MOLECULAR SIMULATION OF PHASE EQUILIBRIA FOR COMPLEX FLUIDS

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1 SUMMARY

The general area of this project was the development and application of novel molecular simulation methods for prediction of thermodynamic and structural properties of complex polymeric, surfactant and ionic fluids. Over this project reporting period, we have made considerable progress in developing novel algorithms to meet the computational challenges presented by the strong or long-range interactions in these systems and have generated data for well-defined models that can be used to test theories and compare to experimental data. In the following paragraphs we describe progress in each of the focus areas of the project, with references [in square brackets] to the accompanying list of publications (§ 2.1). Copies or links to the complete publications are provided in the author's web server at <http://kea.princeton.edu/papers>. Overall, 45 archival papers and many invited and contributed presentations and lectures have been based on work supported by this project. 7 PhD, 1 M.S., 2 postdoctoral fellows and 1 visitor have been associated with this work, as listed in section 3 of the report.

In the area of polymeric systems, we focused on three classes of problems. The first was inspired by experimental observations of shear-induced alignment in thin films of block copolymers in the groups of Paul Chaikin and Rick Register at Princeton. We developed a multiscale modeling approach for both cylindrical [22] and spherical [28] domains that was in good agreement with the experimental results and provided insights on the microscopic mechanism of alignment. The second topic was the effects of stiffness [20] and of confinement [14] on homopolymer solution phase behavior. Finally, we studied phase transitions and critical parameter scaling for branched polymers [27], dendrimers [39] and colloid-polymer mixtures [32]. Our predictions for the effects of branching were recently confirmed by careful measurements by Jacobs *et al.*¹

Studies of model non-ionic surfactant micellization were undertaken as part of the project, using a grand-canonical Monte Carlo methodology that can determine critical micelle concentrations in dilute solutions and can be used at conditions at which large free energy barriers prevent direct sampling of equilibrium micelle formation. In particular, ternary [1] and diblock/triblock binary surfactant systems [3] were investigated. The key finding of [3] was that, depending on surfactant architecture, micellization or phase separation was observed. A first study of a lattice model for ionic surfactants [33] obtained critical micelle concentrations and micelle aggregation numbers in modest agreement to experimental data. This work was extended to ionic surfactants in [43]. Surfactant nanoparticles were investigated in [45].

In the area of ionic systems, we completed studies of the character of ionic criticality in primitive model electrolytes [2,29] in collaboration with the group of Prof. Michael Fisher at the University of Maryland, College Park. These studies conclusively demonstrated that these systems belong to the Ising universality class, thus resolving a long-standing issue in the area of ionic criticality. In a separate study [6] in collaboration with the group of Prof. Rull at Seville, we have elucidated the close connections between ionic and tethered dipolar systems. Critical points of electrolyte mixtures were studied in collaboration with Dr. Dijkstra at Utrecht [24]. Polarizable mixtures were studied in [35]. A study of effective potentials for 1:1 electrolyte solu-

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¹ Jacobs, D.T., C.I. Braganza, A.P. Brinck, et al., Universality in eight-arm star polystyrene and methylcyclohexane mixtures near the critical point. *J. Chem. Phys.*, 127: 124905 (2007).

tions [40] demonstrated how implicit-solvent models can be used to reproduce activity coefficients over broad ranges of concentrations.

A major focus of our work has been on highly asymmetric ionic systems. Early in this project, we obtained phase diagrams and critical parameters for unrestricted primitive model electrolytes with charge asymmetries up to 10:1 [11]. We also completed studies of the influence of short-range interactions and anisotropy on the phase behavior and tricriticality of the lattice restricted primitive model [8, 12, 21]. Novel and potentially useful morphologies were obtained in [21, 34] for systems with short-range interactions in addition to the coulombic forces. The first study of coulombic criticality in polyelectrolyte chains [7] was performed in collaboration with the group of Prof. Sanat Kumar and tethered polyelectrolyte chains were studied in collaboration with Prof. Szleifer [42]. Chains with opposite charges at the two ends were studied in [23]. A major advance was recently achieved in the range of charge asymmetries for which simulation data are available [41]. Explicit calculations of the phase behavior were performed in [41] for systems of charge ratios up to 50:1 using thermodynamic integration and an approximate calculation with minimal systems was used to obtain the scaling of the critical temperature for ratios up to 2000:1. This work was reviewed in [44].

Work on novel Monte Carlo methodologies focused primarily on flat histogram methods for the direct calculation of the density of states [4, 5, 10, 13, 19]. Such methods may have particular advantages in strongly associated coulombic systems or systems with glassy dynamics [31]. We applied flat histogram methods to determine sequence landscapes in proteins [30]. Mixed-filed finite-size scaling techniques with histogram reweighting were used in [37] to obtain critical lines for binary fluid mixtures. We have continued development of fine-lattice discretized methods [16, 17, 18] first proposed in 1999 during a prior DOE project period. We also completed studies of lattice hard sphere models [25] and multi-site rigid objects [38].

