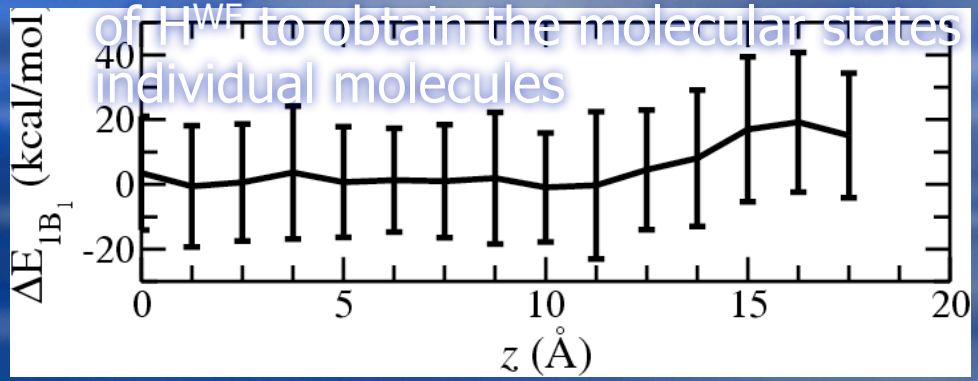


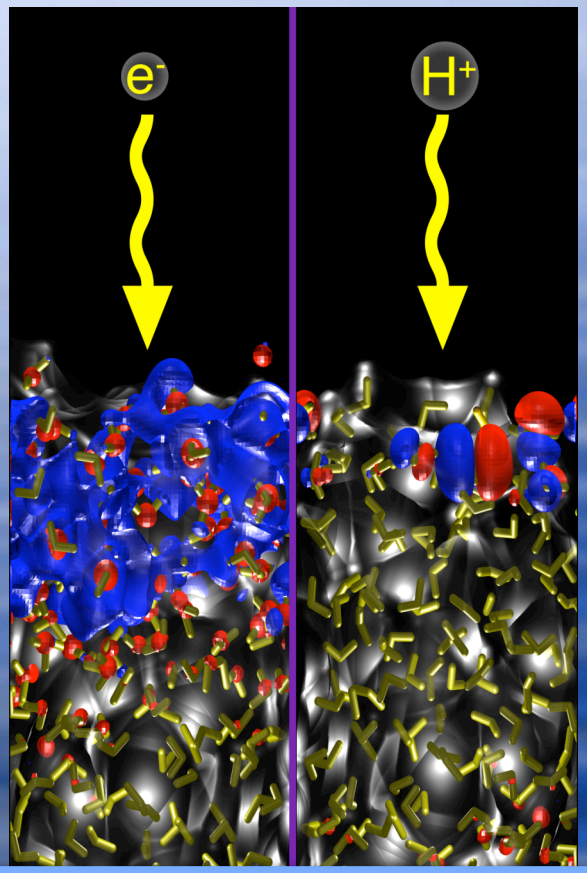
Ab initio simulations can give insight into reactivity of interfacial systems

- Project H^{KS} in a localized (Wannier function) basis **Vuilleumier and Sprik, JCP 115, 3454 (2001)**

$$H_{ij}^{WF} = \sum_k U_{ik}^{*} U_{jk} H_{kk}^{KS}$$

- Rediagonalize each molecular sub-block of H^{WF} to obtain the molecular states of individual molecules





- HOMO and LUMO via

Molecular states eigenvalues reveal interface reactivity

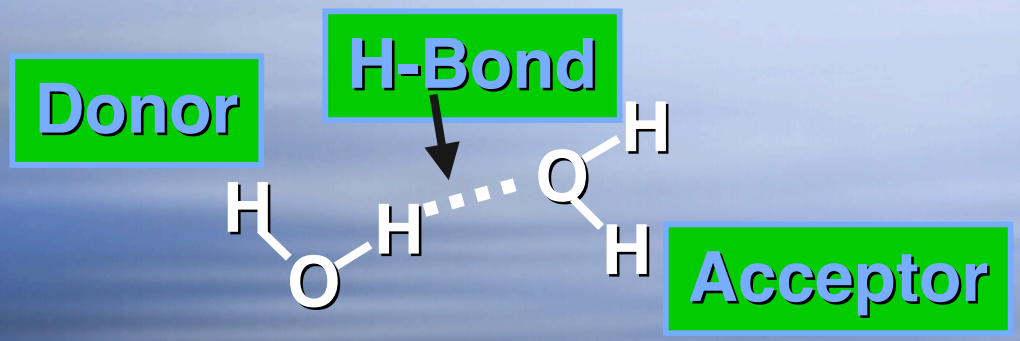
Kuo and Mundy, *Science* 303, 658 (2004)

Classical models of interfaces will provide further calibration of BLYP results

- **TIP4P**
  - Jorgensen, *et al*, JCP 79, 926 (1983)
  - 1500 waters, 28 Å x 28 Å
- **TIP4P-FQ**
  - Rick, Stuart, Berne, JCP 101, 6141 (1994)
  - 1500 waters, 28 Å x 28 Å
- **TIP4P-POL2**
  - Chen, Xing, Siepmann, JPCB 104, 2391 (2000)
  - Breathing LJ radii
  - 1500 waters, 28 Å x 28 Å
- **SPC/E**
  - Berendsen *et al*, JPC 91, 6269 (1987)
  - 1500 waters, 28 Å x 28 Å

