

# Heavy Metal Ion Simulations in Water

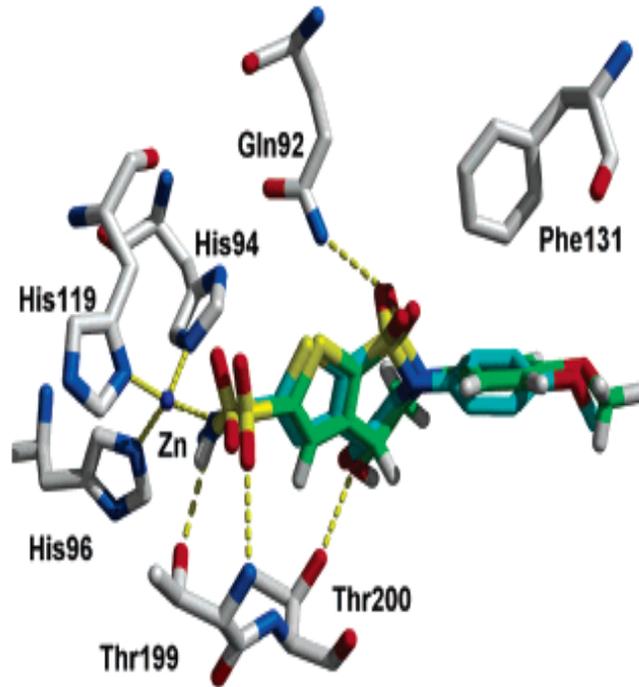
Sean Braet and Dr. Jeb Kegerreis



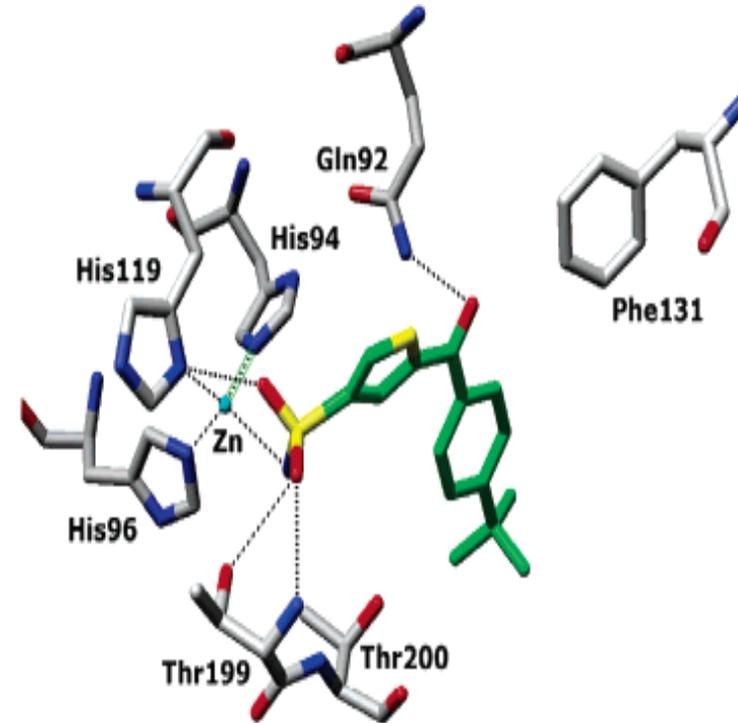
# Understanding Metal Ion Solvation has Varied Applications

- Enzyme cofactors
- Water Pollutants

Ai.