A notable event of the present project period was election of the PI of this project to the National Academy of Engineering. The election citation stated that Prof. Panagiotopoulos was recognized for “the invention of the Gibbs ensemble method of molecular simulation of phase equilibrium and the development of computational techniques for studying complex fluids.” The Office of Basic Energy Science of the Department of Energy has provided major support over the years for the PI’s work being recognized by this honor.

2 PUBLICATIONS AND PRESENTATIONS RESULTING FROM THIS PROJECT (APR. 2002 – NOVEMBER 2007)

2.1 Refereed papers

1. S.-Y. Kim, A. Z. Panagiotopoulos and M. A. Floriano, “Ternary Oil-Water-Amphiphile Systems: Self-Assembly and Phase Equilibria,” *Molec. Phys.*, **100**: 2213-2220 (2002).
2. E. Luijten, M. E. Fisher and A. Z. Panagiotopoulos, “Universality Class of Criticality in the Restricted Primitive Model Electrolyte,” *Phys. Rev. Lett.*, **88**: 185701 (2002).
3. A. Z. Panagiotopoulos, M. A. Floriano and S. K. Kumar, “Micellization and Phase Separation of Diblock and Triblock Model Surfactants,” *Langmuir*, **18**: 2940-8 (2002).
4. M. S. Shell, P. G. Debenedetti and A. Z. Panagiotopoulos, “Molecular structural order and anomalies in liquid silica,” *Phys. Rev. E* **66**: 011202 (2002).
5. M. S. Shell, P. G. Debenedetti and A. Z. Panagiotopoulos, “Generalization of the Wang-Landau method for off-lattice simulations,” *Phys. Rev. E*, **66**: 056703 (2002).

Refereed papers (cont.)

6. J. M. Romero-Enrique, L. F. Rull and A. Z. Panagiotopoulos, "Dipolar origin of the gas-liquid coexistence of the hard-core 1:1 electrolyte model," *Phys. Rev. E*, **66**: 041204 (2002).
7. G. Orkoulas, S. K. Kumar and A. Z. Panagiotopoulos, "Monte Carlo Study of Coulombic Criticality in Polyelectrolytes," *Phys. Rev. Lett.*, **90**: 048303 (2003).
8. A. Diehl and A. Z. Panagiotopoulos, "Phase transitions and tricriticality in the lattice restricted primitive model supplemented by short-range interactions," *J. Chem. Phys.* **118**: 4993-8 (2003).
9. S. Moghaddam and A. Z. Panagiotopoulos, "Lattice discretization effects on the critical parameters of model nonpolar and polar fluids," *J. Chem. Phys.*, **118**: 7556-61 (2003).
10. M. S. Shell, P. G. Debenedetti, and A. Z. Panagiotopoulos, "An improved Monte Carlo method for direct calculation of the density of states," *J. Chem. Phys.*, **119**, 9406-11 (2003).
11. D. Cheong and A. Z. Panagiotopoulos, "Critical parameters of unrestricted primitive model electrolytes with charge asymmetries up to 10:1," *J. Chem. Phys.*, **119**, 8526-8536 (2003).
12. V. Kobelev, A. B. Kolomeisky and A. Z. Panagiotopoulos, "Thermodynamics of electrolytes on anisotropic lattices," *Phys. Rev. E*, **68**, 066110 (2003).
13. M. S. Shell, P. G. Debenedetti and A. Z. Panagiotopoulos, "Saddles in the Energy Landscape: Extensivity and Thermodynamic Formalism," *Phys. Rev. Lett.*, **92**, 035506 (2004).
14. O. J. Hehmeyer, G. Arya and A. Z. Panagiotopoulos, "Phase Transitions of Confined Lattice Homopolymers," *J. Phys. Chem. B*, **108**, 6809-6815 (2004).
15. G. Arya and A. Z. Panagiotopoulos, "Monte Carlo study of shear-induced alignment of cylindrical micelles in thin films," *Phys. Rev. E*, **70**, 031501 (2004).
16. S. Moghaddam and A. Z. Panagiotopoulos, "Determination of second virial coefficients by grand canonical Monte Carlo simulations," *Fluid Phase Equil.*, **222**, 221-224 (2004).
17. C. S. Lock, S. Moghaddam and A. Z. Panagiotopoulos, "Finely discretized lattice simulations of SPC/E water," *Fluid Phase Equil.*, **222**, 225-230 (2004).
18. S. Moghaddam, Y. C. Kim and M. E. Fisher, "Convergence of fine-lattice discretization for near-critical fluids," *J. Phys. Chem. B*, **109**, 6824-37 (2005).
19. M. S. Shell, P. G. Debenedetti, and A. Z. Panagiotopoulos, "Flat-histogram dynamics and optimization in density of states simulations of fluids," *J. Phys. Chem. B*, **108**, 19748-55 (2005).
20. M. A. Floriano, V. Firetto and A. Z. Panagiotopoulos, "Effect of stiffness on the phase behavior of cubic lattice chains," *Macromolecules*, **38**, 2475-81 (2005).
21. A. Diehl and A. Z. Panagiotopoulos, "Phase diagrams in the lattice restricted primitive model: From order-disorder to gas-liquid phase transition," *Phys. Rev. E*, **71**:046118, 7 pp (2005).
22. G. Arya and A. Z. Panagiotopoulos, "Molecular modeling of shear-induced alignment of cylindrical micelles," *Comp. Phys. Comm.*, **169**:262-266 (2005).
23. D. W. Cheong and A. Z. Panagiotopoulos, "Phase Behavior of Polyampholyte Chains from Grand Canonical Monte Carlo Simulations," *Molec. Phys.*, **103**:3031-44 (2005).
24. A.-P. Hynninen, M. Dijkstra, and A. Z. Panagiotopoulos, "Critical Point of Electrolyte Mixtures," *J. Chem. Phys.*, **123**:084903, 9 pp (2005).