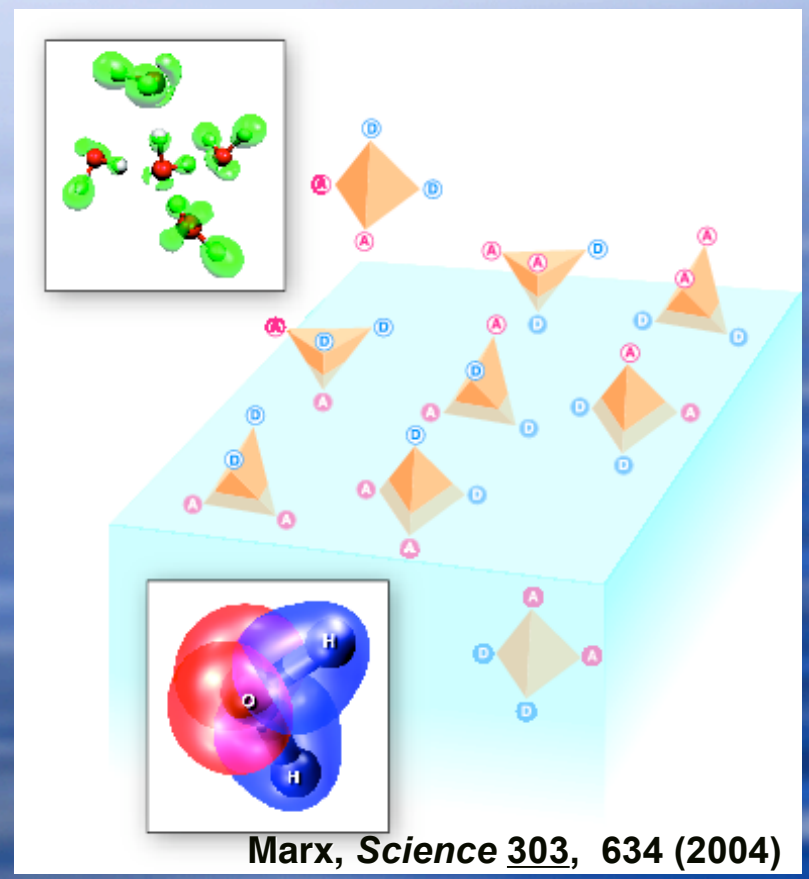
	Surface tension @ 300 K [mN/m]	Saturated vapor pressure @ 373K [kPa]
TIP4P	56	146
TIP4P-fq	82	390
TIP4P-pol2	66	173
SPC/E	-	43
exp	72	101

Are surface moieties sensitive to hydrogen bonding criteria and interaction potential?



		Acceptor only	Single donor
Empirical potentials	Bulk	6-29%	31-42%
	interface	8-34%	51-56%
BLYP	Bulk	3-23%	31-41%
	interface	8-34%	51-56%

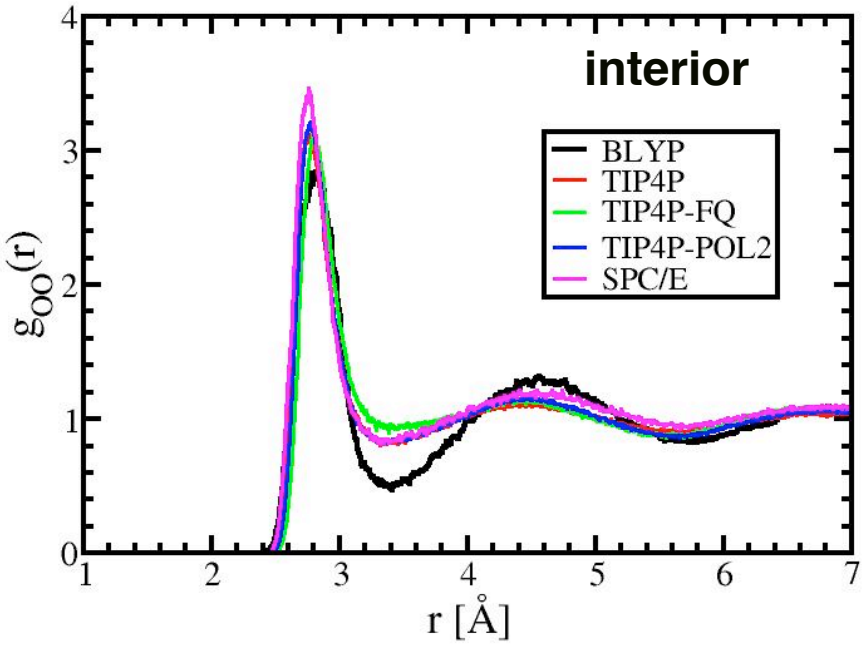
Kuo *et. al.* JCP-B 110, 3738 (2006)

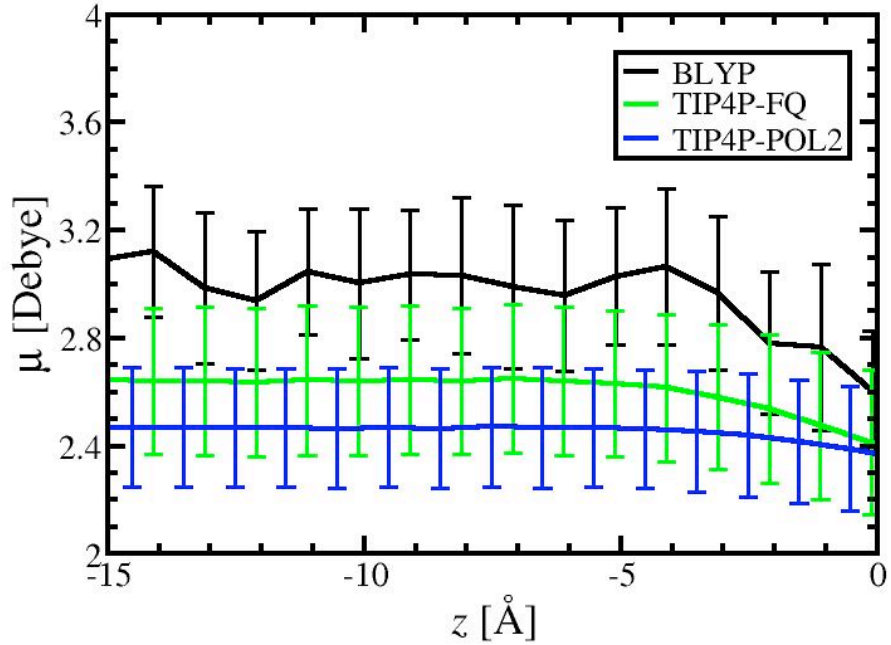


Marx, *Science* 303, 634 (2004)

