



# Extending the Range and Physical Accuracy of High Fidelity Coarse-Grained Models with Ultra-Coarse-Graining



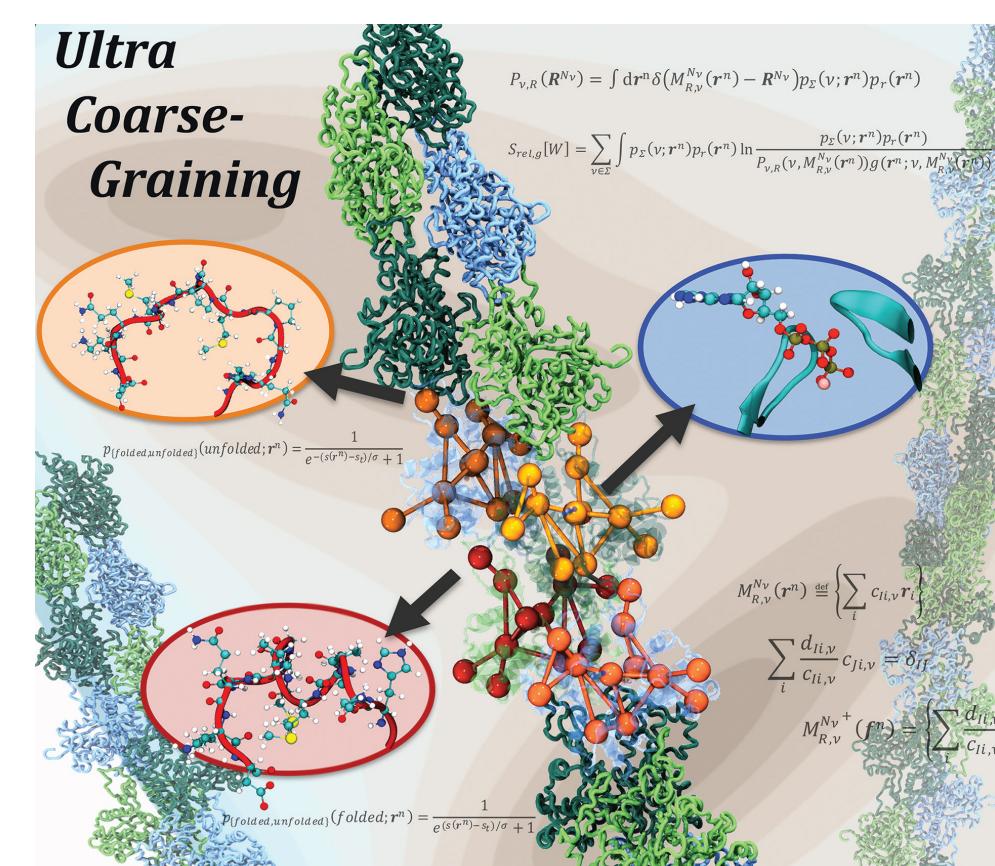
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## Introduction

Coarse-grained (CG) models provide an efficient way to extend the time and length scales of computer simulations by averaging the details beneath the CG resolution. Despite the efficiency and speed-up of the CG model, important information lower than the CG resolution might be lost from the coarse-graining process.

In order to surmount this limitation, **ultra-coarse-graining (UCG)** methodologies have been developed by incorporating discrete state variables into configurational variables. This work presents the general UCG theory designed for frequent changes of internal CG states.



## Theory<sup>1,2</sup>

**UCG effective interaction:** The mixed UCG force field is expressed as the sum of the statewise free energy over the state distribution  $\sigma$ .

$$U_{\text{mix}}^{\text{UCG}}(\mathbf{R}^N) = \sum_{\sigma} p(\sigma | \mathbf{R}^N) (U(\sigma, \mathbf{R}^N) + k_B T \ln p(\sigma | \mathbf{R}^N))$$

**Separability/locality** of substate probabilities provide simple state-wise pair energy  $U^{\text{UCG}}(\mathbf{R}^N)$  and the force term  $\nabla U^{\text{UCG}}(\mathbf{R}^N)$ .

$$U_{\text{mix}}^{\text{UCG}}(\mathbf{R}^N) = \sum_I p(s_I | \mathbf{R}^N) (k_B T \ln p(s_I | \mathbf{R}^N)) + \sum_{I,J \text{ neighbors } s_I, s_J} p(s_I | \mathbf{R}^N) p(s_J | \mathbf{R}^N) U_{2,s_I, s_J}(R_{IJ})$$