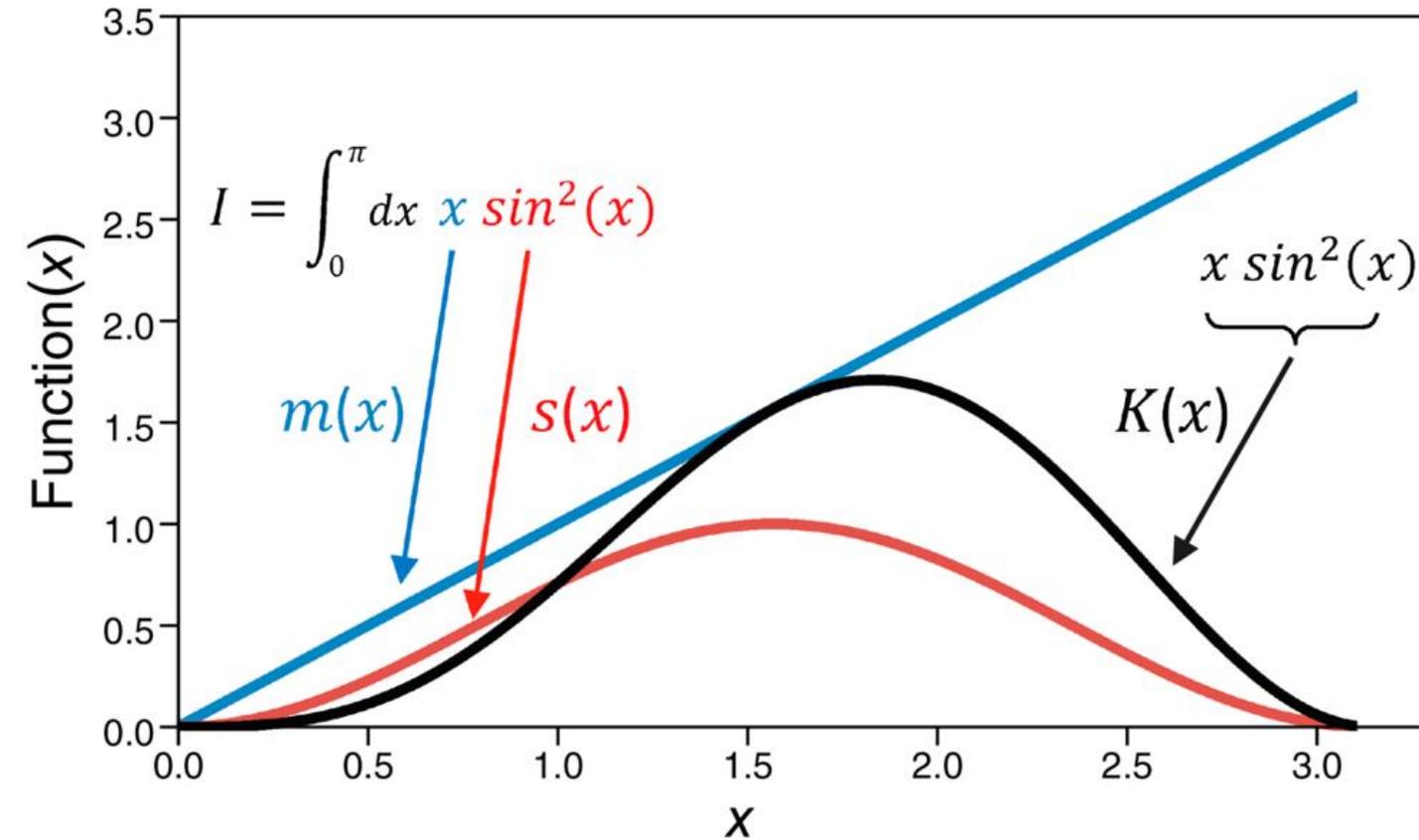
Aii



# Energetics Calculations for Chemical Systems Become Highly Complex

$$\langle V \rangle = \frac{\int dr^N V(r^N) e^{-\beta V(r^N)}}{\int dr^N e^{-\beta V(r^N)}}$$

# Monte Carlo Simulation is a Computationally Efficient Method for Numerically Valuating a System



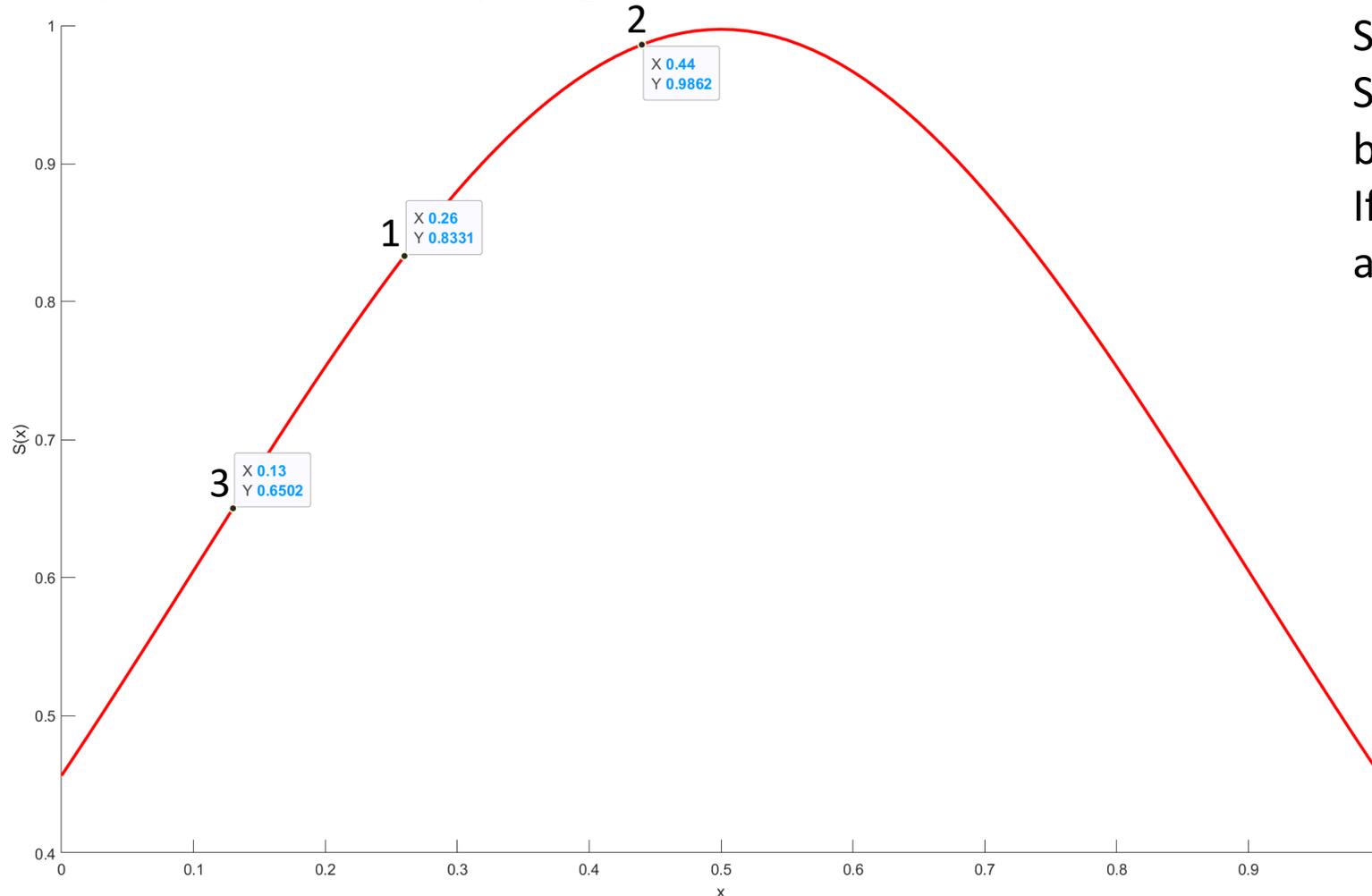
Sampling Function

Monte Carlo Integrand

(2) Hoyer, C. E.; Kegerreis, J. S. A Primer in Monte Carlo Integration Using Mathcad. *J. Chem. Educ.* **2013**, 90 (9), 1186–1190.

