

# Swaminath Bharadwaj G.

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Computational Physical Chemistry  
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## Education

- 2011-2018 Integrated M.Tech-Ph.D, Department of Chemical Engineering  
Indian Institute of Technology Madras, Chennai, India  
**Advisors:** Prof. Abhijit P. Deshpande, Prof. P. B. Sunil Kumar  
**Thesis:** Coarse Grained Simulation and Mean-Field Modeling of LCST in Thermoresponsive Polymer Solutions
- 2007-2011 B.Tech, Department of Chemical Engineering  
Alagappa College of Technology, Anna University, Chennai, India  
G.P.A: 8.91 (scale of 10)

## Work Experience

- 2018-present Post-doctoral Researcher, Computation Physical Chemistry  
Eduard-Zintl-Institut für Anorganische und Physikalische Chemie  
Technical University of Darmstadt, Germany  
**Advisor:** Prof. Nico F. A. van der Vegt

## Research Interests

My research focuses on the modeling of **stimuli-responsive materials** and **interfacial phenomena in soft matter systems** using a combination of molecular simulations, free energy calculations, statistical mechanical and mean-field theoretical approaches. A complimentary focus of my research is to develop methods for the thermodynamic characterization of solute solvation shell, particularly for flexible solutes such as polymer and biopolymers, using a combination of molecular simulations, advanced sampling methods and theoretical frameworks such as small system thermodynamics.

## Publications

1. “Nonadditive ion effects on the coil-globule equilibrium of PNIPAM: A computer simulation study” Y. Zhao, S. Bharadwaj\*, N. F. A. van der Vegt. Accepted in Physical Chemistry Chemical Physics, April 8, 2022 .  
\*Joint first author
2. “Solvation Shell Thermodynamics of Extended Hydrophobic Solutes in Mixed Solvents” M. Tripathy, S. Bharadwaj\*, Nico F. A. van der Vegt. Accepted in The Journal of Chemical Physics, 1st April, 2022.  
DOI:[10.1063/5.0090646](https://doi.org/10.1063/5.0090646)  
\*Joint first author
3. **Review:** “Cononsolvency of thermoresponsive polymers: where we are now and where we are going” S. Bharadwaj, B. J. Niebuur, K. Nothdurft, W. Richtering, N. F. A. van der Vegt, C. M. Papadakis. Accepted in Soft Matter, 2022.  
DOI: [10.1039/D2SM00146B](https://doi.org/10.1039/D2SM00146B)

4. "Small-to-large length scale transition of TMAO interaction with hydrophobic solutes" A. Folberth, S. Bharadwaj, N. F. A. van der Vegt, *Physical Chemistry Chemical Physics* 24 (4), 2080-2087, 2022.  
DOI: [10.1039/D1CP05167A](https://doi.org/10.1039/D1CP05167A)  
**2022 PCCP HOT Articles**
5. "Direct Calculation of Entropic Components in Cohesive Interaction Free Energies" S. Bharadwaj, S. Jabes B., N. F. A. van der Vegt, *The Journal of Physical Chemistry B* 125 (39), 11026-11035, 2021.  
DOI: [10.1021/acs.jpcc.1c05748](https://doi.org/10.1021/acs.jpcc.1c05748)  
**Part of special issue "Dor Ben-Amotz Festschrift"**
6. "An interplay of excluded-volume and polymer-(co) solvent attractive interactions regulates polymer collapse in mixed solvents" S. Bharadwaj, D. Nayar, C. Dalgicdir, N. F. A. van der Vegt, *The Journal of Chemical Physics* 154 (13), 134903, 2021.  
DOI: [10.1063/5.0046746](https://doi.org/10.1063/5.0046746)
7. **Communication:** "A cosolvent surfactant mechanism affects polymer collapse in miscible good solvents" S. Bharadwaj, D. Nayar, C. Dalgicdir, N. F. A. van der Vegt, *Communications Chemistry* 3 (1), 1-7, 2020.  
DOI: [10.1038/s42004-020-00405-x](https://doi.org/10.1038/s42004-020-00405-x)
8. "Characterizing Polymer Hydration Shell Compressibilities with the Small-System Method" M. Tripathy, S. Bharadwaj\*, S. Jabes B., N. F. A. van der Vegt, *Nanomaterials* 10 (8), 1460, 2020.  
DOI: [10.3390/nano10081460](https://doi.org/10.3390/nano10081460)  
\*Joint First Author  
**Part of the special issue "Nanoscale Thermodynamics"**
9. "Does preferential adsorption drive cononsolvency?" S. Bharadwaj, N. F. A. van der Vegt. *Macromolecules* 52 (11), 4131-4138, 2019.  
DOI: [10.1021/acs.macromol.9b00575](https://doi.org/10.1021/acs.macromol.9b00575)
10. "Kosmotropic effect leads to LCST decrease in thermoresponsive polymer solutions" S. Bharadwaj, P. B. Sunil Kumar, S. Komura, A. P. Deshpande, *The Journal of Chemical Physics* 148 (8), 084903, 2018.  
DOI: [10.1063/1.5012838](https://doi.org/10.1063/1.5012838)
11. "Spherically symmetric solvent is sufficient to explain the LCST mechanism in polymer solutions" S. Bharadwaj, P. B. Sunil Kumar, S. Komura, A. P. Deshpande, *Macromolecular Theory and Simulations* 26 (2), 1600073.  
DOI: [10.1002/mats.201600073](https://doi.org/10.1002/mats.201600073)