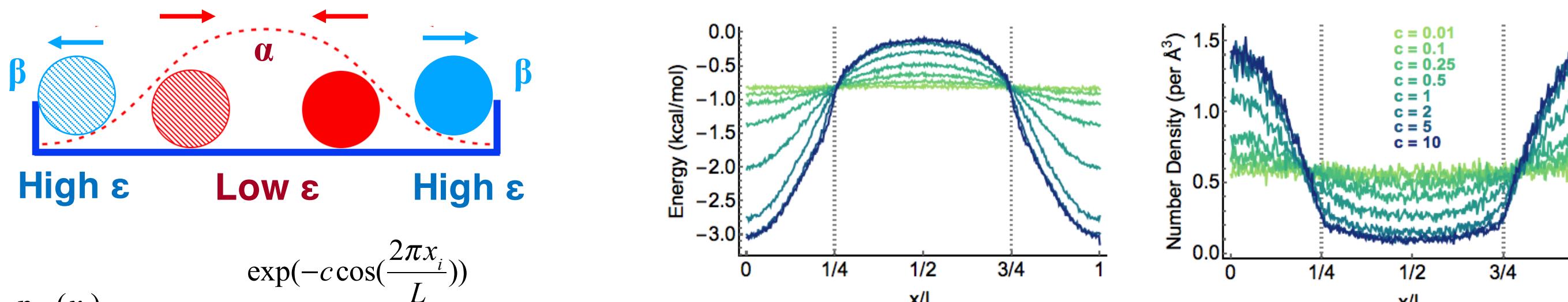
$$\nabla U_{\text{mix}}^{\text{UCG}}(\mathbf{R}^N) = \sum_I (k_B T \ln p(s_I | \mathbf{R}^N)) \nabla p(s_I | \mathbf{R}^N) + \sum_{I,J \text{ neighbors } s_I, s_J} p(s_I | \mathbf{R}^N) p(s_J | \mathbf{R}^N) \nabla U_{2,s_I, s_J}(R_{IJ}) + \sum_{I,J \text{ neighbors } s_I, s_J} U_{2,s_I, s_J}(R_{IJ}) [p(s_I | \mathbf{R}^N) \nabla p(s_J | \mathbf{R}^N) + p(s_J | \mathbf{R}^N) \nabla p(s_I | \mathbf{R}^N)]$$

This UCG methodology can be efficiently **implemented** to the conventional MS-CG framework by variationally minimizing the following residual  $\chi^2$ .

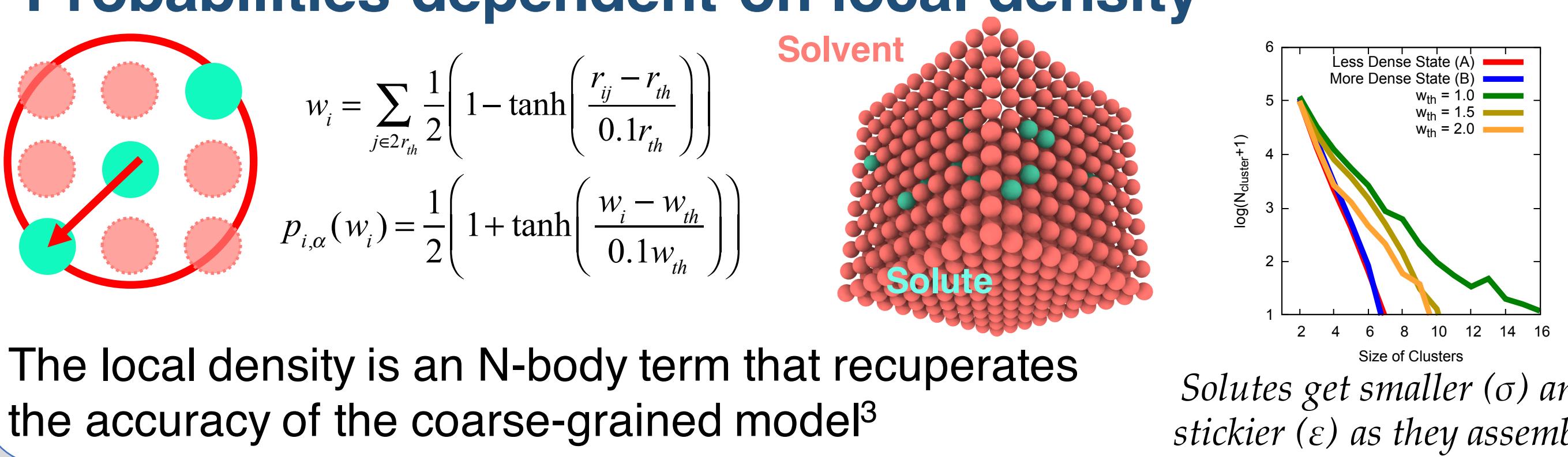
$$\chi^2[U(\sigma, \mathbf{R}^N)] = \lim_{T_s \rightarrow \infty} \frac{1}{T_s} \sum_t \frac{1}{L} \sum_l ||\nabla(U(\sigma_l, M(\mathbf{r}_t^n)) + kT \ln p_\Sigma(\sigma_l | M(\mathbf{r}_t^n))) - M^+(\nabla U(\mathbf{r}_t^n))||^2$$