# Monte Carlo Simulation is a Computationally Efficient Method for Numerically Evaluating a System

## Importance Sampling:



Step 1-2:  $S(2)/S(1) > 1$ , step is accepted  
Step 1-3:  $S(3)/S(1) < 1$ , call a random number between 0 and 1 ( $N$ ):  
If  $S(3)/S(1) > N$ , accept, if  $S(3)/S(1) < N$  reject and recount previous step

# Lennard Jones Potentials Model Van Der Waals Forces

Interaction	$\sigma$ (Å)	$\epsilon$ (kcal/mol)
O-O <sup>3</sup>	3.166	0.1500
O-Zn <sup>4</sup>	1.95	0.2500
O-Cd <sup>5</sup>	2.7	0.0060
O-Pb <sup>5</sup>	3.0	0.1912

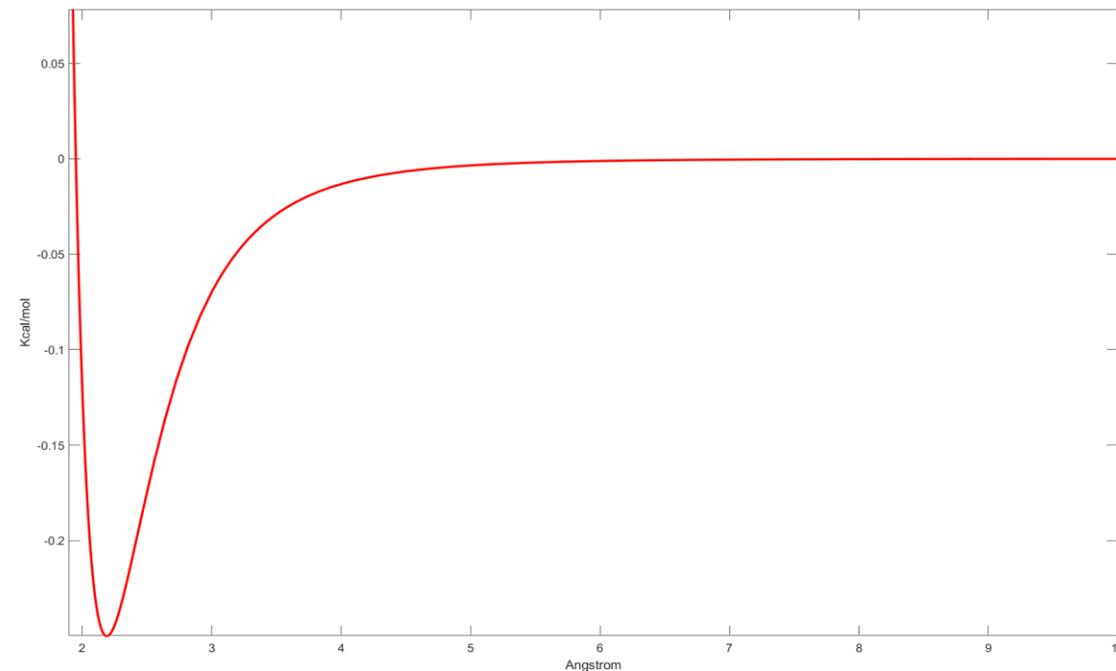
(3) Mark, P.; Nilsson, L. *J. Phys. Chem. A* **2001**, *105* (43), 9954–9960.

(4) Dezfoli, A. A.; Mehrabian, M. A.; Hashemipour, H. *Chemical Engineering Communications* **2015**, *202* (12), 1685–1692.

(5) de Araujo, A. S.; Sonoda, M. T.; Piro, O. E.; Castellano, E. E. *J. Phys. Chem. B* **2007**, *111* (9), 2219–2224.