## Conferences

### Oral Contributions

1. "Nonadditive ion effects on the solvation of thermoresponsive polymers in aqueous solutions," Swaminath Bharadwaj, Yani Zhao, Nico F. A. van der Vegt. *CompFlu*, Indian Institute of Technology Gandhinagar, India, December 13-15, 2021.
2. "A cosolvent surfactant mechanism affects polymer collapse in miscible good solvents," Swaminath Bharadwaj. *Osmolyte and Cosolvent Effects in Stimuli-Responsive Soft Matter Systems*, Virtual conference organized jointly by Technical University of Darmstadt and Technical University of Munich, February 25-26, 2021.
3. "On the mechanism of lower critical solution temperature and its variation with co-solvents in thermoresponsive polymer solutions," Swaminath Bharadwaj, P. B. Sunil Kumar, Shigeyuki Komura, Abhijit P. Deshpande. *CompFlu*, Indian Institute of Technology Madras, Chennai, India, December 18-20, 2017.
4. "Effect of co-solvent on the LCST of thermoresponsive polymers," Swaminath Bharadwaj, P. B. Sunil Kumar, Shigeyuki Komura, Abhijit P. Deshpande. *2nd International Conference on Soft Materials (ICSM)*, Malaviya National Institute of Technology Jaipur, India, December 12-16, 2016. **Best Oral Presentation Award**

## Poster Contributions

1. “Characterizing Polymer Hydration Shell Thermodynamics Using the Small System Method,” Swaminath Bharadwaj, Nico van der Vegt. *Recent progress in the statistical mechanics of solutions through Kirkwood-Buff integrals and related approaches*, Université de Bourgogne, France, September 20-22, 2021
2. “Coil-to-globule transitions in mixed solvents: A cosolvent surfactant mechanism,” Swaminath Bharadwaj, Nico van der Vegt. *11th Liquid Matter Conference*, Prague, July 19-23, 2021
3. “A cosolvent surfactant mechanism affects polymer collapse in miscible good solvents,” Swaminath Bharadwaj, Nico van der Vegt. *CompFlu*, Indian Institute of Technology Bombay, India, December 10-12, 2020.
4. “On the mechanism of lower critical solution temperature and its variation with co-solvents in thermoresponsive polymer solutions,” Swaminath Bharadwaj, P. B. Sunil Kumar, Shigeyuki Komura, Abhijit P. Deshpande. *10th Liquid Matter Conference*, Ljubljana, Slovenia, July 17-21, 2017.
5. “LCST behavior of thermoresponsive polymers in binary solvent mixtures,” Swaminath Bharadwaj, P. B. Sunil Kumar, Shigeyuki Komura, Abhijit P. Deshpande. *CompFlu*, Indian Institutes of Science Education and Research, Pune, India, January 2-4, 2016.
6. “Coil-to-globule transition in thermoresponsive polymer solutions,” Swaminath Bharadwaj, P. B. Sunil Kumar, Shigeyuki Komura, Abhijit P. Deshpande. *Physics of Structural and Dynamical Hierarchy in Soft Matter*, Institute of Industrial Science, University of Tokyo, Japan, March 16-18, 2015.