## Designing substate probabilities<sup>1</sup>

### Probabilities dependent on the position



### Probabilities dependent on local density



The local density is an N-body term that recuperates the accuracy of the coarse-grained model<sup>3</sup>

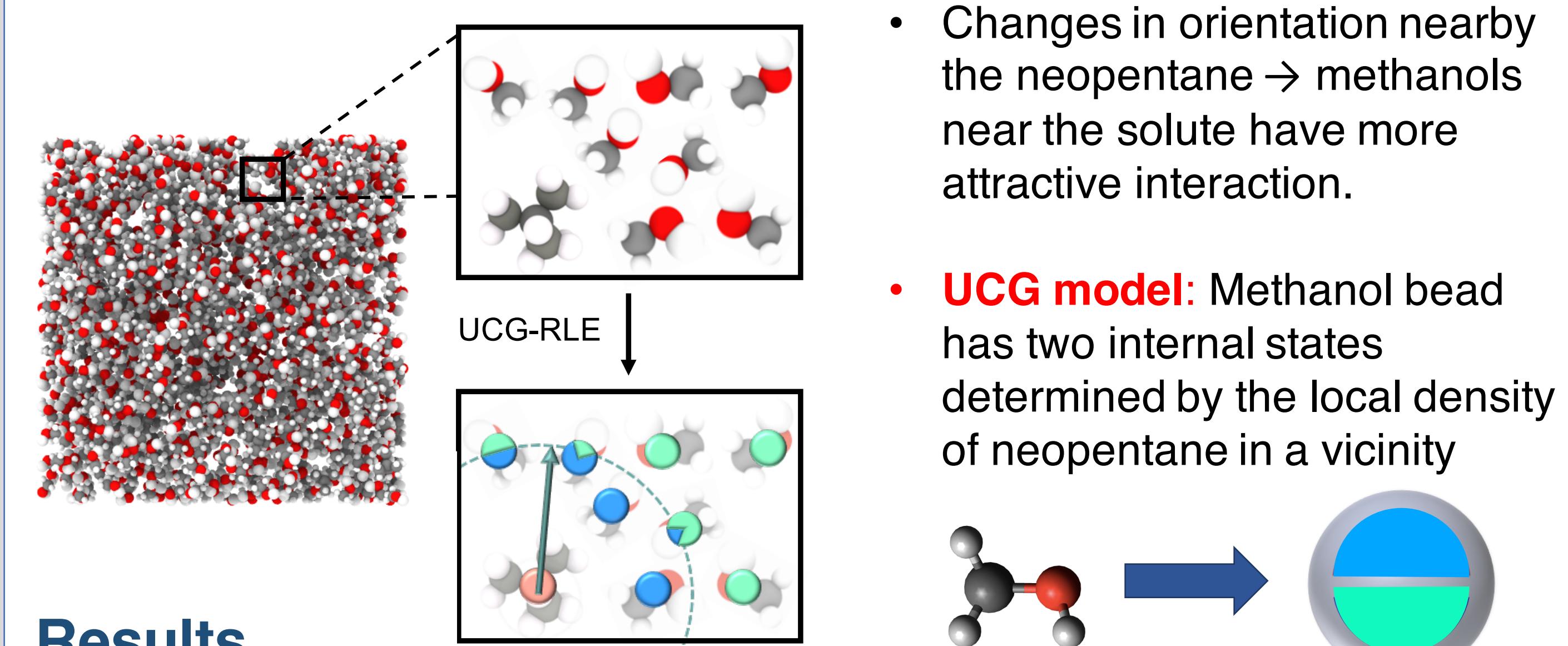
1. J. F. Dama<sup>†</sup>, J. Jin<sup>†</sup>, G. A. Voth. The theory of Ultra-Coarse-Graining. 3. Coarse-grained sites with rapid local equilibrium of internal states. *J. Chem. Theory Comput.* 2017, 13, 1010-1022.