Independent of H-bond criteria and interaction potential the interface is always populated with more acceptor-only and single-donor

Structural and electronic properties of the interfacial systems are in good agreement

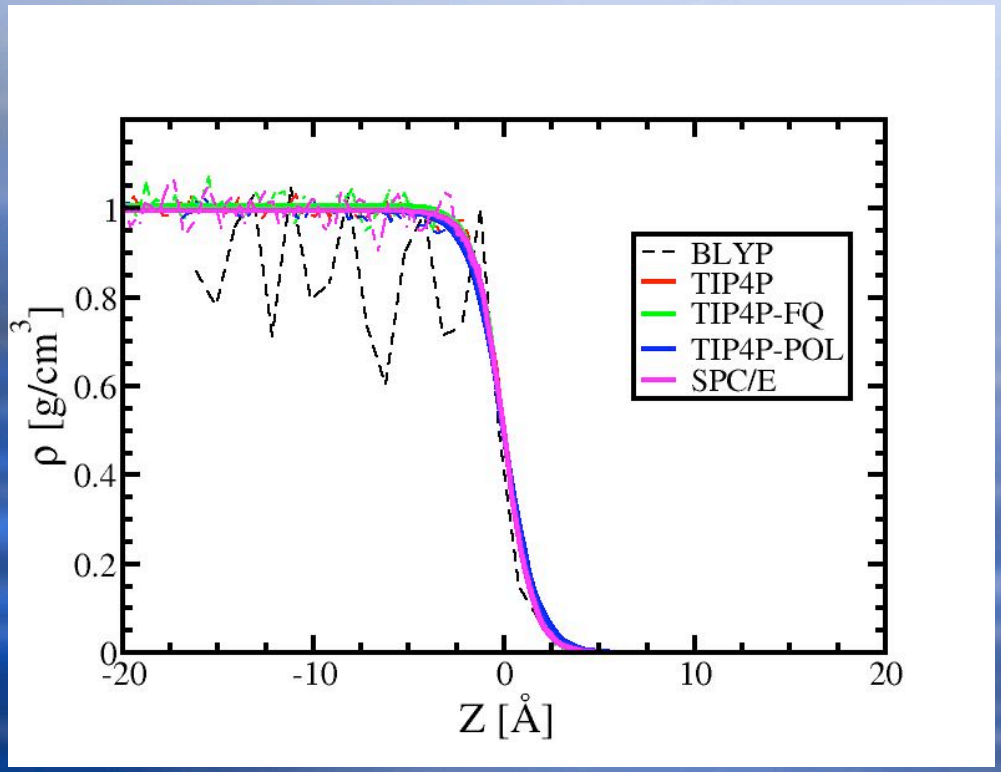




Summary:

- **BLYP RDF is under-structured (bin width 0.02 Å)**
- **BLYP dipole moment decreases more dramatically**

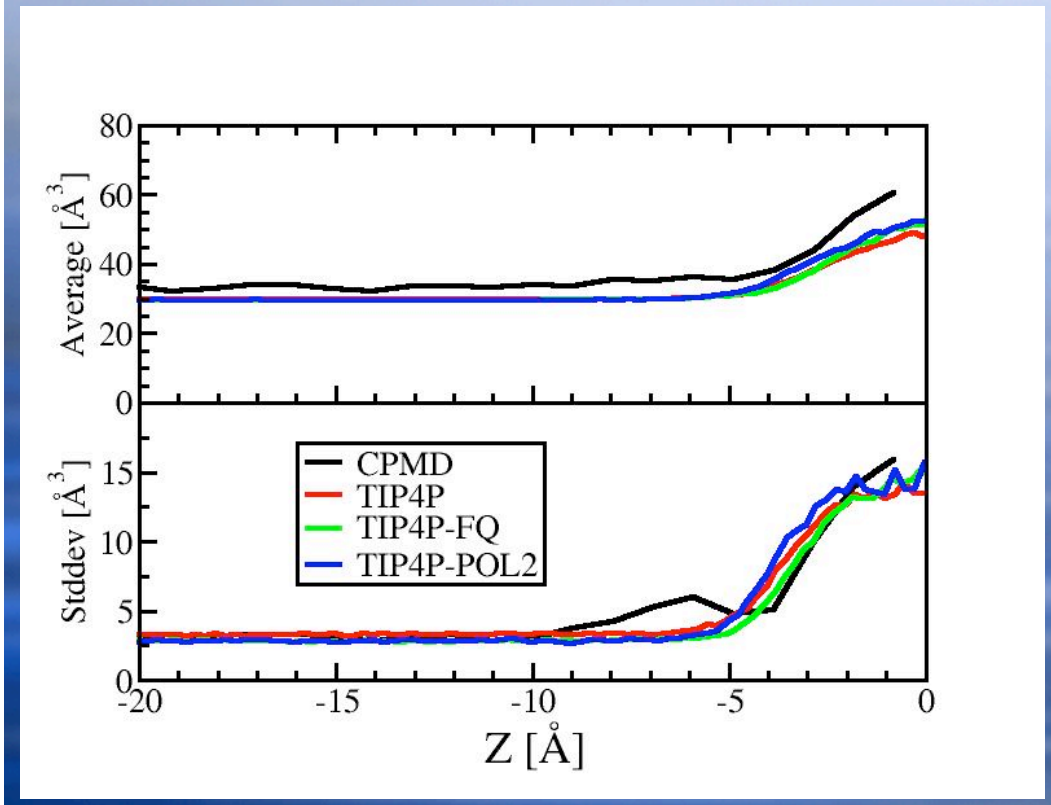
Density profile is the strongest indicator of a stable interface



	ρ [g/cc]	δ [Å]
BLYP	0.857	0.78
TIP4P	0.999	1.57
TIP4P-FQ	1.007	1.57
TIP4P-POL2	0.995	1.78
SPC/E	1.00	1.53

$$\rho(z) = \frac{1}{2}(\rho_l + \rho_v) - \frac{1}{2}(\rho_l + \rho_v)\tanh\left(\frac{z - z_{\mathrm{GDS}}}{\delta}\right)$$