Refereed papers (cont.)

25. A. Z. Panagiotopoulos, "Thermodynamic properties of lattice hard sphere models," J. Chem. Phys., 123:104504, 5 pp (2005).
26. A. Z. Panagiotopoulos, "Simulations of phase transitions in ionic systems," J. Phys.: Condens. Matter, 17:S3205-13 (2005).
27. G. Arya and A. Z. Panagiotopoulos, "Impact of branching on the phase behavior of polymers," Macromolecules, 38, 10596-604 (2005).
28. G. Arya, J. Rottler, A. Z. Panagiotopoulos, D. J. Srolovitz and P. M. Chaikin, "Shear Ordering in Thin Films of Spherical Block Copolymer Micelles," Langmuir, 21, 11518-27 (2005).
29. Y. C. Kim, M. E. Fisher and A. Z. Panagiotopoulos, "Universality of ionic criticality: Size- and charge-asymmetric electrolytes," Phys. Rev. Lett., 95, 195703, 4 pp, (2005).
30. M. S. Shell, P. G. Debenedetti and A. Z. Panagiotopoulos, "Computational characterization of the sequence landscape in simple protein alphabets," Proteins, 62, 232-243 (2006).
31. M. S. Shell, P. G. Debenedetti and A. Z. Panagiotopoulos, "A conformal solution theory for the energy landscape and glass transition of mixtures," Fluid Phase Equil., 241, 147-154 (2006).
32. C.-Y. Chou, T. T. M. Vo, A. Z. Panagiotopoulos and M. Robert, "Computer simulations of phase transitions of bulk and confined colloid-polymer systems," Physica A, 369, 275-290 (2006).
33. D. W. Cheong and A. Z. Panagiotopoulos, "Monte Carlo Simulations of Micellization in Model Ionic Surfactants: Application to Sodium Dodecyl Sulfate," Langmuir, 22, 4076-83 (2006).
34. A. Diehl and A. Z. Panagiotopoulos, "Phase behavior of the Lattice Restricted Primitive Model with nearest-neighbor exclusion," J. Chem. Phys., 124, 194509, 6 pp (2006).
35. P. J. Lenart and A. Z. Panagiotopoulos, "Phase Behavior of Binary Stockmayer and Polarizable Lennard-Jones Fluid Mixtures Using Adiabatic Nuclear and Electronic Sampling," Ind. Eng. Chem. Research, 45, 6929-6938 (2006).
36. V. Firetto, M. A. Floriano and A. Z. Panagiotopoulos, "Effect of stiffness on the micellization behavior of model H4T4 surfactant chains," Langmuir, 22, 6514-22 (2006).
37. P. J. Lenart and A. Z. Panagiotopoulos, "Tracing the Critical Loci of Binary Fluid Mixtures Using Molecular Simulation," J. Phys. Chem. B, 110, 17200-6 (2006).
38. J. R. Davis, M. V. Piccarreta, R. B. Rauch, T. K. Vanderlick, and A. Z. Panagiotopoulos, "Phase Behavior of Rigid Objects on a Cubic Lattice," Ind. Eng. Chem. Res., 45, 5421-5425 (2006).
39. A. N. Rissanou, I. G. Economou and A. Z. Panagiotopoulos, "Monte Carlo simulation of the phase behavior of model dendrimers," Macromolecules, 39, 6298-6305 (2006).
40. P. J. Lenart, A. Jusufi, and A. Z. Panagiotopoulos, "Effective potentials for 1:1 electrolyte solutions incorporating dielectric saturation and repulsive hydration," J. Chem. Phys., 126, 044509, 7 pp (2007).
41. A.-P. Hynninen and A. Z. Panagiotopoulos, "Disappearance of the Gas-Liquid Phase Transition for Highly Charged Colloids," Phys. Rev. Lett., 98, 198301 (2007).
42. O. J. Hehmeyer, G. Arya, A. Z. Panagiotopoulos and I. Szleifer, "Monte Carlo simulation and molecular theory of tethered polyelectrolytes," J. Chem. Phys., 126, 244902 (2007).
43. A. Jusufi, A.-P. Hynninen and A. Z. Panagiotopoulos, "Implicit-solvent Models for Micellization of Ionic Surfactants," J. Phys. Chem. B, 112, 13783-92 (2008).