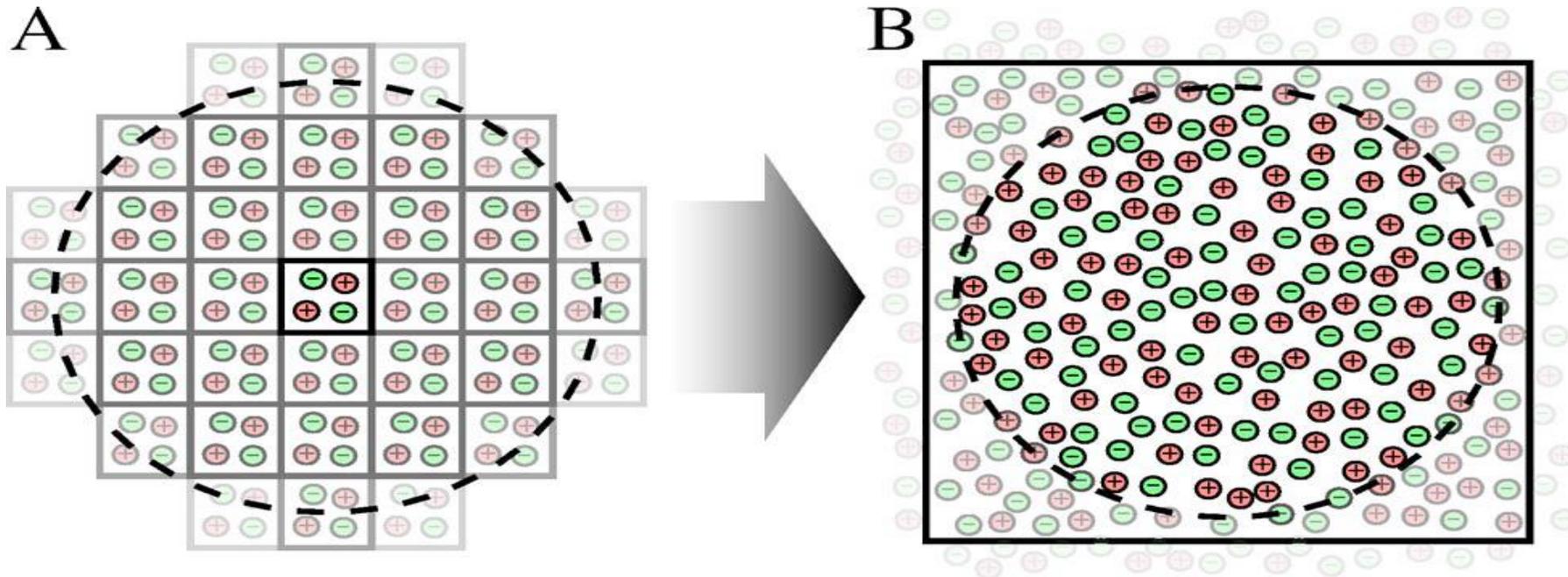
$$V_{ij} = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$

$\epsilon_{ij}$  relates to the potential well minimum  
 $\sigma_{ij}$  relates to the zero potential distance



# Wolfe's Method Provides a Computationally Efficient Method for Evaluating Long Range Interactions

$$V_{ij}(r) = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^6 \right] + q_i q_j \left[ \frac{\operatorname{erfc}(\alpha r)}{r_{\text{coff}}} - \frac{\operatorname{erfc}(\alpha r_{\text{coff}})}{r_{\text{coff}}} + \left( \frac{\operatorname{erfc}(\alpha r_{\text{coff}})}{r_{\text{coff}}^2} + \frac{2\alpha e^{(-\alpha^2 r_{\text{coff}}^2)}}{\sqrt{\pi} r_{\text{coff}}} \right) (r - r_{\text{coff}}) \right],$$



(6) Fennell, C. J.; Gezelter, J. D. Is the Ewald Summation Still Necessary? Pairwise Alternatives to the Accepted Standard for Long-Range

Electrostatics. *The Journal of Chemical Physics* **2006**, *124* (23), 234104.

# Solvation Energies were Calculated, and Radial Distribution Functions were Generated

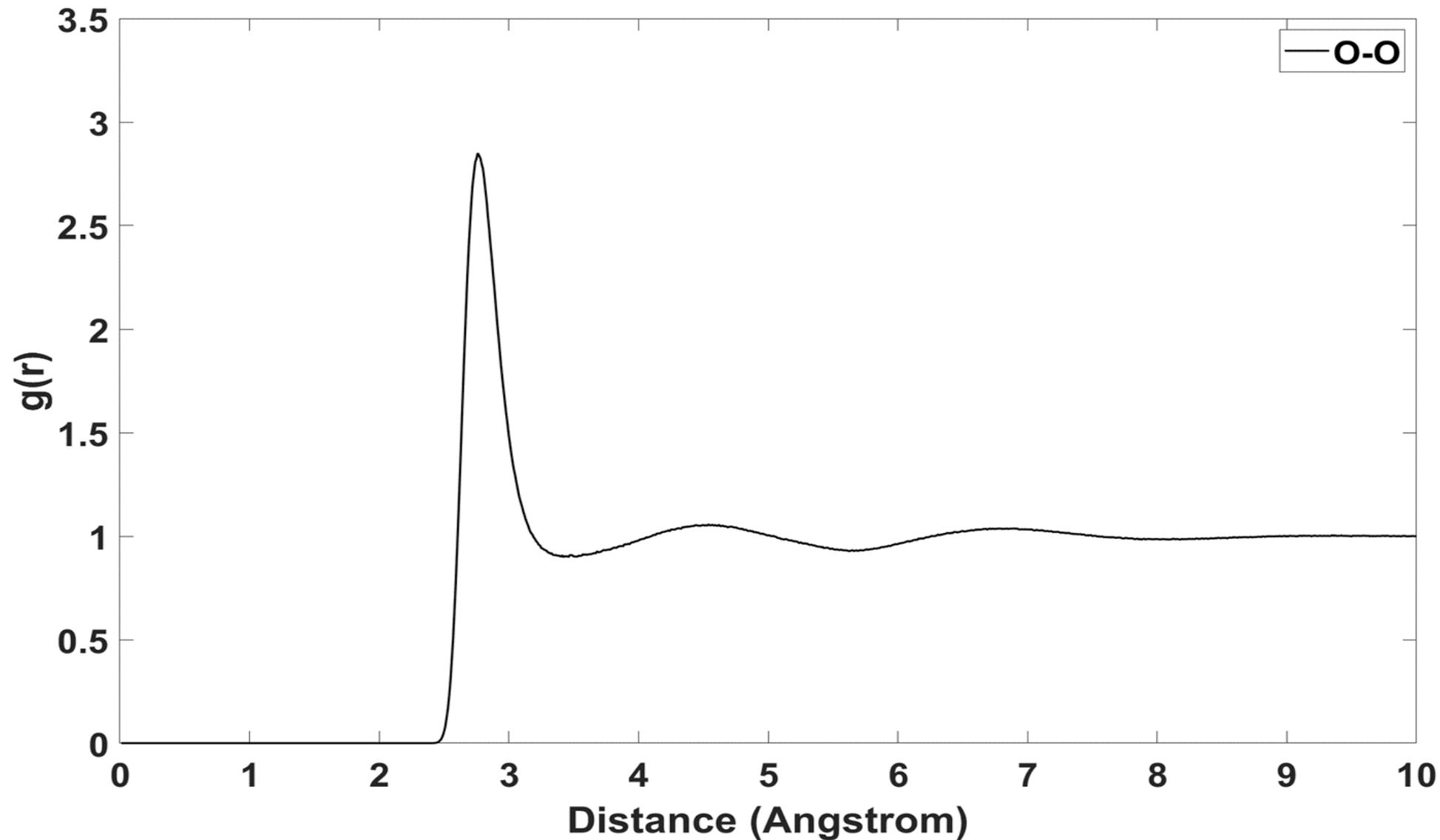
Sampling Function:  $e^{-\beta V_{ij}(r)}$

