

# Water Diffusion in NaCl/CsI Solutions

Zhi Wang  
June 11th, 2014

- What is diffusion coefficient?
- How do we calculate coefficient?
- How is simulation compared to the experiment?
- How to parameterize the ions?
- How to judge the new parameters? Which reference should I choose to compare with?
- How will the new parameters affect my target — water diffusion coefficient in salt solution?

# What is diffusion coefficient?

- Flux goes from high concentration region to low concentration region, described by Fick's first law.

in 1 dimensional diffusion  $\frac{dn}{dt}/A = -D\frac{d\rho}{dx}$

*e.g.*  $n$ : mol;  $t$ : s;  $A$ : m<sup>2</sup>;  $D$ : m<sup>2</sup>/s;

$\rho$ : mol/m<sup>3</sup>;  $x$ : m.

- The coefficient  $D$  is diffusion coefficient.

# How to calculate $D$ ?

- Fick's second law.
- Fick's second law: concentration/density/probability density/*etc.* in space change with time.

$$\frac{\partial \rho(x, t)}{\partial t} = D \frac{\partial^2 \rho(x, t)}{\partial x^2}$$

$$\lim_{x \rightarrow \infty} \rho(x, t) = \lim_{t \rightarrow \infty} \rho(x, t) = 0 \quad \rho(x, 0) = \delta(x)$$

$$\rho(x, t) = \frac{1}{\sqrt{4\pi Dt}} e^{-\frac{x^2}{4Dt}}$$

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} \rho(x, t) x^2 dx = 2Dt \quad D = \frac{\langle r^2 \rangle}{6t}$$

- Why we can, and how we can calculate  $D$  in 3 dimensional space.

# Experiments and Simulations

*D* of Water at 25 °C (10)

	3 M NaCl	Water	3M CsI
Experiment	1.87	2.299	2.79
AIMD	1.412↓	2.135	2.305↑
AMOEBA09	1.8193↓	2.1317	1.8897↓

<sup>a</sup> R. Mills, *The Journal of Physical Chemistry*, **1973**, 77, 685

<sup>b</sup> K. J. Müller and H. G. Hertz, *The Journal of Physical Chemistry*, **1996**, 100, 1256

<sup>c</sup> Y. Ding, A. A. Hassanali and M. Parrinello, *Proceedings of the National Academy of Sciences*, **2014**, 111, 3310

<sup>d</sup> NPT ensemble

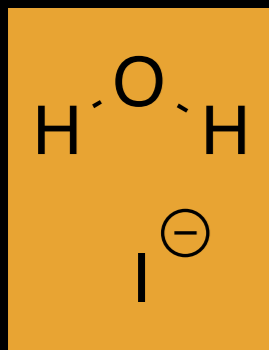
# Parametrization and Energy References

Parameters of Cs

	vdW Radius	Depth of Energy Well	Polarizability	Damping
Cs	4.37	0.53	2.26	0.39
I	4.66	0.52	7.25	0.39

$$\phi_{\text{vdW}} = \varepsilon \left( \left( \frac{\sigma}{r} \right)^m - \left( \frac{\sigma}{r} \right)^n \right)$$

Energy References



	Measurement	Cs	I <sup>-</sup>
Quantum	X + H	—	-10.0256
TINKER	X + H	—	-9.7898
Experiments	solvation free energy	-61.66	-67.64
TINKER	solvation free energy	-58.5	-69.2

# Problems

## Energy References

	Measurement	Cs	I <sup>-</sup>
Quantum	X + H	—	-10.0256
TINKER	X + H	—	-9.7898
Experiments	solvation free energy	-61.66	-67.64
TINKER	solvation free energy	-58.5	-69.2

<sup>a</sup> An appropriate basis set for Cesium **to be found**.

<sup>b</sup> TATB assumption — **incorrect**.

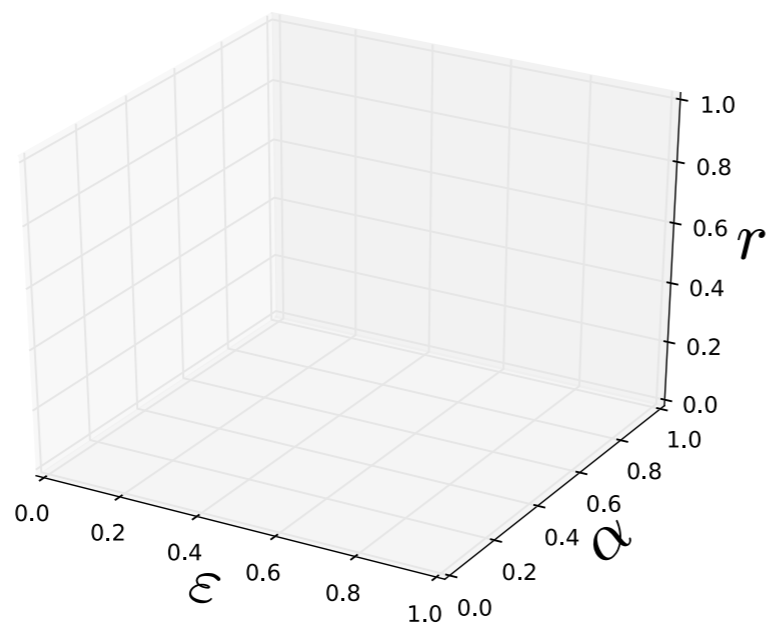
<sup>c</sup> OSRW: Orthogonal Space Random Walk — **no reference**.