2. J. F. Dama<sup>†</sup>, J. Jin<sup>†</sup>, G. A. Voth. *J. Chem. Theory Comput.* 2018, 14, 2288-2288.

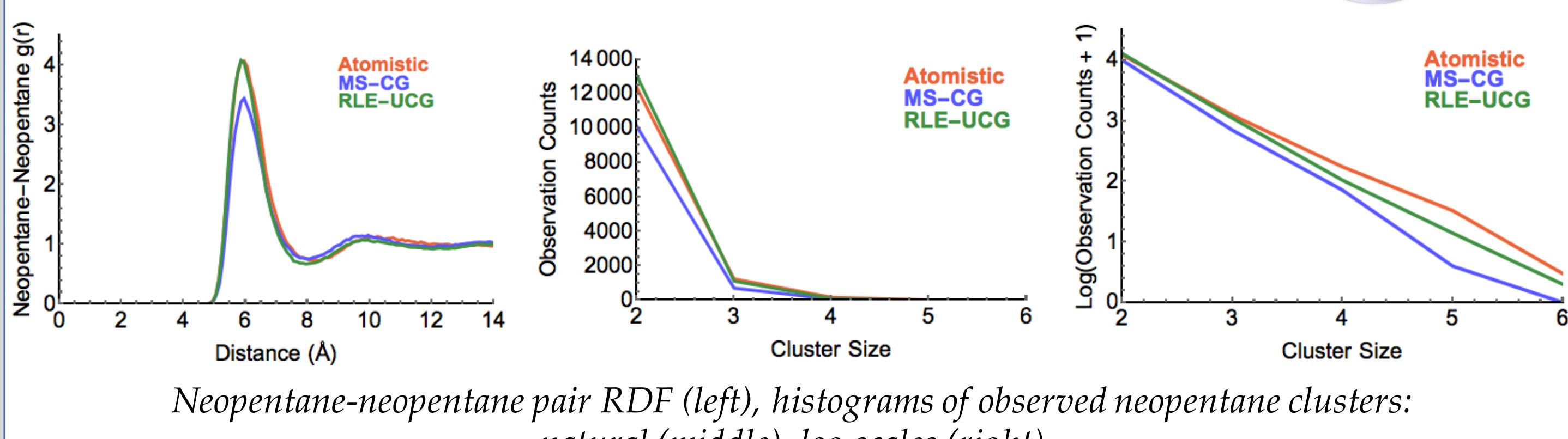
3. J. W. Wagner, T. Dannenhoffer-Lafage, J. Jin, G. A. Voth. Extending the range and physical accuracy of coarse-grained models: Order parameter dependent interactions. *J. Chem. Phys.* 2017, 147, 044113.

## Cooperative hydrophobic association<sup>1</sup>

**Solvophobic effect:** When methanol is close to neopentane, it will rarely form hydrogen bonds with the alkane and therefore have more freedom to form bonds with other nearby methanols