Monte Carlo Integrand:  $V_{ij}(r)$

Solvation Energy:  $V_{sol} = V_{ionic} - V_{water}$

Radial Distribution Function Calculation:  $g(r) = 4\pi\rho \int g(r)r^2 dr$

# Simulations of Pure Water Established the Validity of the Method



# Simulations of Pure Water Established the Validity of the Method

System	Coordination Number	1 <sup>st</sup> Peak Position (Å)	1 <sup>st</sup> Peak Maximum	2 <sup>nd</sup> Peak Position (Å)	2 <sup>nd</sup> Peak Maximum
H <sub>2</sub> O	5.2	2.76	2.85	4.55	1.05
Lit. H <sub>2</sub> O <sup>3</sup>	4.7	2.87	3.09	4.48	1.14

(3) Mark, P.; Nilsson, L. Structure and Dynamics of the TIP3P, SPC, and SPC/E Water Models at 298 K. *J. Phys. Chem. A* **2001**, *105* (43), 9954–9960.

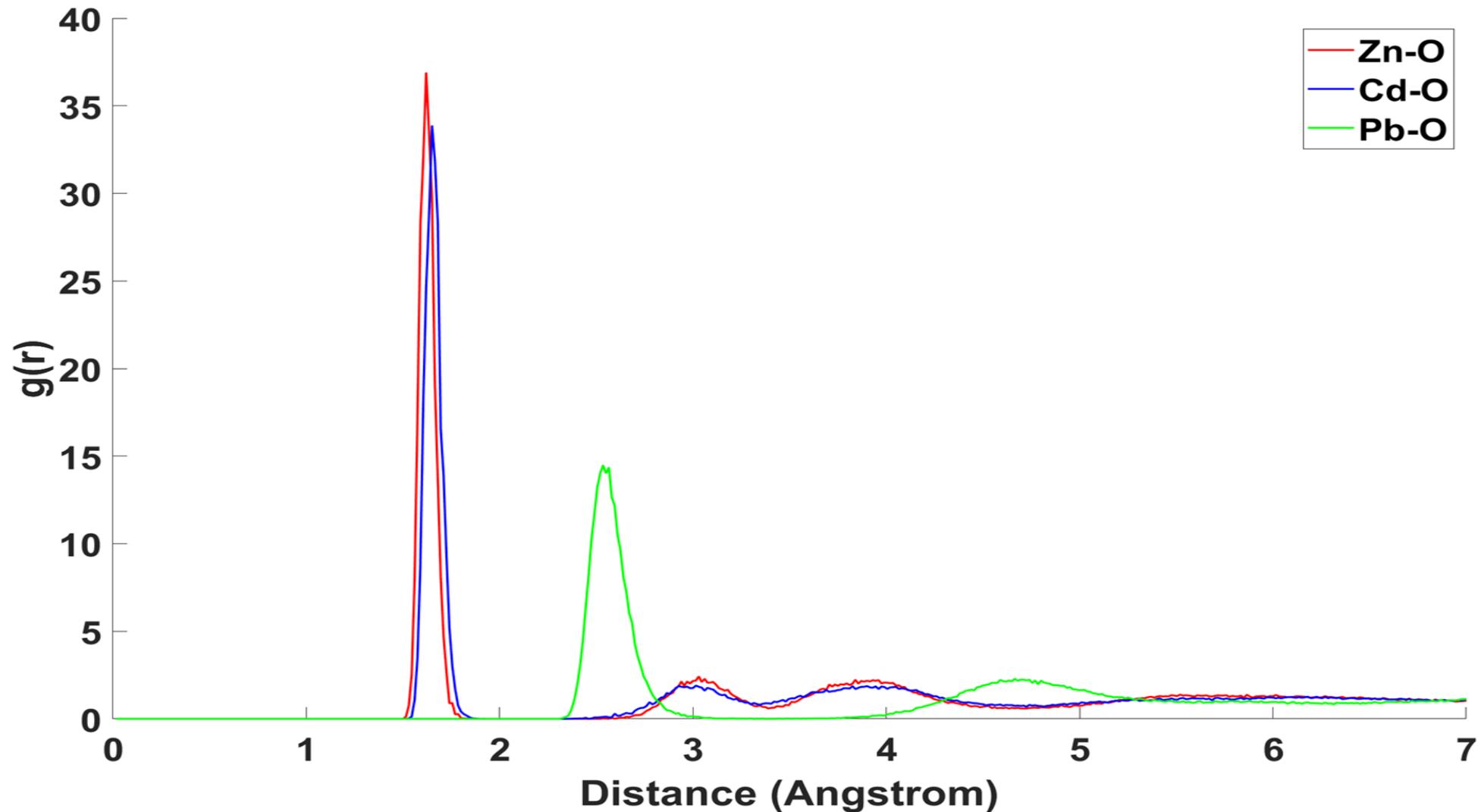
# Simulations of Aqueous Ionic Systems Yielded Varied Results