44. A.-P. Hynninen and A. Z. Panagiotopoulos, "Invited topical review: Simulations of phase transitions and free energies for ionic systems," *Molec. Phys.* 106, 2039-2051 (2008).
45. J. R. Davis and A. Z. Panagiotopoulos, "Monte Carlo simulations of amphiphilic nanoparticle self assembly," *J. Chem. Phys.* 129, 194706, 7 pp (2008).

2.2 Conference presentations

1. "Chain conformations, effective attractions and phase transitions in flexible polyelectrolytes", presented at Gordon Research Conference in Polymer Physics, August 11-16, 2002, Salve Regina University, Newport, RI (with G. Orkoulas and S. K. Kumar).
2. "Direct Monte Carlo Calculation of the Configurational Density of States", presented at the Annual AIChE meeting, Indianapolis, IN, Nov. 3-8, 2002 (with M. S. Shell and P. G. Debedenetti).
3. "Computer Simulations of Two- and Three-Dimensional Colloid-Polymer Systems," presented at the Annual APS Meeting, March 3-7, 2003 (with C.-Y. Chou, T. Vo and M. Robert).
4. "Polyelectrolyte Phase Behavior" presented at the Annual APS Meeting, March 3-7, 2003 (with S. Kumar and G. Orkoulas).
5. "Role of Associated Pairs in the Gas-Liquid Transition of 1:1 Electrolyte Primitive Models," presented at the Thermodynamics 2003 Conference, Cambridge, UK April 9-11, 2003 (with J. M. Romero-Enrique and L. F. Rull).
6. "Phase Behavior of Asymmetric Ionic Fluids" oral presentation at the 15th Symposium on Thermophysical Properties, Boulder, CO June 23-27, 2003 (with D. Cheong).
7. "Phase Transitions and Tricriticality in the Lattice-Restricted Primitive Model Supplemented by Short-Range Interactions" oral presentation at the 15th Symposium on Thermophysical Properties, Boulder, CO June 23-27, 2003 (with A. Diehl).
8. "Role of Associated Pairs in the Gas-Liquid Transition of 1:1 Electrolyte Primitive Models" oral presentation at the 15th Symposium on Thermophysical Properties, Boulder, CO June 23-27, 2003 (with J.M. Romero-Enrique and L.F. Rull).
9. "Phase Transitions in Colloid/Polymer Systems," poster presentation at the "Foundations of Molecular Modeling and Simulation" conference, Keystone, CO, July 6-11, 2003 (with Owen Hehmyer). "The Energy Landscape: Towards a Unified View of Supercooled Liquids and Glasses," presented at the Annual AIChE meeting in San Francisco, CA Nov. 16-21, 2003 (with M. S. Shell and P. G. Debedenetti).
10. "A new Monte-Carlo Paradigm: Density of States Methods," presented at the Annual AIChE meeting in San Francisco, CA Nov. 16-21, 2003 (with M. S. Shell and P. G. Debedenetti).
11. "Kinetic Approach to Rare Events: Application to Micelle Assembly and Breakup," presented at the Annual AIChE meeting in San Francisco, CA Nov. 16-21, 2003 (with D. I. Kopelevich and I. G. Kevrekidis).
12. "Phase Transitions in Highly Asymmetric Ionic Systems," presented at the Annual AIChE meeting in San Francisco, CA Nov. 16-21, 2003 (with D. Cheong).
13. "Monte Carlo Simulations of Phase Behavior of Bulk and Confined Colloid-Polymer Mixtures," presented at the Annual AIChE meeting in San Francisco, CA Nov. 16-21, 2003 (with C.-Y. Chou, T.T.M. Vo and M. A. Robert).