## Organization

1. Organization of the virtual conference “Osmolyte and cosolvent effects in stimuli-responsive soft matter systems” in February, 2021 with Prof. Nico van der Vegt, TU Darmstadt and Prof. Christine M. Papadakis, TU Munich  
Website: <https://sites.google.com/view/ocesrms2021/>
2. Assisted in the organization of the conference “Complex Fluids”, IIT Madras and IIT Palakkad in 2017
3. Initiated and organized the yearly “In-house Symposium” in the Department of Chemical Engineering, IIT Madras

## Research Highlights

**Cosolvent Effects on the Phase Behavior of Responsive Polymers:** The coil-globule transition of aqueous polymers is of profound significance in understanding the structure and function of responsive soft matter. In particular, the remarkable effect of amphiphilic cosolvents (e.g., alcohols) that leads to both swelling and collapse of stimuli-responsive polymers has been hotly debated in the literature, often with contradictory mechanisms proposed. A predominant focus in the literature has been placed on the role of polymer-cosolvent attractive interactions whereas the role of *excluded volume interactions (repulsive interactions)* has been largely neglected. Using molecular dynamics simulations and free energy calculations, we demonstrated that alcohols *preferentially adsorb* on the polymer and reduce the free energy cost of creating a repulsive polymer-solvent interface via a *surfactant-like mechanism* which surprisingly *drives polymer collapse* at low alcohol concentrations. This hitherto neglected role of interfacial solvation thermodynamics is common to all coil-globule transitions, and rationalized the experimentally observed effects of higher alcohols and polymer molecular weight on the coil-to-globule transition of thermoresponsive polymers. Further, we showed that polymer-(co)solvent attractive interactions reinforce or compensate this mechanism and it is this interplay which drives polymer swelling or collapse. The surfactant-like mechanism proposed in our study is generic and applicable to other polymer solutions containing amphiphilic cosolvents.

**Salt Effects on the Coil-to-Globule Transitions of Thermoresponsive Polymers:** The anion Hofmeister series classifies anions in order of their ability to salt out proteins:  $\text{CO}_3^{2-} > \text{SO}_4^{2-} > \text{S}_2\text{O}_3^{2-} > \text{H}_2\text{PO}_4^- > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^- > \text{I}^- > \text{ClO}_4^- > \text{SCN}^-$ . Specifically, anions on the right hand side of this series are *weakly hydrated* and *partition to nonpolar surfaces* such as polymer/water or air-water interfaces. On the other hand, *strongly hydrated* anions (left hand side of the series) tend to *strongly interact with water* molecules and remain in the bulk water environment. Recent experiments have indicated that the combined

effect of a weakly hydrated and a strongly hydrated anion on the lower critical solution temperature (LCST) of poly(N-isopropylacrylamide)(PNIPAM) is nonadditive. Our study focused on this nonadditive effect on the coil-to-globule of PNIPAM using large scale atomistic simulations. The simulations were able to capture the experimentally observed effect of mixed salts (NaI-Na<sub>2</sub>SO<sub>4</sub>) on the coil-globule equilibrium of PNIPAM. Interestingly, the predicted change in LCST as a function of salt concentration from simulations, through a semi-quantitative analysis, is in quantitative agreement with experimental measurements. We showed that non-additive ion effects on the coil-to-globule transitions of PNIPAM arise due to the interplay between *depletion of the strongly hydrated sulfate ions* and the preferential accumulation of the iodide ions on the polymer leading to *favourable PNIPAM-I<sup>-</sup> interactions*. This correlates with the *partitioning of the Na<sup>+</sup> cations* from the counterion cloud of the weakly hydrated iodide ions to the counterion cloud of the strongly hydrated sulfate ions. The proposed mechanism is applicable to other solutions containing a mixture of a weakly hydrated and strongly hydrated anion.

