Water Diffusion in NaCl/CsI Solutions

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- 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 $\quad \dfrac{\mathrm{d}n}{\mathrm{d}t}/A = -D\dfrac{\mathrm{d}\rho}{\mathrm{d}x}$

$e.g.\ n$: mol; t: s; A: m^2; D: m^2/s;

ρ: $\mathrm{mol}/\mathrm{m}^3$; 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.

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

$$\lim_{x\to\infty} \rho(x,t) = \lim_{t\to\infty} \rho(x,t) = 0 \qquad \rho(x,0) = \delta(0)$$

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

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

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

Experiments and Simulations

	D of Water at 25 ºC (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↓

[a] R. Mills, *The Journal of Physical Chemistry,* **1973,** *77,* 685
[b] K. J. Müller and H. G. Hertz, *The Journal of Physical Chemistry,* **1996,** *100,* 1256
[c] Y. Ding, A. A. Hassanali and M. Parrinello, *Proceedings of the National Academy of Sciences,* **2014,** *111,* 3310
[d] NPT ensemble

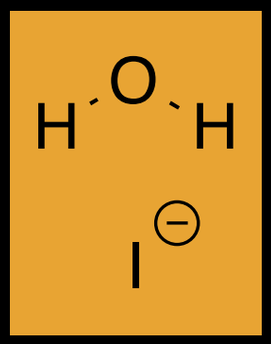
Parametrization and Energy References

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

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

Energy References



	Measurement	Cs	I^-
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

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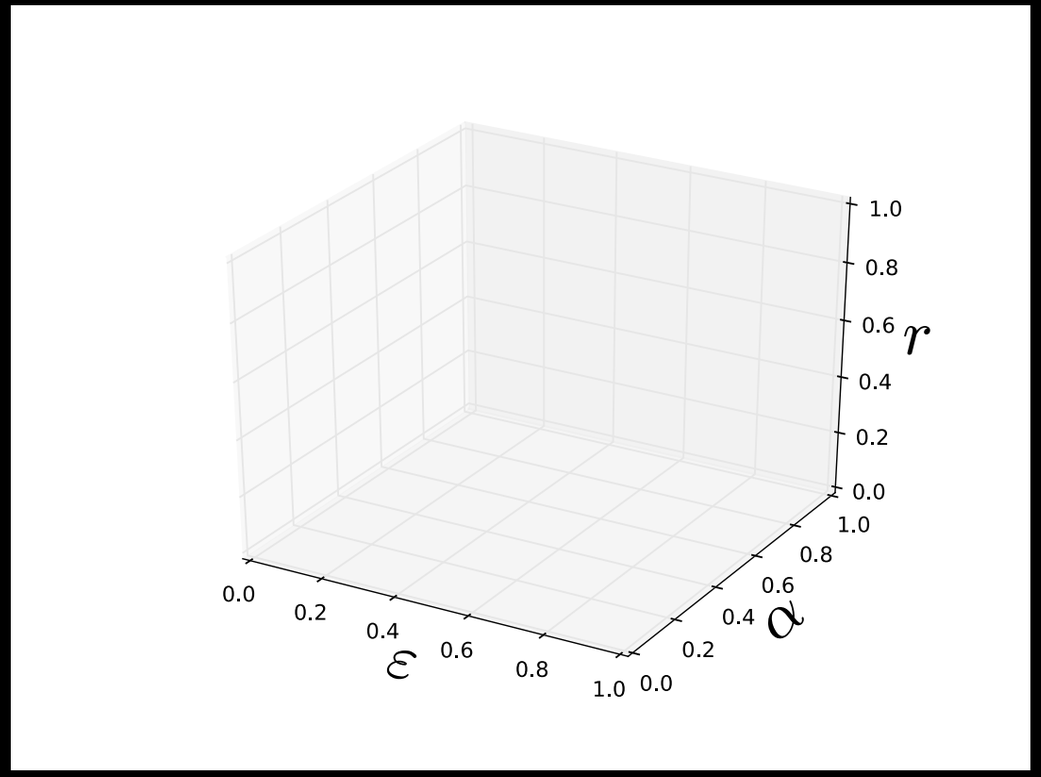
[a] An appropriate basis set for Cesium to be found.
[b] TATB assumption — incorrect.
[c] OSRW: Orthogonal Space Random Walk — no reference.