14. "Effect of chain stiffness on the phase behavior of model polymers and surfactants" presented at the 5th Symposium of the Italian Computational Chemistry Group, Siena, Italy, Dec. 18-19, 2003 (with M. A. Floriano and V. Firetto).
15. "Phase behavior and structure of confined lattice homopolymers," paper 341h presented at the Annual AIChE meeting in Austin, TX, Nov. 7 – 12, 2004 (with O. J. Hehmeyer and G. Arya).
16. "Molecular simulation study of shear-induced alignment of cylindrical micelles in thin films," paper 575c presented at the Annual AIChE meeting in Austin, TX, Nov. 7 – 12, 2004 (with G. Arya).
17. "Flat histogram methods for the calculation of free energies, from liquids to proteins," paper 50a presented at the Annual AIChE meeting in Austin, TX, Nov. 7 – 12, 2004 (with M. S. Shell and P. G. Debenedetti).
18. "Molecular Dynamics studies of charged, tethered polymer systems," paper 338h presented at the Annual AIChE meeting in Austin, TX, Nov. 7 – 12, 2004 (with O. J. Hehmeyer and M. J. Stevens).
19. "Phase transitions in polyampholyte chains from Monte Carlo simulations," paper 164c presented at the Annual AIChE meeting in Austin, TX, Nov. 7 – 12, 2004 (with D. Cheong).
20. "Computer simulation of confined colloid-polymer systems," paper 346e presented at the Annual AIChE meeting in Austin, TX, Nov. 7 – 12, 2004 (with C. Y. Chou and M. A. Robert).
21. "Computer Simulation of Depletion Effects in Three-Dimensional Colloid-Polymer Systems," paper 346f presented at the Annual AIChE meeting in Austin, TX, Nov. 7 – 12, 2004 (with T. T. M. Vo and M. A. Robert).
22. "Micellization and shear alignment in model surfactant systems," invited paper presented at the 229th ACS National Meeting, San Diego, CA, March 13-17, 2005 (with G. Arya).
23. "Computer Simulation Study of the Phase Behaviour of Polymer and Surfactant Solutions: from Linear to Rigid Chains, paper presented at the Division of Chemical Physics, Italian Chemical Society 34th National Meeting, Siena, 20-24 June 2005 (with V. Firetto and M. A. Floriano).
24. "Phase diagrams in the lattice restricted primitive model: From order-disorder to gas-liquid phase transition," poster P 3.15 presented at the 6th Liquid Matter Conference, Utrecht, The Netherlands, July 1-5, 2005 (with A. Diehl).
25. "Monte Carlo simulations of aggregation phenomena in model polymer and surfactant solutions," poster presented at the "International School of Solid State Physics: 34th Course," Erice, Italy, 20 July – 1 August 2005 (with M. A. Floriano and V. Firetto).
26. "Estimation Strategies for Stochastic Systems in "Equation Free" Methods," poster presentation at Applications of Methods of Stochastic Systems and Statistical Physics in Biology, U. of Notre Dame, Notre Dame, IN, October 28-30, 2005 (with C. Calderon and Y. Kevrekidis).
27. "Tracing the Critical Locus for Binary Fluid Mixtures Using Molecular Simulations," paper 87a, Annual AIChE meeting, Cincinnati, OH, Oct. 31 – Nov. 4, 2005 (with P. Lenart).
28. "Monte Carlo Simulations and Self-Consistent Mean Field Theory of Polyelectrolyte Brushes," paper 518e, Annual AIChE meeting, Cincinnati, OH, Oct. 31 – Nov. 4, 2005 (with O. J. Hehmeyer).

29. "Characterization of Protein Sequence Landscapes Using Flat-Histogram Monte Carlo Algorithms," paper 456d, Annual AIChE meeting, Cincinnati, OH, Oct. 31 – Nov. 4, 2005 (with M. S. Shell and P. G. Debenedetti).
30. "Self-Assembly and Phase Behavior of Model Nanoparticles with Attached Chains," paper 493d, Annual AIChE meeting, Cincinnati, OH, Oct. 31 – Nov. 4, 2005 (with J. R. Davis and T. K. Vanderlick).
31. "Long Range and Quantitative Alignment of Diblock Copolymer Monolayers by Shear," (with P. M. Chaikin, R. A. Register, K. Asakawa), PCCM-Rhodia Symposium, Princeton, NJ November 4-5, 2005.
32. "Phase behavior of the lattice restricted primitive model with nearest neighbor repulsion and exclusion," presented at the XXIX National Meeting of Condensed Matter Physics, Sao Lourenco, Brazil, May 9-13, 2006 (with Alexandre Diehl).
33. "Computational studies of POSS - based materials," poster presentation at the 2nd International Symposium on nanostructured and functional polymer-based materials and composites, Lyon, France, 29-31 May 2006 (with Vanessa Firetto, G. Camino and Michele A. Floriano).
34. "Computational studies of nanostructured POSS materials," presented at the 22nd Italian Chemical Society Meeting, Florence, Italy, Sept. 10-15, 2006 (with Vanessa Firetto, Michele A. Floriano and Daniela Tabuani).
35. "Computational studies of self-assembly in model copolymer solutions," presented at the 22nd Italian Chemical Society Meeting, Florence, Italy, Sept. 10-15, 2006 (with Vanessa Firetto and Michele A. Floriano).
36. "Monte Carlo Simulation of the Phase Behavior of Model Dendrimers," presented at the 6th Panhellenic Conference on Polymers, Patras, Greece, Nov. 3-5, 2006 (with Anastassia N. Rissanou and Ioannis G. Economou).
37. "Monte Carlo Simulations of Self-Assembly for Amphiphilic Nanoparticles," paper 272a, AIChE Annual Meeting, San Francisco, CA, Nov. 12-17, 2006 (with J. R. Davis and T. K. Vanderlick).
38. "Critical Point of Electrolyte Mixtures," paper 162t, AIChE Annual Meeting, San Francisco, CA, Nov. 12-17, 2006 (with A.-P. Hynninen and M. Dijkstra).
39. "Monte Carlo Simulations of the Thermal Denaturation Transition of Model DNA Chains in Solution," paper 209b, AIChE Annual Meeting, San Francisco, CA, Nov. 12-17, 2006 (with J. C. Araque and M. A. Robert).
40. "Influence of Block Lengths and Symmetries on Phase Behavior of Multiblock Copolymers," AIChE Annual Meeting, San Francisco, CA, Nov. 12-17, 2006 (with R.K. Prud'homme and M. Gindy).
41. "Orientation of surfactant self-aggregates on graphite," presented at the APS March meeting, Denver, CO, March 5th – 9th, 2007 (with M. Sammalkorpi, A.-P. Hynninen and M. Haataja).
42. "Molecular Simulations of DNA Hybridization in Solution and in Microarrays," presented at the APS March meeting, Denver, CO, March 5th – 9th, 2007 (with J. C. Araque and M. Robert).
43. "Disappearance of the gas-liquid phase transition for highly charged colloids," poster presentation at the 81st ACS Colloid & Surface Science Symposium, Newark, DE, June 24-27, 2007 (with A.-P. Hynninen).
44. "Lattice Monte Carlo simulations of amphiphilic nanoparticles," poster presentation at the PPEPPD 2007 conference, Crete, Greece, May 20-25, 2007 (with J. R. Davis).