BLYP interface shows more expansion in the vicinity of Gibb's dividing surface



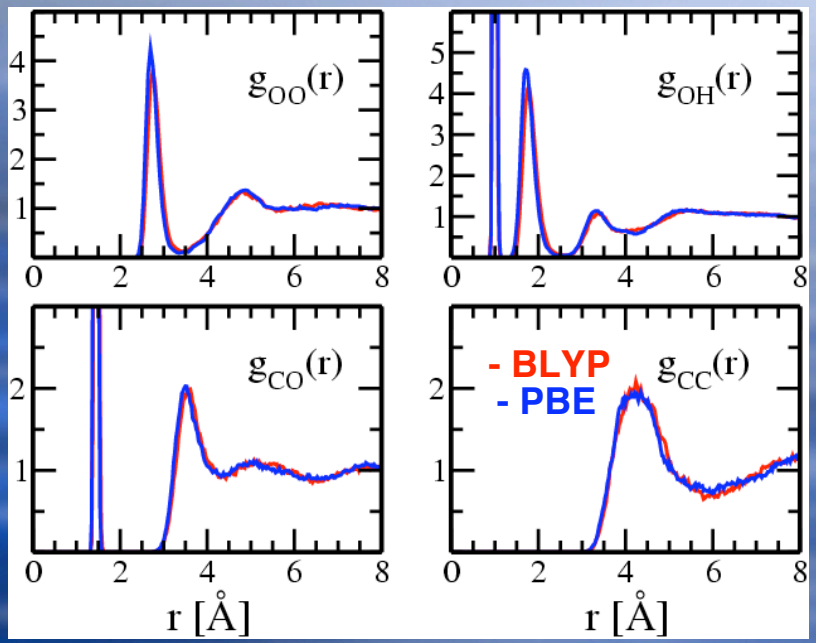
	$\langle r_{OO} \rangle$ [Å]	
	interior	surface
BLYP	2.93	2.96
TIP4P	2.96	2.94
TIP4P-FQ	2.99	2.99
TIP4P-POL2	2.97	2.94
SPC/E	2.95	2.93

All analysis point to surface relaxation for BLYP interface in agreement with x-ray

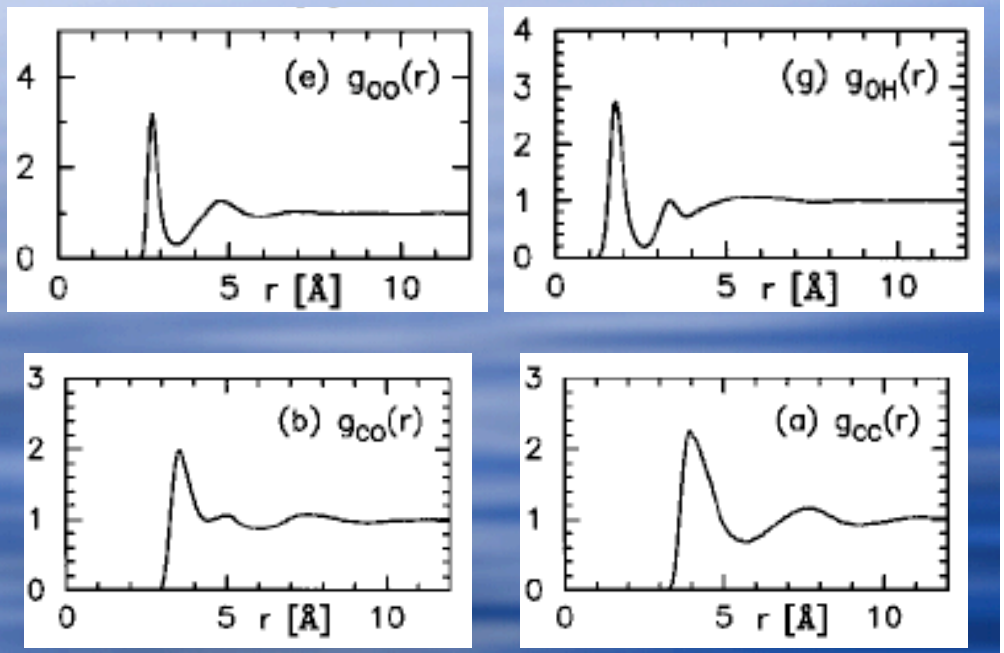
Wilson *et. al., J. Chem. Phys.* 117, 7738 (2002)

Can DFT interaction potentials give accurate structural data for bulk methanol?

Simulation



EXPT. (Soper)