IODIDE

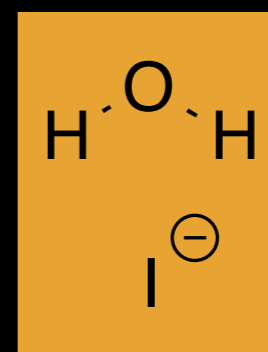
# Parametrization of Iodide

## Parametrization of I

	vdW Radius ( $r$ )	Depth of Energy Well ( $\epsilon$ )	Polarizability ( $\alpha$ )
I	4.66	0.52	7.25
Increment	0.03	0.005	0.1
min	3.16	0.27	2.25
max	6.16	0.77	12.25

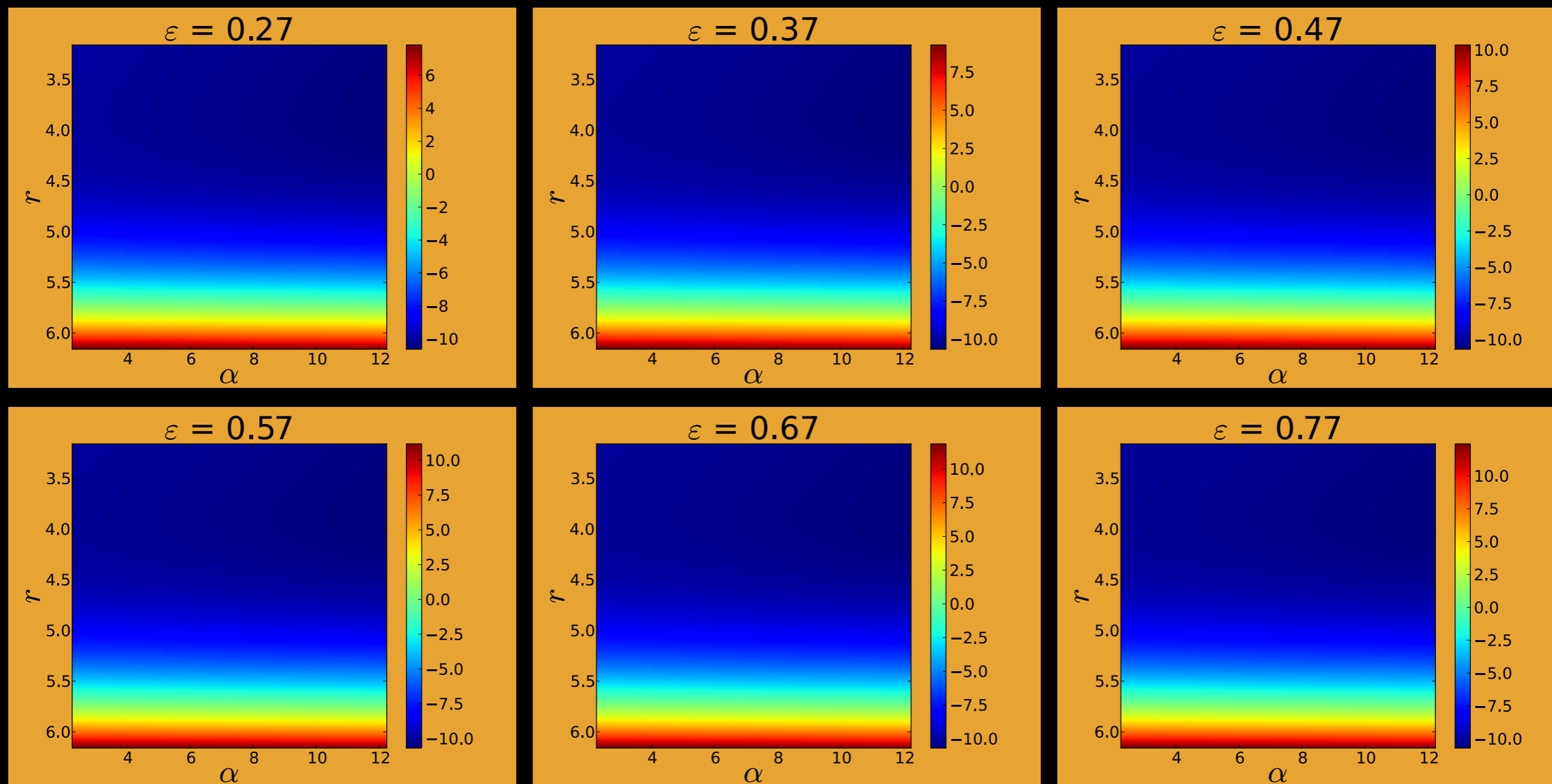