System	Potential Energy (kcal/mol)	Solvation Energy (kcal/mol)	Literature Solvation Energy (kcal/mol) <sup>5,7</sup>	% Difference
Zn <sup>2+</sup> (aq)	-5465.9	-518.2	-334.4*	43.11%
Cd <sup>2+</sup> (aq)	-5451.8	-507.0	-436.9	14.86%
Pb <sup>2+</sup> (aq)	-5314.4	-366.8	-359.0	2.15%

(5) de Araujo, A. S.; Sonoda, M. T.; Piro, O. E.; Castellano, E. E. Development of New Cd<sup>2+</sup> and Pb<sup>2+</sup> Lennard-Jones Parameters for Liquid Simulations. *J. Phys. Chem. B* **2007**, *111* (9), 2219–2224.

(7) Johnson, K. J.; Cygan, R. T.; Fein, J. B. Molecular Simulations of Metal Adsorption to Bacterial Surfaces. *Geochimica et Cosmochimica Acta* **2006**, *70* (20), 5075–5088.

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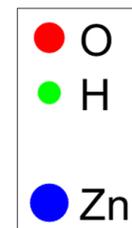
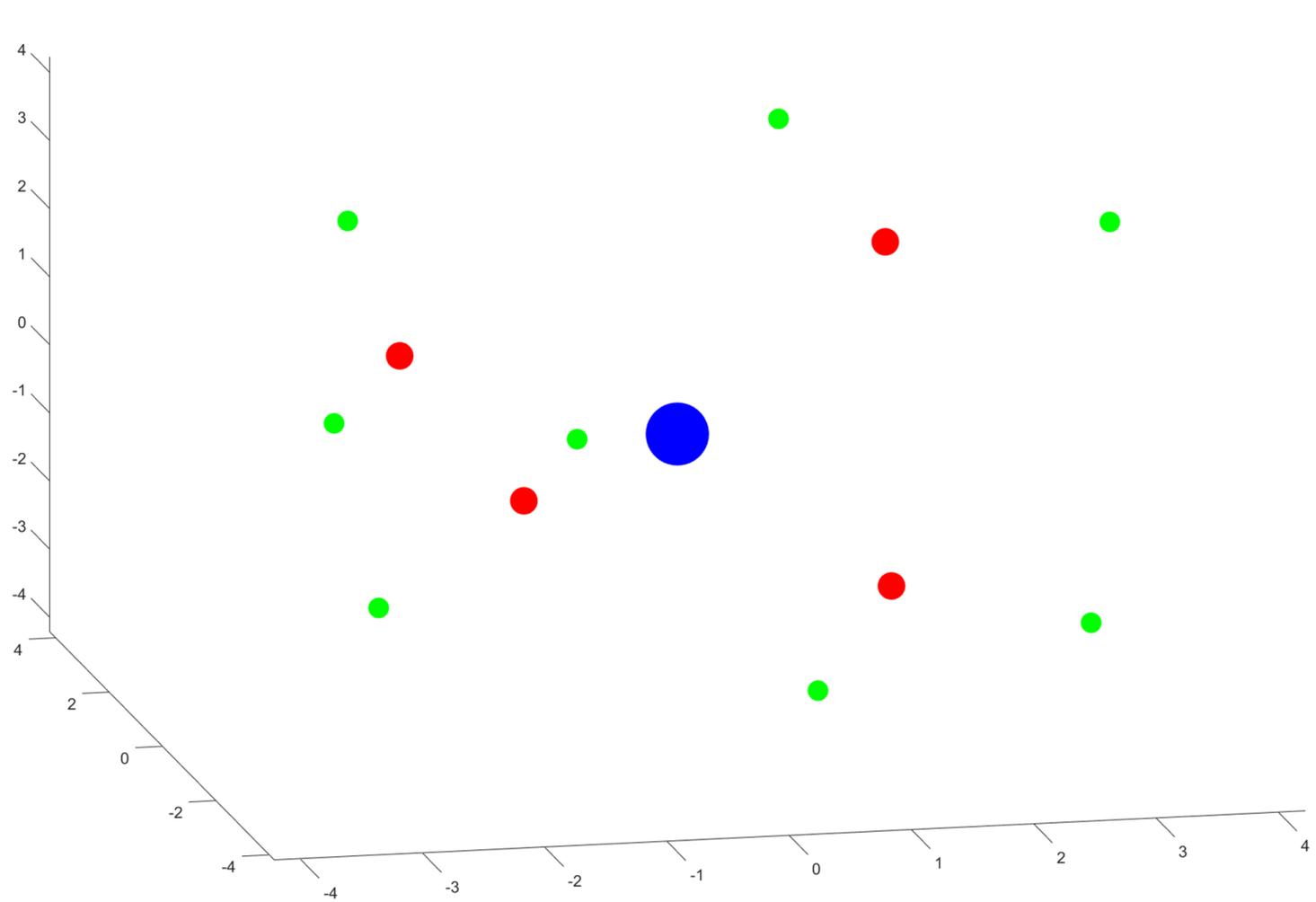
# Simulations of Aqueous Ionic Systems Yielded Varied Results