IODIDE

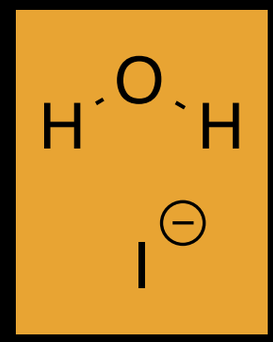
Parametrization of Iodide

Parametrization of I

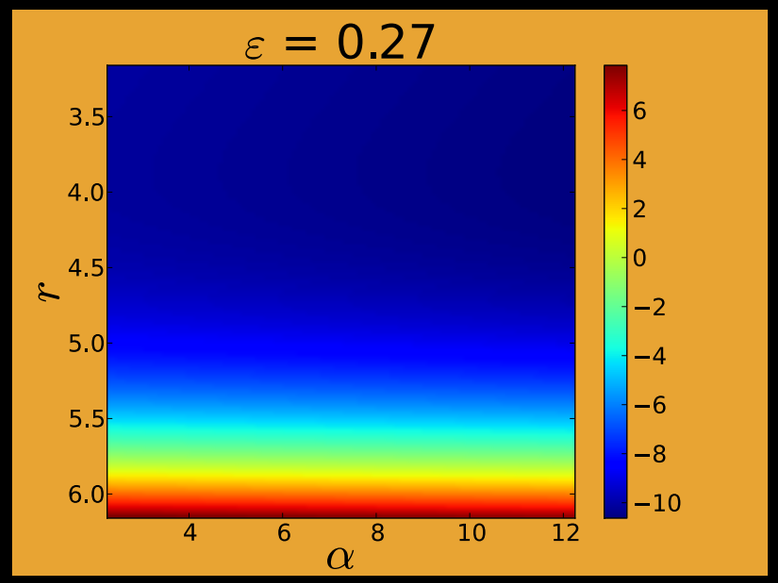
	vdW Radius (r)	Depth of Energy Well (ε)	Polarizability (α)
I	4.66	0.52	7.25
Increment	0.03	0.005	0.1
min	3.16	0.27	2.25
max	6.16	0.77	12.25