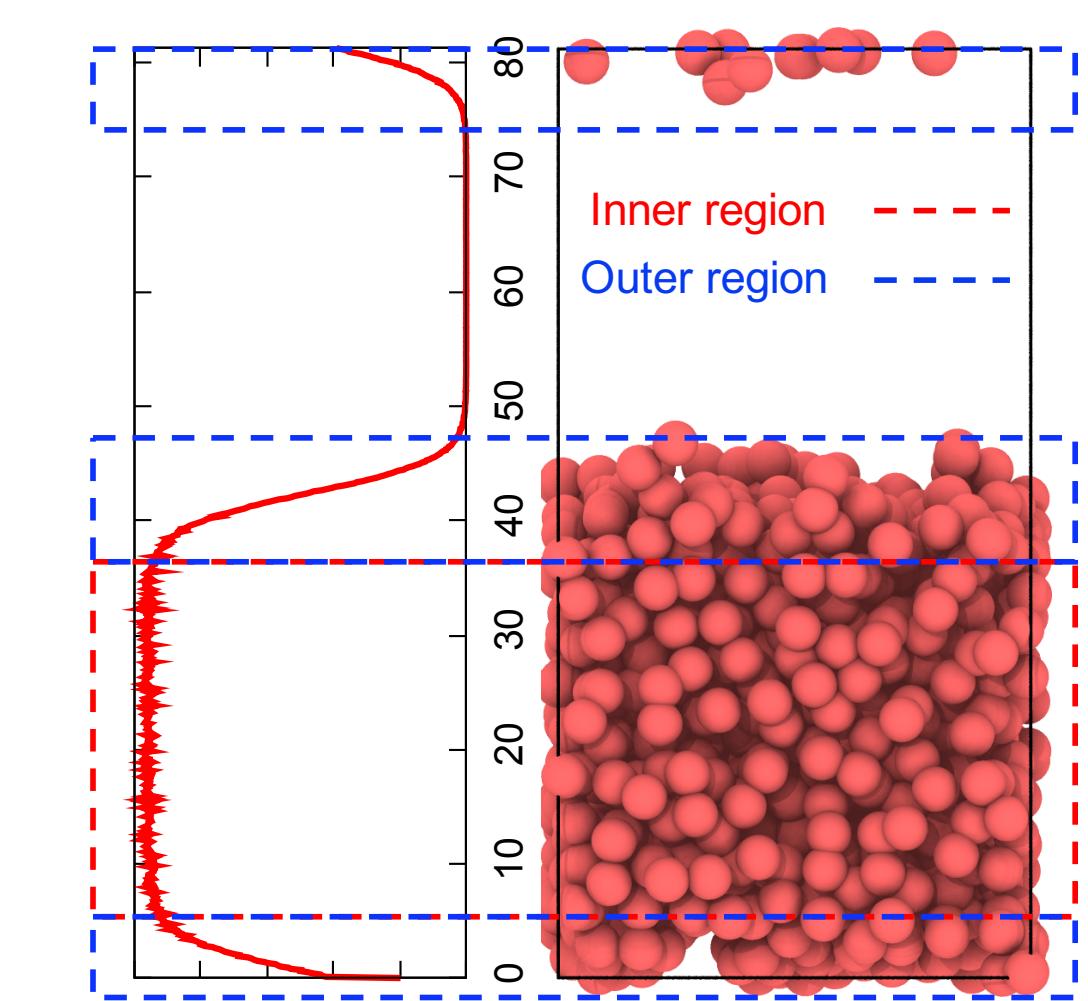
## Results



## Liquid/vapor interface modeling<sup>4</sup>

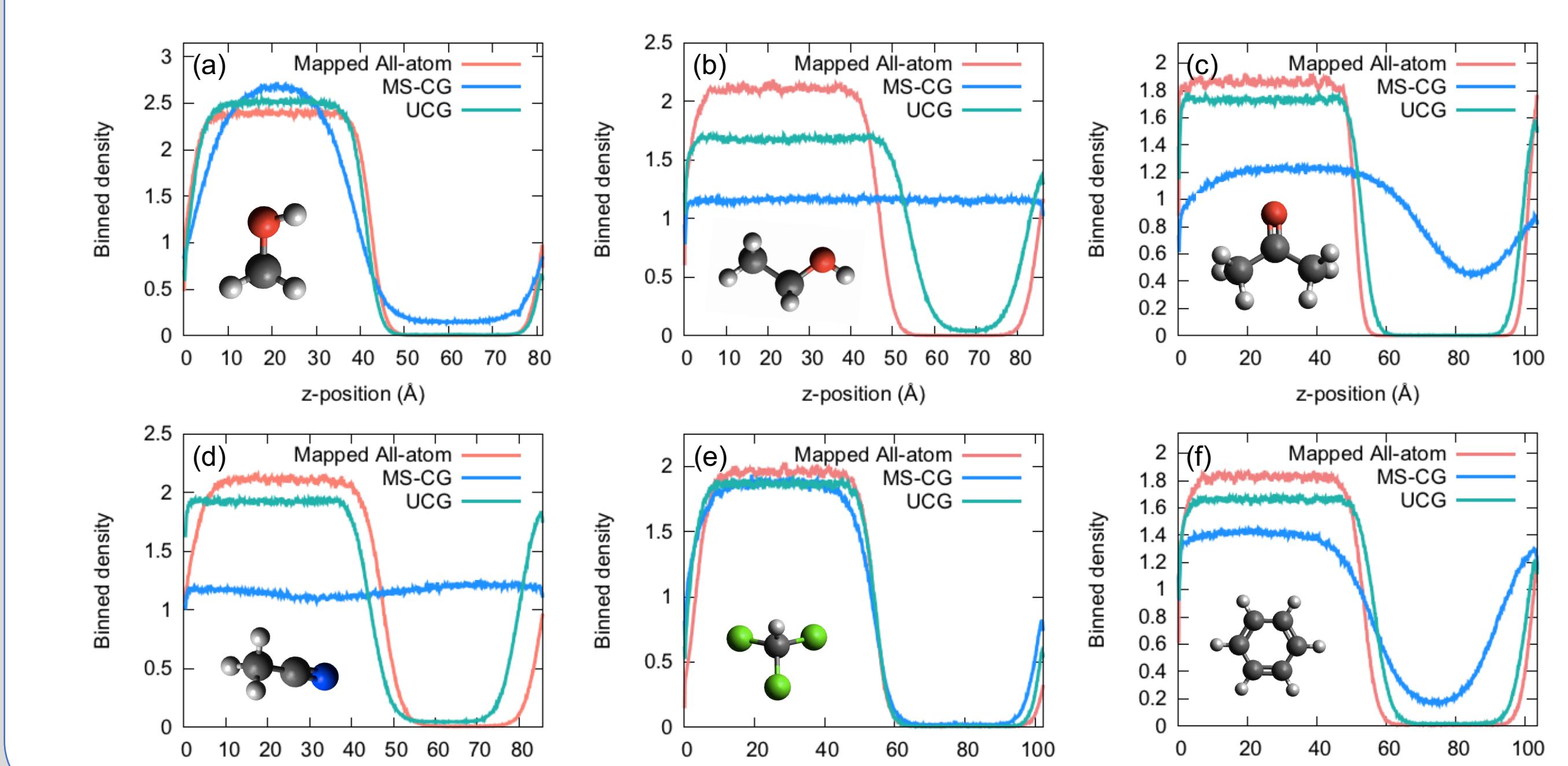
### Limitations and Challenges<sup>3,4</sup>