Conference presentations (cont.)

45. "Theory and simulations of thermally sensitive telechelic star polymers" poster presentation at the CECAM workshop on "Fluid phase behaviour and critical phenomena from liquid state theories and simulation," Lyon, France, July 5 – 8, 2007 (with F. Lo Verso and C. N. Likos).
46. "Telechelic star-like micelles: characterization of the molecular aggregation processes," poster presentation at the Soft, Complex, and Biological Matter Conference, Terrasini, Sicily, July 15 – 19, 2007 (with F. Lo Verso and C. N. Likos).
47. "Disappearance of the gas-liquid phase transition for highly charged colloids," poster presentation at the Soft, Complex, and Biological Matter Conference, Terrasini, Sicily, July 15 – 19, 2007 (with A.-P. Hynninen).
48. "Phase Behavior of Binary Amphiphile Mixtures," poster presentation at the Soft, Complex, and Biological Matter Conference, Terrasini, Sicily, July 15 – 19, 2007 (with J. R. Davis).
49. "Crystal Structures Of Dipolar Colloids and Binary Hard- and Charged Spheres," paper 527c, Annual AIChE meeting, Salt Lake City, UT, Nov. 4-9, 2007 (with A.-P. Hynninen).
50. "Like-Charge Attraction of Spheres - Global Phase Diagram and Critical Scaling," paper 139e, Annual AIChE meeting, Salt Lake City, UT, Nov. 4-9, 2007 (with A.-P. Hynninen).
51. "Monte Carlo Simulations Of Binary Amphiphile Mixtures," paper 408i, Annual AIChE meeting, Salt Lake City, UT, Nov. 4-9, 2007 (with J. R. Davis).
52. "Implicit Water Model of Ionic Surfactant Micelles" Arben Jusufi, Antti-Pekka Hynninen, and Athanassios Z. Panagiotopoulos paper 174d, AIChE Spring National Meeting, New Orleans, LA, April 6-10, 2008.
53. "A Computational Investigation of the Solubility of Heavy n-Alkanes in Water," Andrew Ferguson, Athanassios Z. Panagiotopoulos and Pablo G. Debenedetti, paper PHYS 192, ACS National Meeting, Philadelphia, PA, August 17-21, 2008.
54. "A Computational Investigation of the Solubility and Hydrophobic Collapse of Heavy N-Alkanes in Water," Andrew L. Ferguson, Athanassios Z. Panagiotopoulos, and Pablo G. Debenedetti, paper 253g, Annual AIChE meeting, Philadelphia, PA, November 16-21, 2008.

2.3 Invited seminars and lectures

1. "Phase transitions and microstructure formation in ionic and surfactant solutions," Department of Chemistry, Rice University, April 11, 2002.
2. "Phase transitions in ionic systems," invited lecture at the Thermodynamics-2002 conference, Univ. of Maryland, April 20th, 2002.
3. "Self-assembly and Phase Separation in Model Surfactant Systems," invited seminar, Dept. of Physical Chemistry, Complutense University, Madrid, Spain, May 17, 2002.
4. "Phase transitions in ionic systems," invited seminar, Dept. de Fisica Atomica, Molecular y Nuclear, Universidad de Sevilla, May 21, 2002.
5. "Phase transitions and microstructure formation in ionic and surfactant solutions," plenary lecture at the XI Congreso de Física Estadística, Tarragona, Spain, May 23-25, 2002.
6. "Phase transitions in ionic systems," invited lecture at the 6th Liblice Conference, -2002 conference, Špindlerův Mlýn, Czech Republic, June 9-14, 2002.