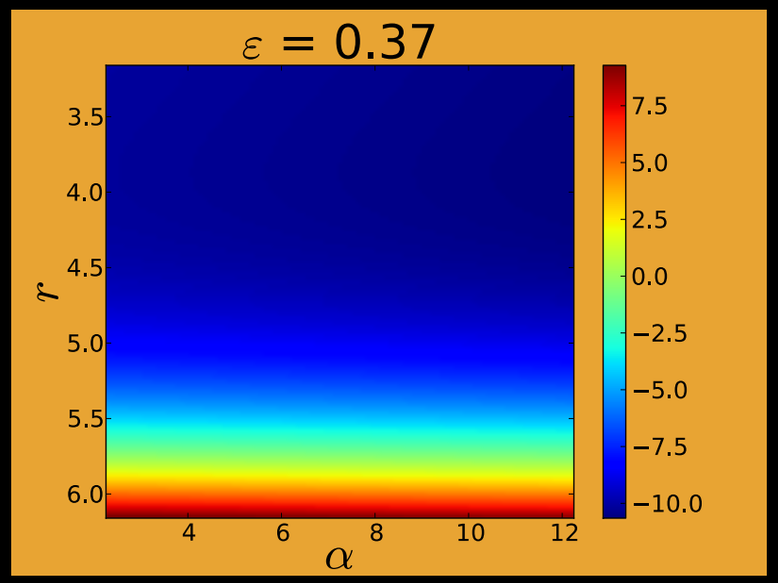


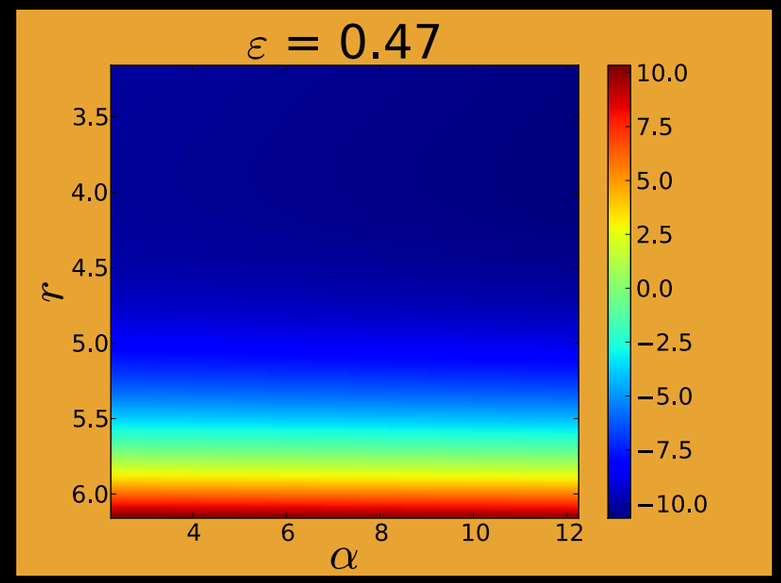
Intermolecular Energy

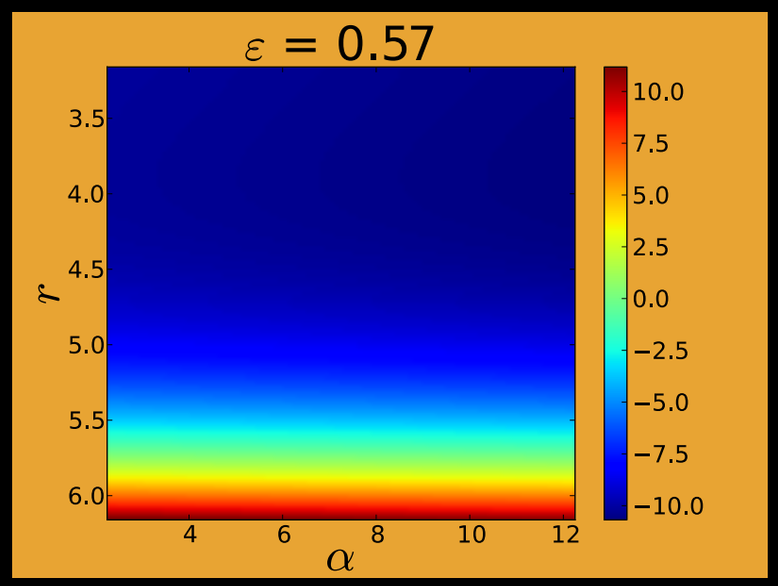


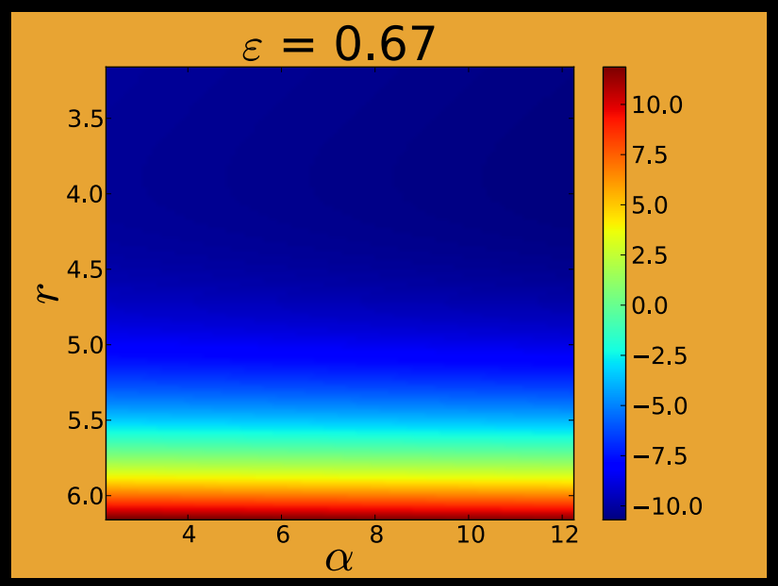
Screening: TINKER ANALYZE