## Intermolecular Energy





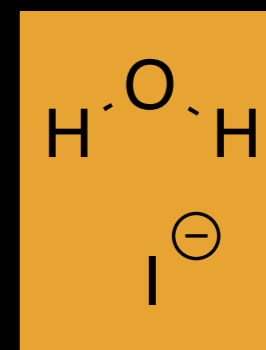
# Screening: TINKER ANALYZE



Radius:  $\uparrow$  — Energy: **obviously** less.

Epsilon:  $\uparrow$  — Energy: less.

Alpha:  $\uparrow$  — Energy: **slightly** more.



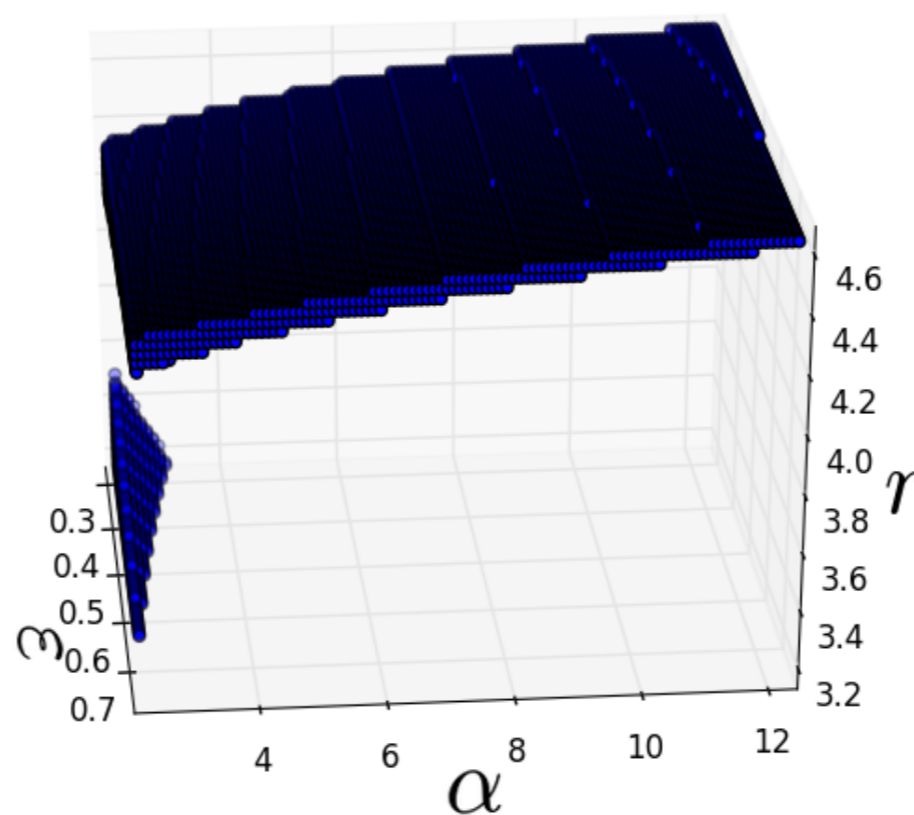
# Screening

Q: How to choose parameters from these graphs?