- Liquid and vapor phases have different averaged molecular interactions
- Standard force fields are designed & able to match one phase at a time
- Conventional MS-CG representation of the single-bead model failed to identify the directionality of a molecule
- MS-CG approach was unable to reproduce the correct phase coexistence for aspherical molecule



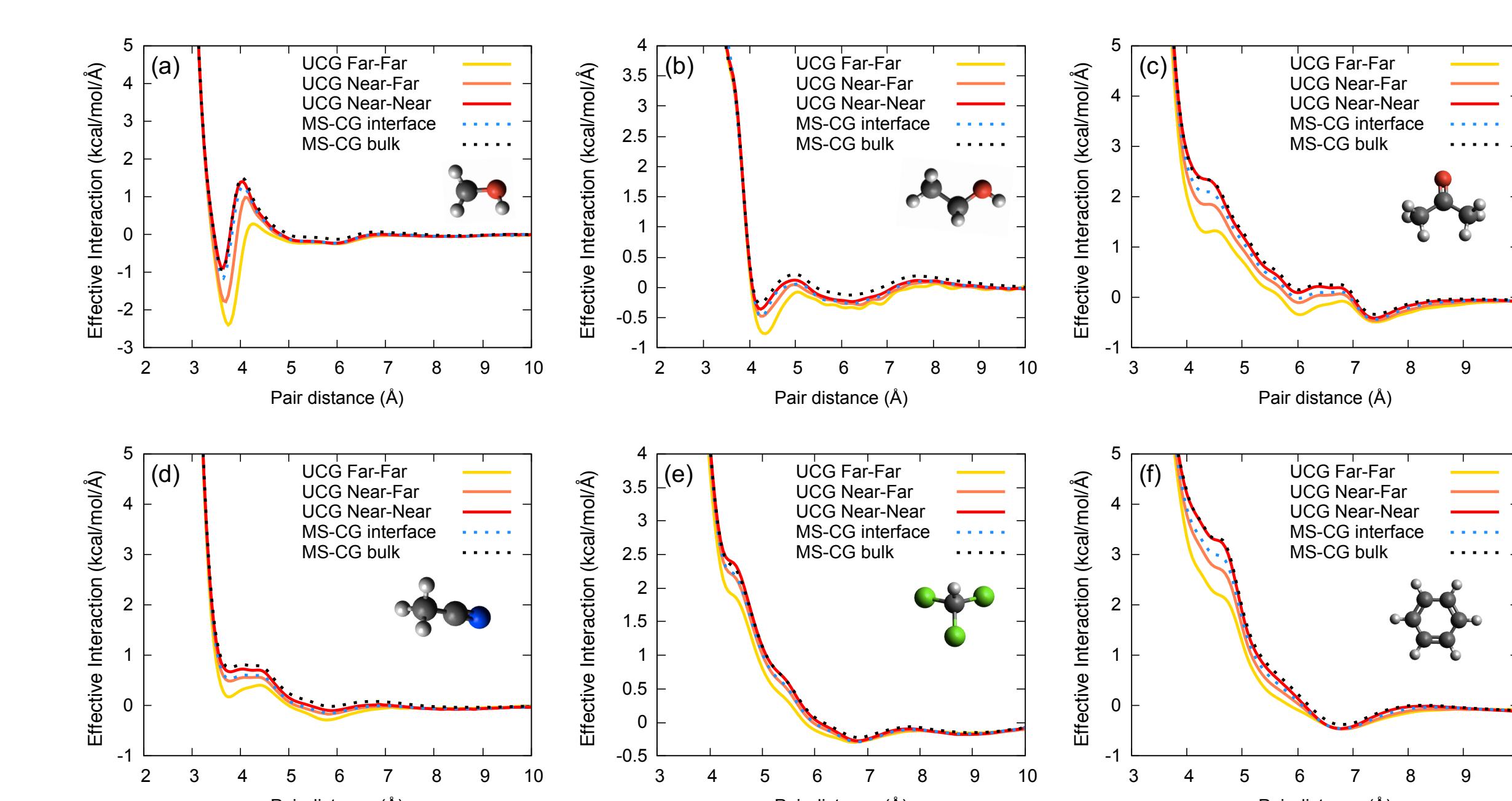
However, UCG can overcome these challenges!