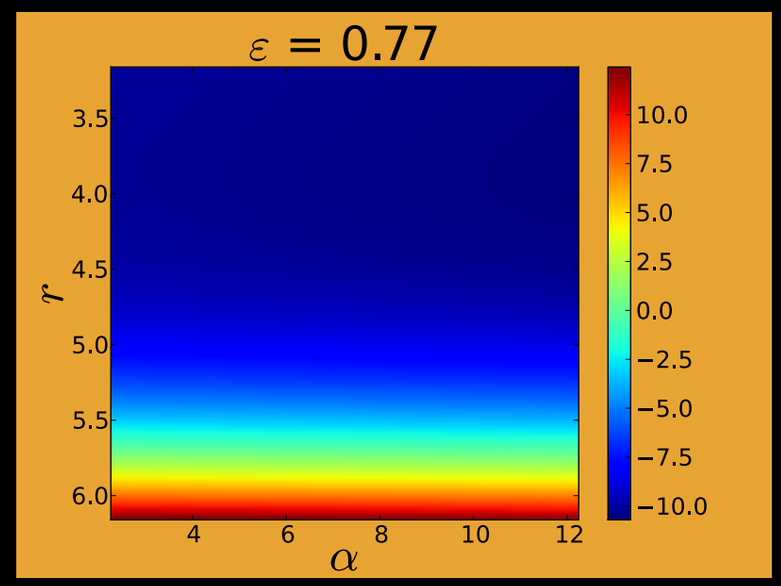




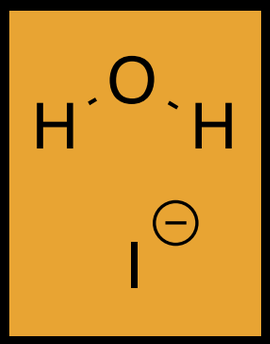








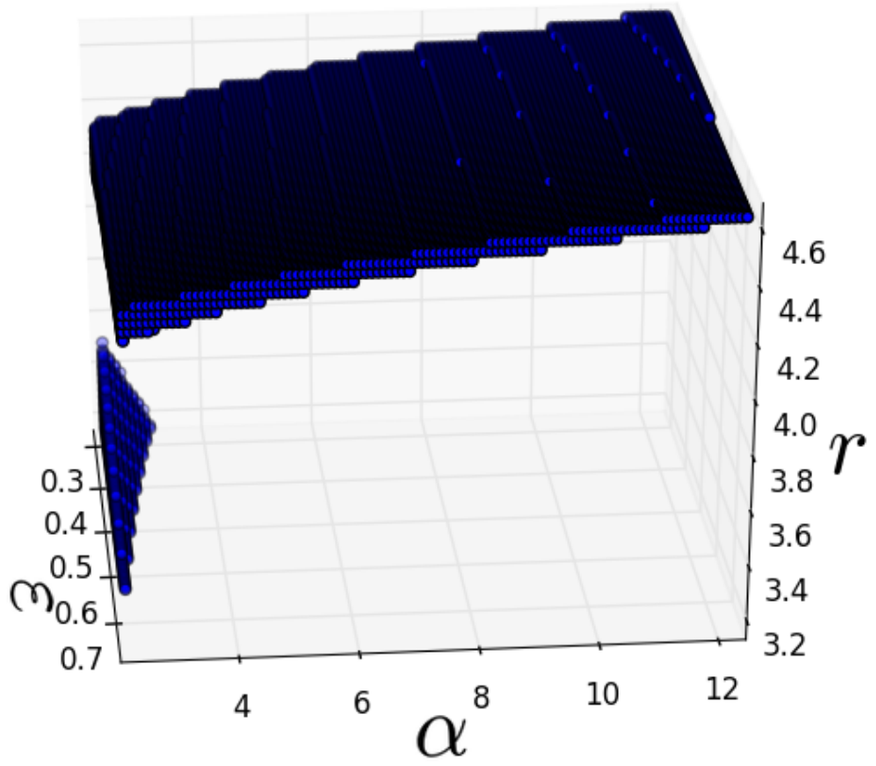
Radius: ↑ — Energy: obviously less.
Epsilon: ↑ — Energy: less.
Alpha: ↑ — Energy: slightly more.