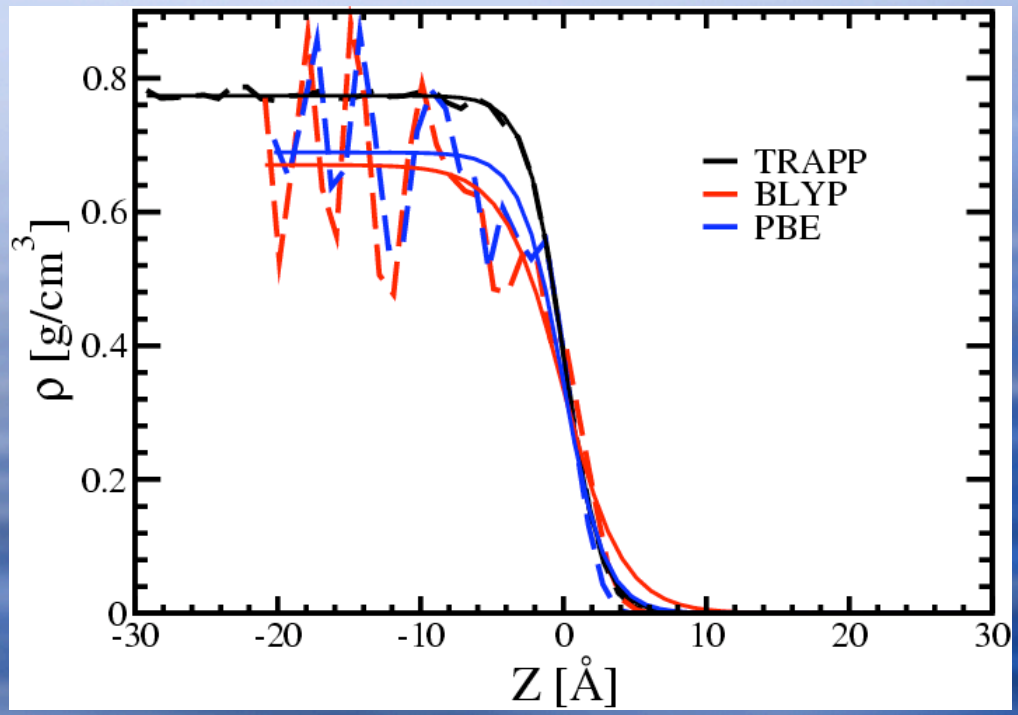


64 molecules, 300K, .792 g/cc, 15 ps using CP2K/QUICKSTEP

DFT gives a slightly over structured RDF for bulk liquid

Reproducing structural properties of methanol liquid-vapor interface is another test of DFT

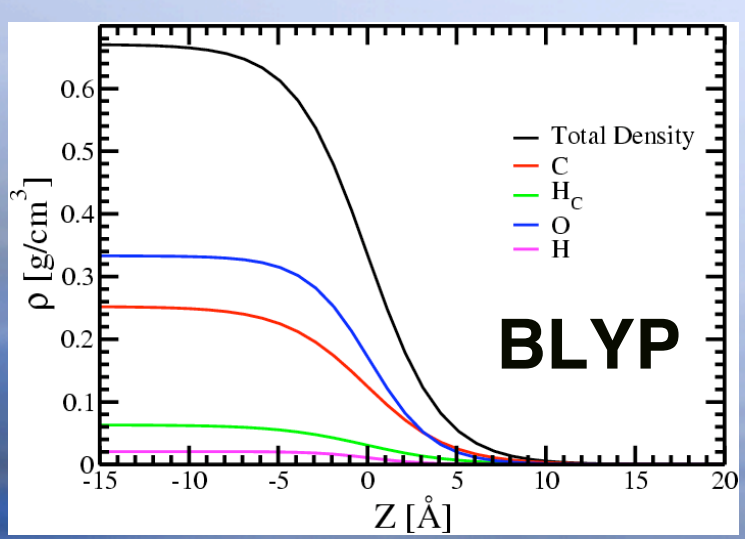
- BLYP and PBE
  - CP2K/Quickstep, NVT
  - 15 ps, 15Å x 15Å x 73Å
  - 120 methanols
- TRAPP
  - TOPMON, GEMC
  - 4 x 10^5 cycles
  - 800 methanols
- LLNL's THUNDER Linux cluster

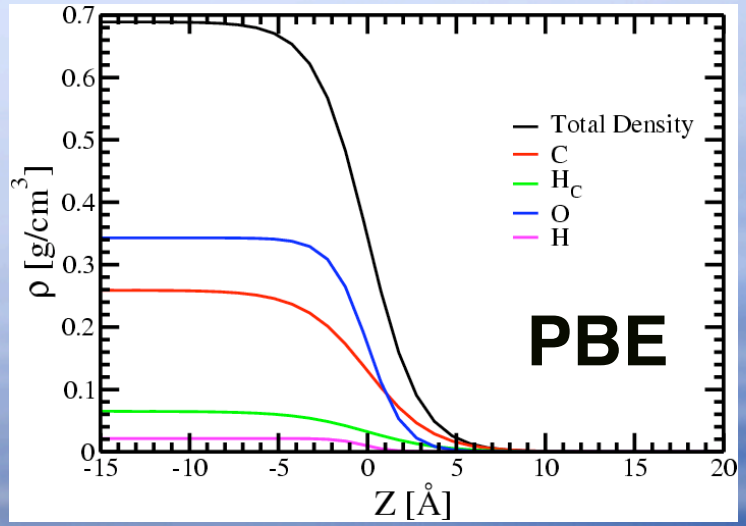


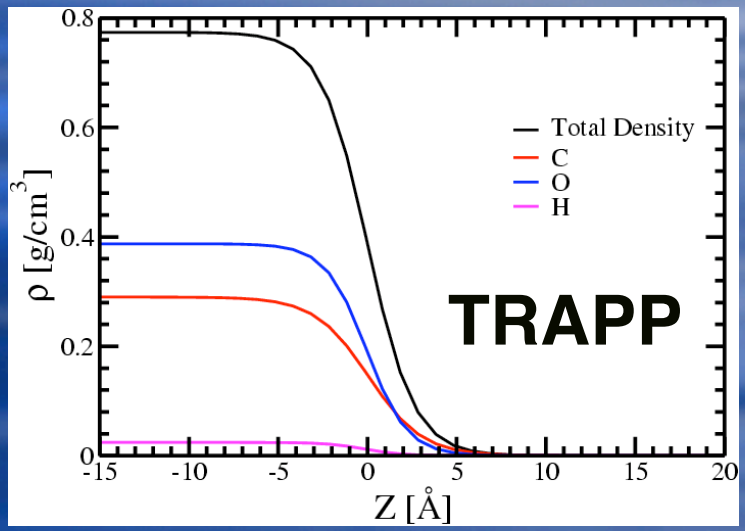
$$\rho(z) = \frac{1}{2}(\rho_l + \rho_v) - \frac{1}{2}(\rho_l + \rho_v)\tanh\left(\frac{z - z_{GDS}}{\delta}\right)$$