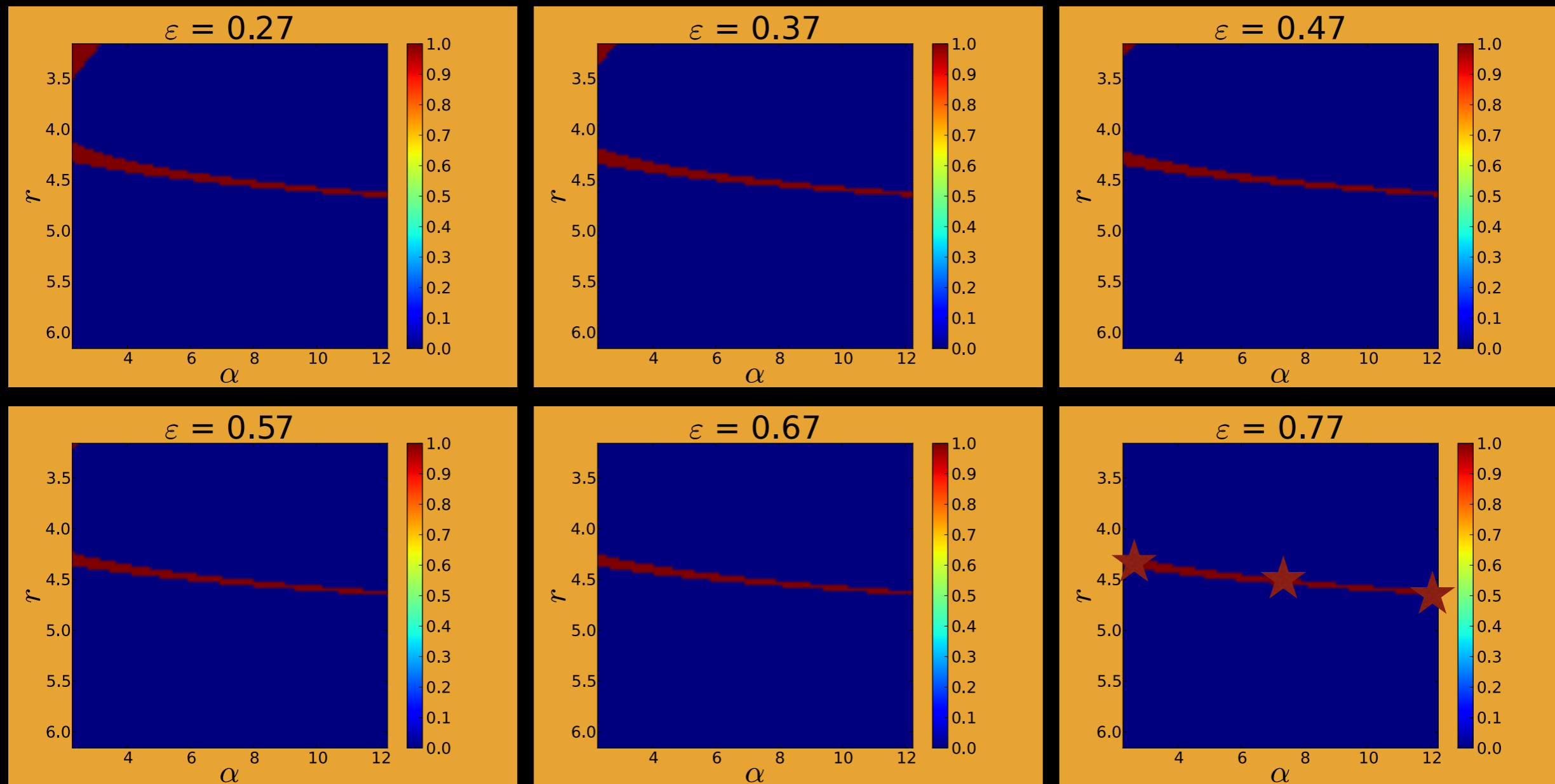
A: Ask quantum. w/ BSSE: -10.0256, w/o BSSE: -11.6659 kcal/mol

**Arbitrarily** choose a small range: -10.02 ~ -10.12 kcal/mol

$$\{(r, \varepsilon, \alpha) \mid U(r, \varepsilon, \alpha) \in (-10.12, -10.02]\}$$



# Screening



Within the range of  $-10.02 \sim -10.12$ : red; otherwise: blue.

# Results

		Simulation Results				
$\alpha$	items	$\varepsilon$				
		0.27	0.395	0.52	0.645	0.77
	$r$	4.225	4.27	4.30	4.315	4.315
2.25	$\Delta G$	-82.0 +/- 0.2	-80.0 +/- 0.2	-78.4 +/- 0.3	-77.8 +/- 0.2	-77.6 +/- 0.4
	$D$	2.0023	2.0035	—*	2.0114	1.8997
	$r$	4.51	4.525	4.525	4.525	4.525
7.25	$\Delta G$	-75.0 +/- 0.4	-74.1 +/- 0.1*	-73.4 +/- 0.3	-73.2 +/- 0.2	-73.0 +/- 0.4
	$D$	1.8930	1.9487	1.8256	2.0365	2.0217
	$r$	4.645	4.645	4.645	4.63	4.63
12.25	$\Delta G$	-79.0 +/- 0.7	-76.9 +/- 0.3	-76.4 +/- 0.5	-76.1 +/- 0.4	-77.0 +/- 0.8
	$D$	1.3069*	1.3433	1.4353	1.4442	1.3437

\* predicted by less data or no data reported due to the unexpected situations in cluster

# Conclusion

- No idea for Cesium.
- Iodide: original parameters — intermolecular energy close to MP2/6-311G result.
- Iodide: (maybe) smaller polarizability?

# Further More

- The range of intermolecular energy is arbitrary. What if ...
- How does everything change with radius?
- A wild guess: the polarizability of Cesium cation is too large?
- ...

The End