7. "Phase transitions in ionic and colloid/polymer systems," Chemical Engineering Colloquium, MIT, Sept. 13, 2002.
8. "Phase transitions in ionic and colloid/polymer systems," Instituto Mexicano del Petróleo, Mexico City, Mexico, Sept. 19, 2002.
9. "Self-assembly and Phase Separation in Model Surfactant Systems," Dept. of Physics, Universidad Nacional Autónoma de México, Sept. 20, 2002.
10. "Phase transitions in ionic and colloid/polymer systems," Chemical Engineering Colloquium, Univ. of Pennsylvania, Sept. 30, 2002.
11. "Phase transitions in ionic and colloid/polymer systems," Chemical Engineering Colloquium, Drexel Univ., Oct. 21, 2002.
12. "New simulation approaches for modeling phase transitions in complex fluids," invited talk at the 225th ACS National Meeting, New Orleans, LA March 23-27, 2003.
13. "Phase transitions in ionic and colloid/polymer systems," Department of Chemical Engineering, U. of Wisconsin, Madison, April 1, 2003.
14. "Monte Carlo Studies of Phase Transitions in Ionic and Colloid/Polymer Systems," invited talk at the 50th Anniversary of the Metropolis Algorithm, Los Alamos, NM, June 9-11, 2003.
15. "Monte Carlo Simulations of Phase Transitions in Confined Fluids," invited talk at the 3rd International TRI/Princeton Workshop on Characterization of Porous Materials, Princeton, NJ, June 23-25, 2003.
16. "Molecular Simulation Methods for Prediction of Phase Equilibrium Properties," invited talk at the 15th Symposium on Thermophysical Properties, Boulder, CO, June 22-27, 2003.
17. "Phase Transitions in Colloid/Polymer Systems in 2 and 3 Dimensions," invited talk at the CECAM Workshop on Many-Body Interactions in Simple Liquids, Lyon, France, July 7-9, 2003.
18. "Phase Transitions in Ionic and Colloid/Polymer Systems," invited talk at the Telluride Workshop on Polymer Physics, July 20-25, 2003.
19. "Molecular and mesoscopic simulations of phase equilibria," invited talk at the 226th ACS National Meeting, New York, Sept. 7-11, 2003.
20. "Multiscale Modeling and Coarse Graining for Simulations of Self-Assembly," invited talk at the APS Annual Meeting, Montreal, Canada, March 22-26 2004.
21. "Monte Carlo Simulations of Phase Transitions in Ionic Systems," invited talk at the George Stell Symposium, Stony Brook University, April 24th, 2004
22. "Molecular and mesoscopic simulations of phase equilibria: Surfactant solutions and thin films," Chemical Engineering Colloquium, Univ. of Texas at Austin, April 30th, 2004.
23. "Molecular-modeling methods and use for product and process design," plenary talk at the 6th International Conference on "Foundations of Computer-Aided Process Design," Princeton, NJ (with P. R. Westmoreland), July 11-16, 2004.
24. "Phase transitions, micellization and shear alignment in surfactant systems," invited talk at the Conference on Computational Physics, Genoa, Italy, Sept. 1-4, 2004.
25. "Monte Carlo Simulations of Phase Transitions in Ionic Systems," invited talk at the CCP5 Meeting on "New Perspectives in Modeling and Simulation," Sheffield, UK, Sept. 2-4, 2004.
26. "Phase transitions, micellization and shear alignment in surfactant systems," Department of Chemical Engineering Colloquium, University of Washington, Seattle, Nov. 1, 2004.

27. "Monte Carlo Simulations of Phase Transitions in Ionic Systems," Department of Chemical Engineering Colloquium, University of California, Berkeley, Dec. 1, 2004.
28. "Nanostructured block copolymer thin films via directed self-assembly: A computational study," Department of Chemical Engineering, National Technical University of Athens, Jan. 25, 2005.
29. "Flat histogram methods for the calculation of free energies, from liquids to proteins," Institute for Physical Chemistry, NRCPS "Demokritos," Jan. 26, 2005.
30. "Molecular and mesoscopic simulations of phase transitions in ionic and surfactant systems," Department of Chemical Engineering, "Collaboratus" Lecture Series, Rutgers Univ., March 24, 2005.
31. "Monte Carlo simulations of phase transitions in ionic systems," plenary talk at the 6th Liquid Matter Conference, Utrecht, The Netherlands, July 1-5, 2005.
32. "Phase transitions, micellization and shear alignment in surfactant systems" plenary talk at the International School on "Monte Carlo and Molecular Dynamics of Condensed Systems" Erice, Italy July 20 – Aug. 1, 2005.
33. "Simulations of Phase Transitions and Micellization in Ionic Systems," seminar at the Institute for Theoretical Physics II, Heinrich Heine Univ., Düsseldorf, Germany, Dec. 5, 2005.
34. "Phase transitions and micellization in surfactant and polymer systems," seminar at the Inst. for Theoretical Physics, Univ. Utrecht, The Netherlands, Dec. 6, 2005.
35. "Simulations of Phase Transitions and Micellization in Dendrimers and Ionic Systems," seminar at the National Technical University of Athens, Greece, Jan. 27, 2006.
36. "Phase transitions in polyelectrolytes, polyampholytes and charged colloids," Distinguished Lecture, Chemical Engineering, Materials Science and Physics, University of Southern California, Los Angeles, Feb. 17, 2006.
37. "Simulations of Phase Transitions and Micellization in Ionic Systems," Chemical Engineering, Vanderbilt University, Nashville, TN, Feb. 27, 2006.
38. "Molecular Simulation Studies of Fluids and Proteins: What can modern computers tell us about material properties?" Wilson College Fellows Lunch, April 19, 2006.
39. "Simulations of Phase Transitions and Micellization in Ionic Systems," 22nd European Symposium on Applied Thermodynamics, Elsinore, Denmark, June 28 – July 1, 2006.
40. "Molecular Simulation of Phase Equilibria," Symposium to honor Prof. Robert C. Reid, MIT Chemical Engineering Dept., Oct. 13, 2006.
41. "Phase transitions and micellization in surfactant and polymer systems," Purdue University, Chemistry Dept., Physical Chemistry Colloquium, Oct. 18, 2006.
42. "Simulations of Phase Transitions and Micellization in Ionic Systems," Columbia University / CCNY Chemical Engineering IGERT Colloquium, April 17th, 2007.
43. "Disappearance of the gas-liquid phase transition for highly charged colloids," invited talk at the CECAM workshop on "Fluid phase behavior and critical phenomena from liquid state theories and simulation," Lyon, France, July 5 – 8, 2007.
44. "Simulations of Phase Transitions and Micellization in Ionic Systems," plenary talk at the Soft, Complex, and Biological Matter Conference, Terrasini, Sicily, July 15 – 19, 2007.
45. "Origins and Development of the Gibbs Ensemble Methodology," opening talk of the session on "20 Years of the Gibbs Ensemble" at the Annual AIChE Meeting, Salt Lake City, UT, Nov. 4-9, 2007.