System	Coordination	1 <sup>st</sup> Peak	1 <sup>st</sup> Peak	2 <sup>nd</sup> Peak	2 <sup>nd</sup> Peak
	Number	Position (Å)	Maximum	Position (Å)	Maximum
Zn <sup>2+</sup> (aq)	4.0	1.62	36.90	3.02	2.18
Lit. Zn <sup>2+</sup> (aq) <sup>1</sup>	6.0	2.12	19.10	4.10	1.95
Cd <sup>2+</sup> (aq)	4.0	1.65	33.88	3.02	1.90
Lit. Cd <sup>2+</sup> (aq) <sup>5</sup>	6.0	2.08	23.75	4.24	2.1
Pb <sup>2+</sup> (aq)	9.0	2.535	14.48	4.70	2.23
Lit. Pb <sup>2+</sup> (Lit) <sup>5</sup>	6.0	2.56	12.96	4.79	1.95

(1) Irwin, J. J.; Raushel, F. M.; Shoichet, B. K. Virtual Screening against Metalloenzymes for Inhibitors and Substrates <sup>†</sup>. *Biochemistry* **2005**, *44* (37), 12316–12328.

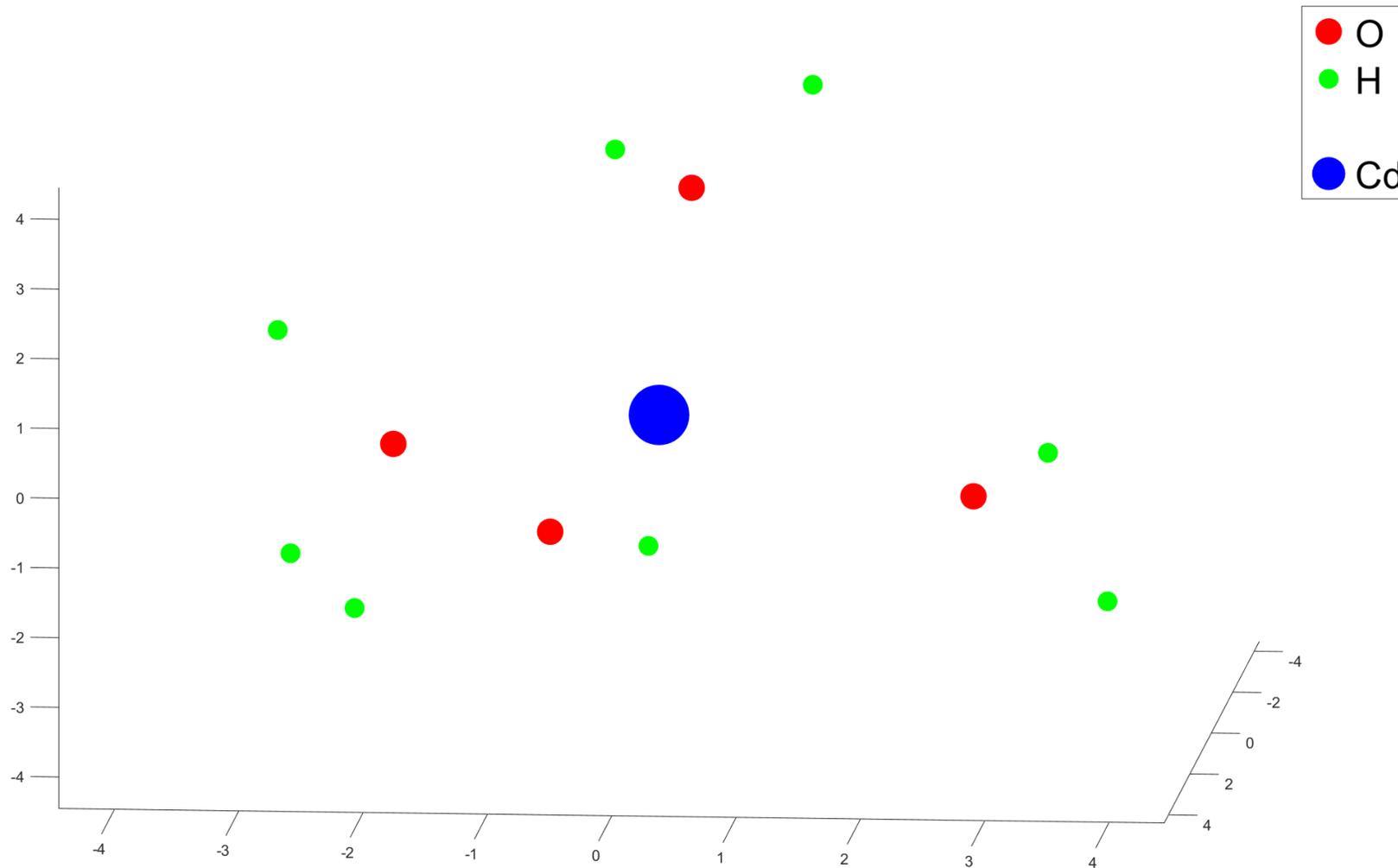
(5) de Araujo, A. S.; Sonoda, M. T.; Piro, O. E.; Castellano, E. E. Development of New Cd<sup>2+</sup> and Pb<sup>2+</sup> Lennard-Jones Parameters for Liquid Simulations. *J. Phys. Chem. B* **2007**, *111* (9), 2219–2224.