**Hydrophobic Length Scale Dependence of Osmolyte Effects:** Osmolytes such as Trimethylamine N-oxide (TMAO) regulate the thermodynamic stability of proteins and polymers, and are shown to play an important role in biological systems. The effect of TMAO on the solvation of nonpolar solutes is not well understood. Our study focused on the effect of TMAO on the hydrophobic hydration and hydrophobic interactions of “small” and “large” hydrophobic solutes using molecular dynamics (MD) simulations and free-energy calculations. Interestingly, the simulation data indicated the occurrence of a *length scale crossover* in the TMAO interaction with repulsive Weeks–Chandler–Andersen (WCA) solutes: while TMAO is *depleted* from the hydration shell of a *small WCA solute* (methane) and increases the free-energy cost of solute-cavity formation, it *preferentially binds* to a *large WCA solute* ( $\alpha$ -helical polyalanine), reducing the free-energy cost of solute-cavity formation via a *surfactant-like mechanism*. Significantly, the study shows that this surfactant-like behaviour of TMAO reinforces the solvent-mediated attraction between large WCA solutes by means of an entropic force linked to the interfacial accumulation of TMAO. It therefore *favours* solute–solute contact states that *minimise the surface area* exposed to the solvent and have a small overall number of TMAO molecules adsorbed.

**Solvation Shell Thermodynamics:** The ability of various cosolutes and cosolvents, in aqueous solutions, to enhance or quench interfacial solvent density fluctuations have crucial implications on the conformational equilibrium of macromolecules such as polymers and proteins. Therefore characterizing the thermodynamics of the solvation shell and their dependence on stimuli such as cosolvent/cosolute concentration is very important. The small system method (SSM) exploits the unique nature of finite sized open systems in which, *thermodynamic quantities scale with the inverse system size*. This scaling allows for the *accurate estimation of properties* in the thermodynamic limit in finite size simulations. Our study extends the SSM to characterize the thermodynamics of the hydration shell of a model extended hydrophobic solute in water and water-urea/methanol mixtures. In parallel, our other study was aimed at computing the contribution to the solvation free energy arising from fluctuating solute-solvent cohesive interactions which is known as “Fluctuation entropy”. The fluctuation entropy is usually computed through *indirect or approximate methods* which are not applicable to solutes with *flexible conformational degrees of freedom* such as macromolecules. This study proposed a direct method based on the indirect umbrella sampling (INDUS) method to *directly compute the fluctuation entropy* which can be applied to macromolecules.

## Computational Skills

- **Molecular Simulations**  
GROMACS, LAMMPS and PLUMED
- **Free energy methods**  
Thermodynamic Integration, Free energy perturbation, Umbrella sampling
- **Programming Languages**  
Extensive use of C, bash and awk for writing scripts and analysis codes. Knowledge of L<sup>A</sup>T<sub>E</sub>X for document preparation.
- **Related computational software**  
VMD, Gnuplot, Matplotlib and Git. Extensively worked with Linux OS.

## Teaching Experience

Over the course of my PhD and postdoc tenure, I have had the opportunity to be a formal teaching assistant for different courses. My responsibilities included preparation of weekly exercises, holding problem solving sessions for students, preparation and correction of written examinations and taking part in oral examinations. In some of the courses, I had the privilege to deliver one or two lectures.

1. Teaching assistant with Prof. Nico van der Vegt for the graduate course “Physical Chemistry of Soft Matter” from October, 2021 - February, 2022
2. Teaching assistant with Prof. Nico van der Vegt for the undergraduate course “Computer Applications in Chemistry” from April-July, 2021
3. Teaching assistant with Prof. Nico van der Vegt for the graduate course “Statistical Thermodynamics” from April-July, 2019
4. Teaching assistant with Prof. Abhijit P. Deshpande for the graduate course “Rheology of Complex Materials” from July-November, 2016 and July-November, 2017
5. Teaching assistant with Prof. P. B. Sunil Kumar for the graduate course “Methods of Computational Physics” from July-November, 2014
6. Teaching assistant with Prof. P. B. Sunil Kumar for the undergraduate course “Statistical Physics and Applications” from July-November, 2013

## References

- **Prof. Nico F. A. van der Vegt**  
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- **Prof. Abhijit P. Deshpande**  
Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai, India  
E-mail: abhijit@iitm.ac.in
- **Prof. P. B. Sunil Kumar**  
Department of Physics, Indian Institute of Technology Palakkad, Ahalia Integrated Campus, Kozhippara, Palakkad, India  
E-mail: sunil@iitpkd.ac.in
- **Dr. Shigeyuki Komura**  
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- **Prof. Walter Richtering**  
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E-mail: richtering@rwth-aachen.de
- **Prof. Christine M. Papadakis**  
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