Stable ab initio air/methanol interface

Atomic density profile at the interface



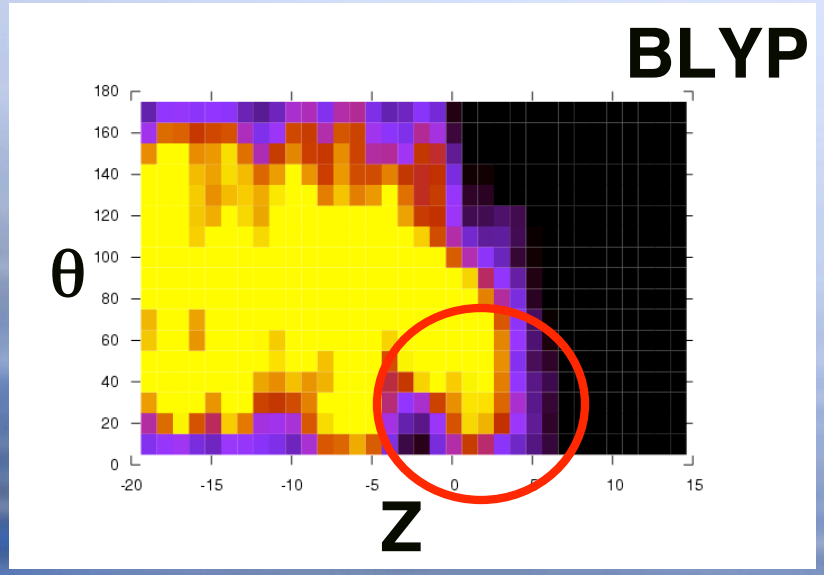


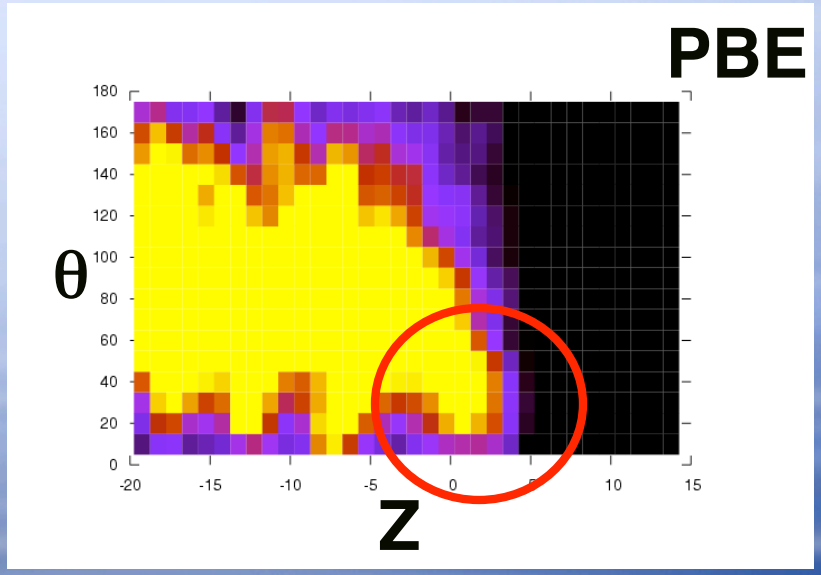


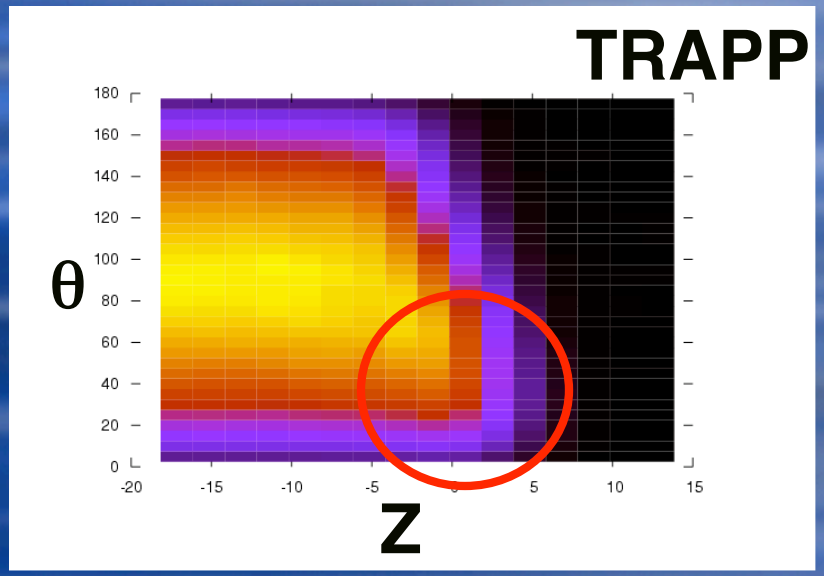
	ρ [g/cc]	δ [Å]	Z_{GDS} [Å]
BLYP	0.670	4.16	20.89
PBE	0.689	2.918	20.24
TRAPP	0.774	2.61	29.16

Hint of special orientation for methanol near the interface.