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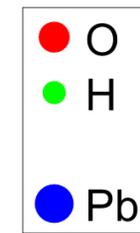
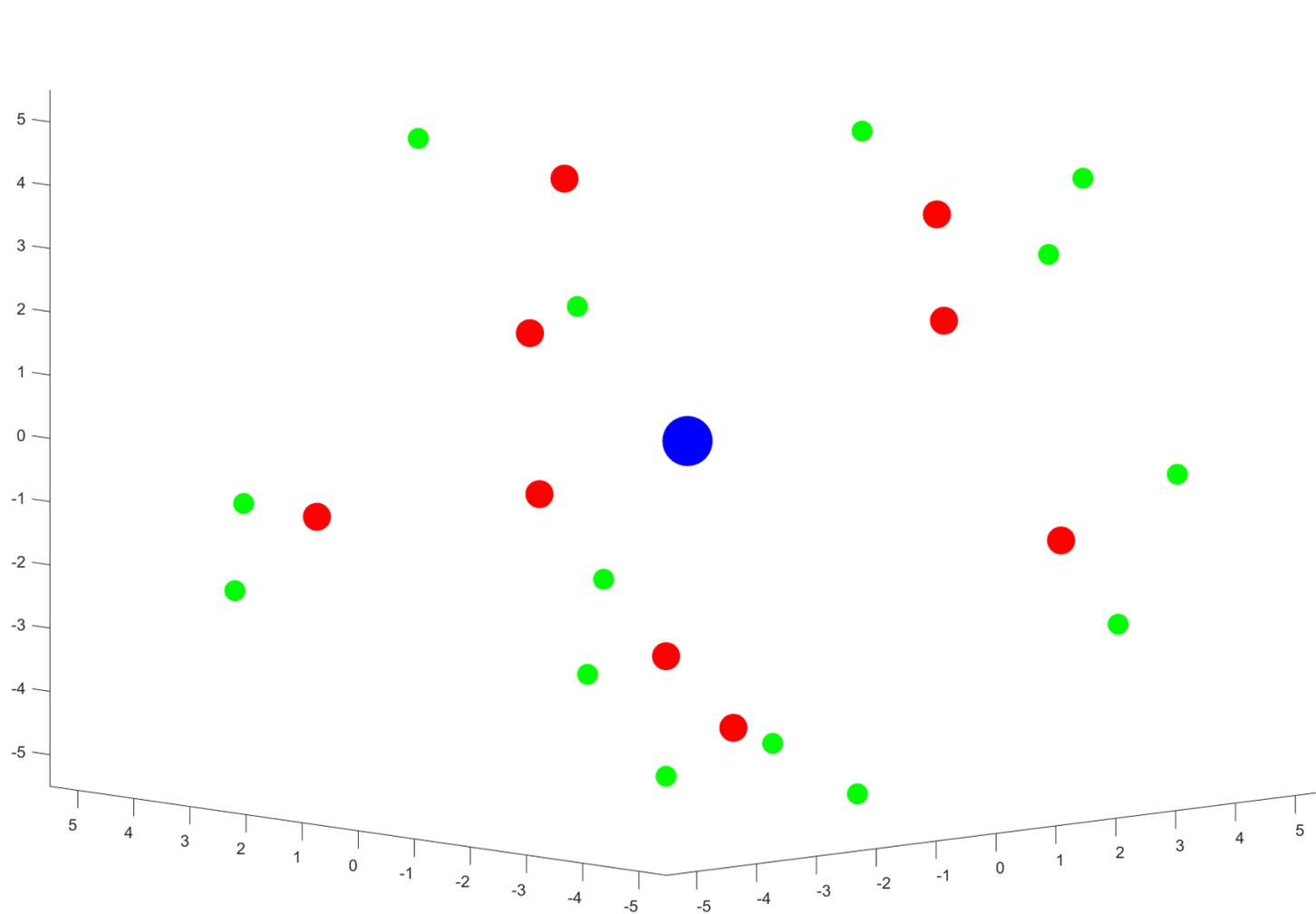
Zinc simulations yielded a tetrahedral shaped first coordination sphere

# Simulations of Aqueous Ionic Systems Yielded Varied Results



Cadmium simulations yielded a tetrahedral shaped first coordination sphere

# Simulations of Aqueous Ionic Systems Yielded Varied Results



Lead simulations yielded a first coordination sphere with 9 waters

# Future Directions

- Using other potential functions
  - Lennard Jones 12-6-4
  - Further exploring the validity of Wolfe's method for this charged system
- Using a flexible model for water
- Applications to other metal ions
- Application to more complex systems

# Acknowledgements

- Thank you to Dr. James A. Beres and Merry Jean Beres for their financial support through the Beres Grant.
- Dr. Kegerreis
- The Shippensburg University Chemistry Department



# References

- (1) Irwin, J. J.; Raushel, F. M.; Shoichet, B. K. Virtual Screening against Metalloenzymes for Inhibitors and Substrates <sup>†</sup>. *Biochemistry* **2005**, *44* (37), 12316–12328.
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- (4) Dezfoli, A. A.; Mehrabian, M. A.; Hashemipour, H. Molecular Dynamics Simulation of Heavy Metal Ions in Aqueous Solution Using Lennard-Jones 12-6 Potential. *Chemical Engineering Communications* **2015**, *202* (12), 1685–1692.
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