### Results (Slab density profile)



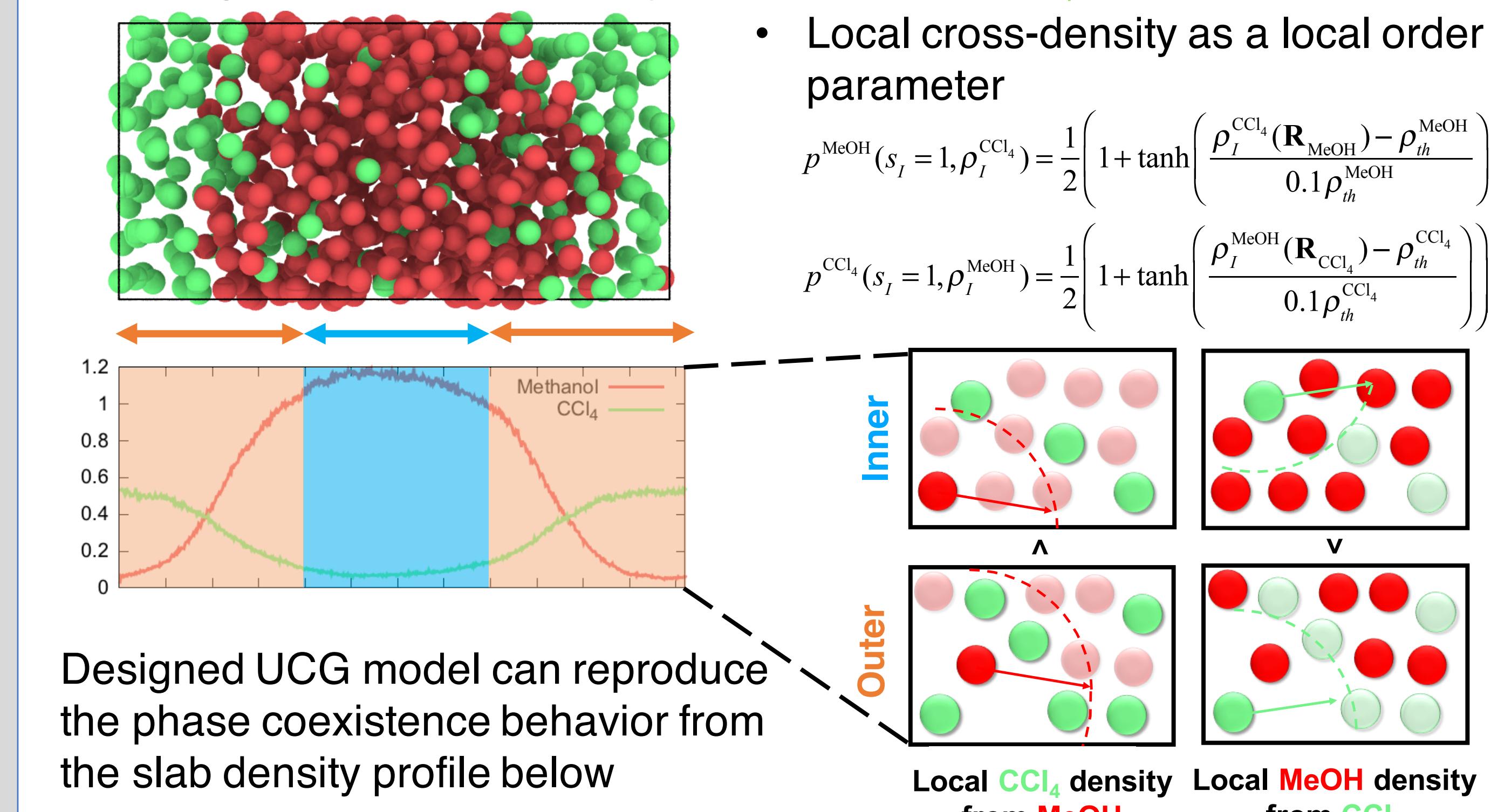
## Transferable Interaction

Dense-dense (near-near) UCG statewise interaction from liquid/vapor interface is transferable to the pure interaction from bulk liquid phase