Orientational order near methanol interface



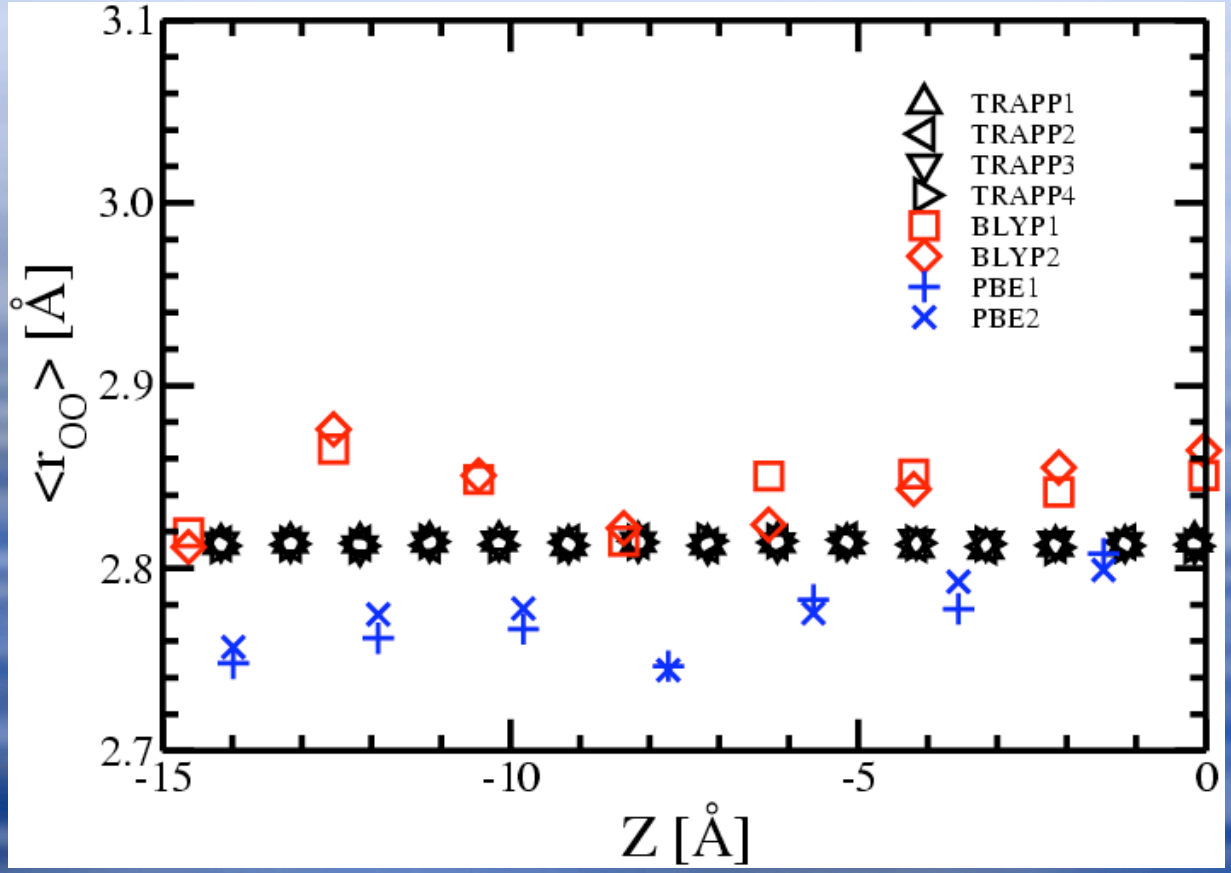




$$\cos\theta = \hat{v}_{\mathrm{O-C}} \cdot \hat{z}$$

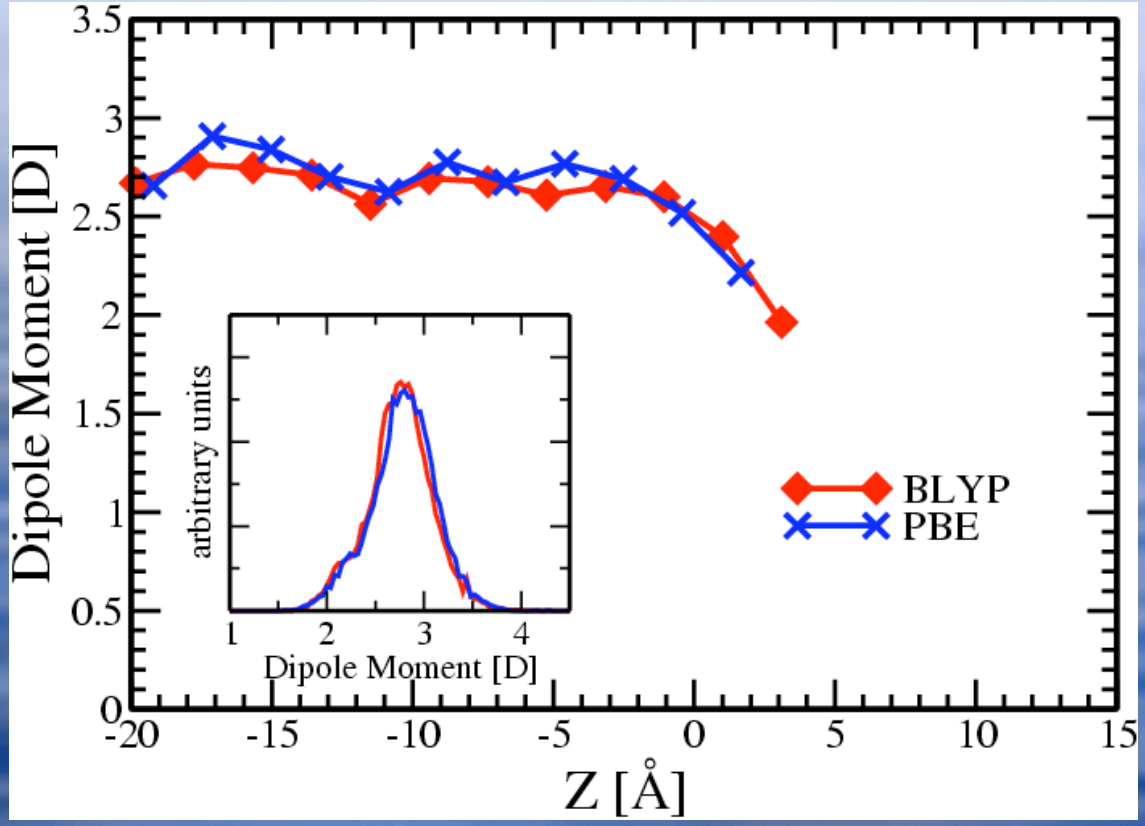
Methanol prefers a perpendicular orientation at the interface

Average O-O distance at air-methanol interface



- **Both functionals show no decrease in average O-O distance seemingly at odds with experiment**
  - **Lack of dispersion?**

Average molecular dipole at air-methanol interface



- **Similar to the aqueous interface, we see a decrease in the molecular dipole moment for methanol at the interface**

Conclusions

- First ab initio simulation of stable air/liquid interface for water and methanol at 300K.
- Observed surface relaxation in air/water interface but no surface contraction in air/methanol interface.
- Quantified the population of different surface moieties as well as explored the chemical reactivity at the interface through the use of frontier molecular orbitals.
- Classical empirical potential can be use to obtain qualitatively similar structural features.
- Interest in chemical reactions still dictates ab initio methods must be used.