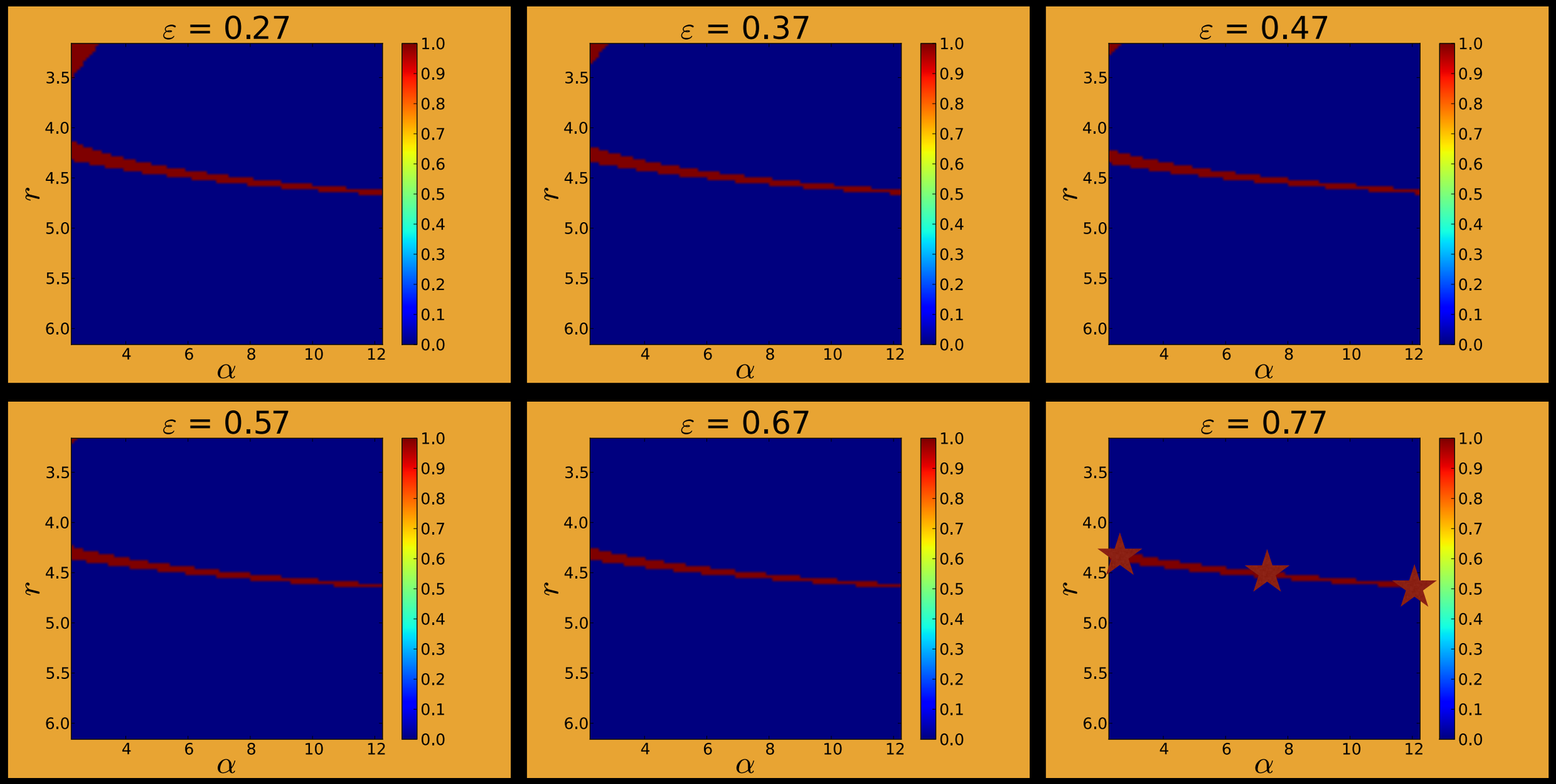
Screening

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 ~ -10.12: red; otherwise: blue.

Results

Simulation Results

a	items	*ε*				
		0.27	0.395	0.52	0.645	0.77
2.25	*r*	4.225	4.27	4.30	4.315	4.315
	ΔG	-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
7.25	*r*	4.51	4.525	4.525	4.525	4.525
	ΔG	-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
12.25	*r*	4.645	4.645	4.645	4.63	4.63
	ΔG	-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