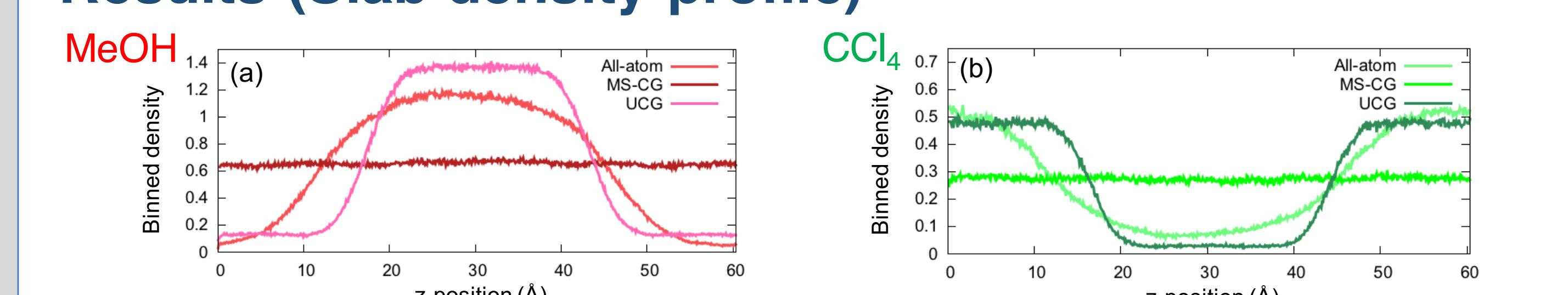
## Liquid/liquid interface modeling<sup>4</sup>

**Inhomogeneous interfacial system:** Methanol/CCl<sub>4</sub> interface



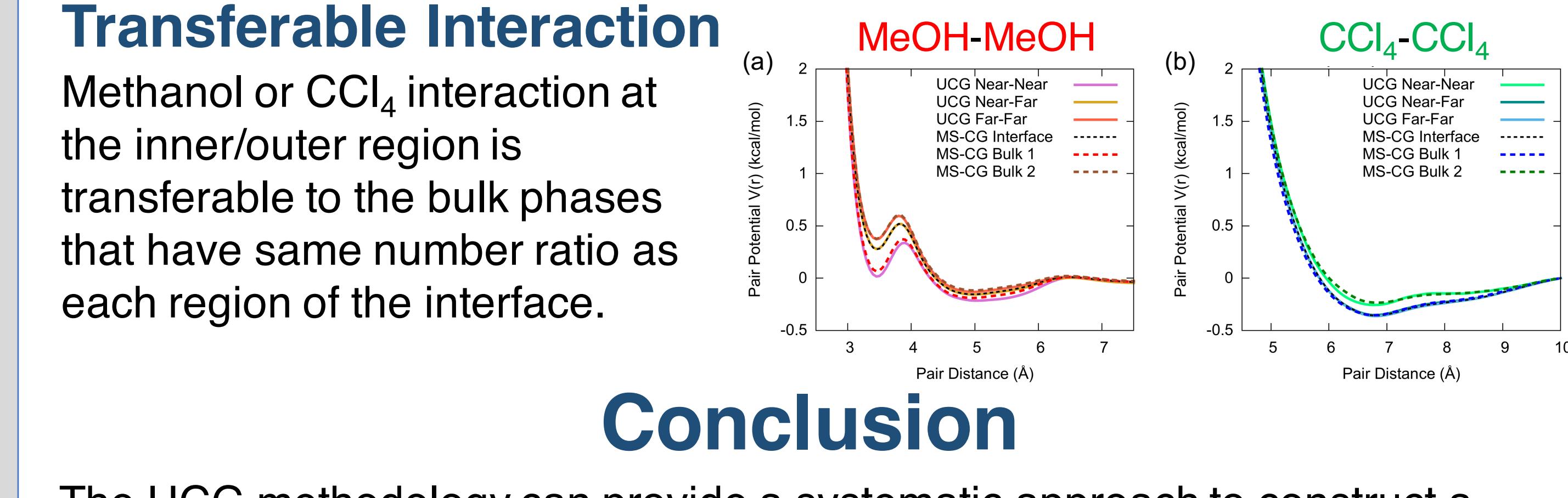
Designed UCG model can reproduce the phase coexistence behavior from the slab density profile below

### Results (Slab density profile)



## Transferable Interaction

Methanol or CCl<sub>4</sub> interaction at the inner/outer region is transferable to the bulk phases that have same number ratio as each region of the interface.



## Conclusion

The UCG methodology can provide a systematic approach to construct a transferable CG interactions in complex systems

## Acknowledgements



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