Acknowledgements

- CPMD Consortium
- CP2K Mannschaft
- J. Hutter
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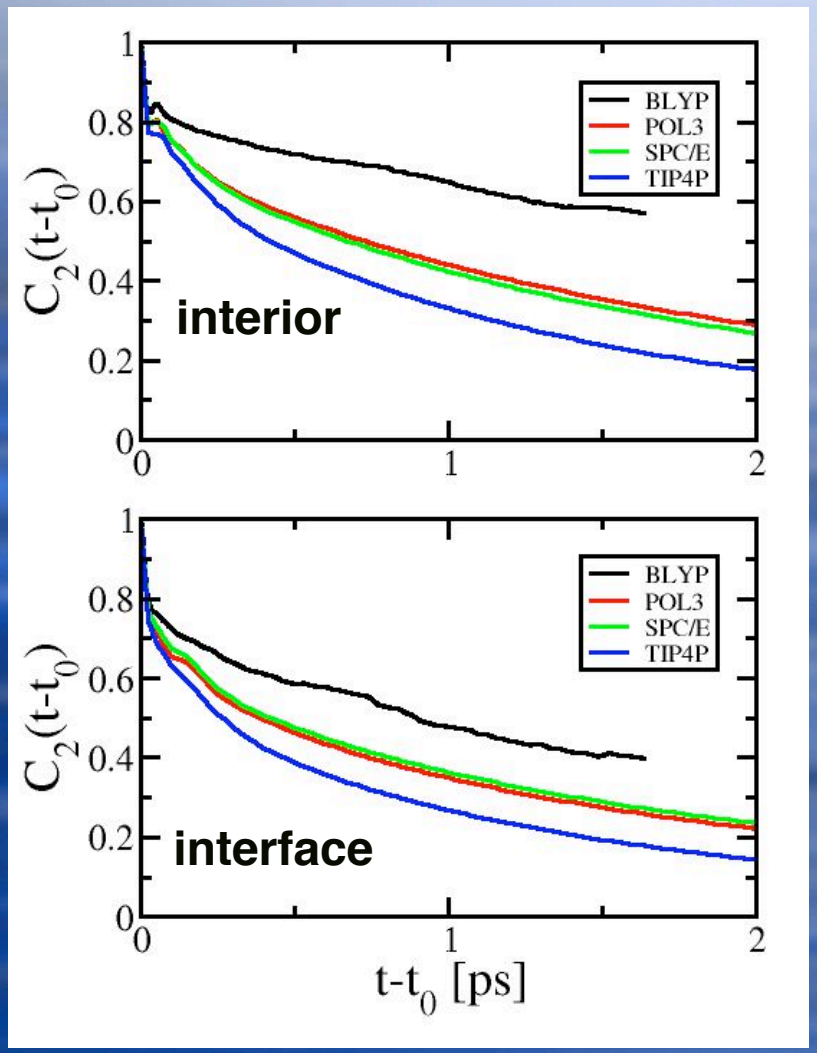
- A. Kubota
- C. Shereda
- A. Moody

We can compare short time CPMD dynamics to classical empirical potentials



- Interfacial reorientation is faster for all models
- BLYP dynamics is consistently slower
- We have also computed retention times for empirical models. All are in good agreement

Kuo *et. al.* JCP-B 110, 3738 (2006)

Our results indicate that BLYP can capture different H-bonded surface population

Increasing # H-bonds/H_2O

2.1 Å, θ=20

	0_D	1_D	2_D
0_A	6%	11%	5%
	11%	15%	4%
1_A	12%	27%	14%
	15%	27%	10%
2_A	5%	13%	8%
	4%	9%	5%
	30%	51%	

2.9 Å, θ=30

0_D	1_D	2_D
1%	3 %	2%
3%	8%	2%
3 %	19 %	20%
8 %	34%	15%
2%	18 %	31 %
2 %	14%	13 %
14%	56%	

3.2 Å, θ=40

0_D	1_D	2_D
0 %	1 %	1%
1 %	3%	1 %
1 %	14 %	19 %
4 %	25%	18 %
1 %	16%	46%
1 %	16%	30%
7%	44%	

The interface is always populated with more acceptor-only and single-donor

Analysis for classical interfaces show H-bond populations consistent with BLYP results

Bulk

	0_D	1_D	2_D
	1.25%	4.31%	4.32%
0_A	1.19%	4.04%	3.20%
	0.79 %	3.63%	3.24%
	5.50%	21.04%	20.88%
1_A	3.52%	18.97%	18.67%
	3.46%	21.16%	20.18%
	3.62%	17.02%	20.93%
2_A	1.76%	16.77%	29.62%
	2.08%	18.20%	25.75%

TIP4P
TIP4P-FQ
TIP4P-POL2

Surface

	0_D	1_D	2_D
	3.20%	7.48%	4.12%
0_A	4.08%	8.81 %	2.53%
	1.87%	6.70%	2.37%
	9.93%	28.00%	17.38%
1_A	8.08%	31.09%	14.57%
	6.25%	33.42%	16.34%
	3.54%	13.87%	12.08%
2_A	1.81%	13.90%	14.58%
	1.80%	15.79%	14.99%

6-15%

50-61%

H-Bond population for Methanol using Wernet hydrogen bond criteria

Bulk

	0_D	1_D	2_D
	1.70%	11.72%	0.00%
0_A	1.63%	8.34%	0.00%
	0.68 %	7.13%	0.00%
	6.23%	74.76%	0.00%
1_A	3.54%	80.79%	0.00%
	2.11%	83.43%	0.00%
	0.22%	5.36%	0.00%
2_A	0.05%	5.66%	0.00%
	0.00%	6.65%	0.00%

TRAPP
BLYP
PBE

Surface

	0_D	1_D	2_D
	2.32%	12.49%	0.00%
0_A	4.02%	8.25%	0.00%
	2.96%	9.06%	0.00%
	6.36%	74.16%	0.00%
1_A	3.60%	81.96%	0.00%
	1.38%	83.04%	0.00%
	0.18%	4.48%	0.00%
2_A	0.02%	2.15%	0.00%
	0.03%	3.53%	0.00%

There are no major differences in the hydrogen bond population between interior and surface methanols