46. “Monte Carlo Simulations of Phase Transitions in Ionic Systems,” “Lectures at the Leading Edge” series, Chemical Engineering and Applied Chemistry, Univ. of Toronto, Canada, Nov. 14, 2007.
47. “Simulations of phase transitions and activity coefficients in ionic systems,” Invited talk at the Spring ACS Meeting, New Orleans, LA, April 6-10, 2008.
48. “Thermodynamic Properties by Simulation,” plenary talk at the 7th International Symposium of ESIQIE, Mexico City, Mexico, May 19-22, 2008.
49. “Fundamentals of Monte Carlo Simulations” invited mini-course presented at the 7th International Symposium of ESIQIE, Mexico City, Mexico, May 19-22, 2008.
50. “Monte Carlo Simulations of Phase Transitions and Micellization in Ionic Systems,” Soft and Biological Matter seminar, Oxford University, Oxford, UK, June 5, 2008.
51. Applications of enhanced ergodic sampling: Solubility and conformations of n-alkanes in water,” invited lecture at the Workshop on Mathematical and Numerical Methods for Free Energy Calculations in Molecular Systems, Banff, Canada, June 15-20, 2008.

3 PERSONNEL ASSOCIATED WITH THE PROJECT (APR. 2002 – DEC. 2008)

A. Principal Investigator: Athanassios Z. Panagiotopoulos

B. Post-doctoral Associates / Visitors

Alexandre Diehl (Assistant Professor, Physics, Universidade Federal do Ceará, Brazil). Prof. Diehl joined our group at Princeton in January 2001 and returned to Brazil in January of 2003. He worked on ionic systems with additional short-range interactions.

Gaurav Arya (Post-doctoral Associate, PhD Chem. E., Univ. of Notre Dame). Dr. Arya worked in our group from September of 2003 to August of 2005. His work was on surfactant systems in thin films and under shear.

Antti-Pekka Hynninen (Post-doctoral Fellow, PhD Chemistry, Univ. of Utrecht). Dr. Hynninen came to Princeton as a PCCM postdoctoral fellow in January of 2006. He has worked on highly asymmetric ionic systems.

C. Graduate Students

Sarvin Moghaddam (M.S., Ohio State U., 1998). Ms. Moghaddam joined the group in January 1999. Her research focused on finely discretized lattice models. She completed her PhD from the Univ. of Maryland in October of 2003, followed by a “mini-postdoctoral” at Princeton University in Jan. 2004 – April 2004.

Daniel Cheong (B.S., Carnegie Mellon U., 1997). Mr. Cheong joined our group in January 2001. His research focused on asymmetric electrolyte, polyampholyte and ionic surfactant systems. He completed his PhD in the fall of 2005 and is presently a researcher at the Institute for High Performance Computing in Singapore.

M. Scott Shell (B.S., Carnegie Mellon U., 2000). Mr. Shell was jointly supervised by Prof. Debenedetti and me since January 2001. His work in our group focused on devel-

opment of flat histogram Monte Carlo methods. He was the recipient of a Princeton-Hertz Fellowship that covers most of his stipend and tuition, with a supplement provided by the DOE grant. In 2004, he was named “Jacobus Fellow.” The Jacobus award is the top honorific fellowship for graduate students at Princeton. He completed his PhD in the fall of 20005 and is presently an Assistant Professor at the University of California, Santa Barbara.

Carrie S. Lock (B.S., U. Virginia, 2000). Ms. Lock joined our group in January 2001. Her work, for which she was awarded the M.S. degree in May 2003, focused on development of finely discretized models for water and aqueous solutions.

Owen J. Hehmeyer (B.S., U. Texas at Austin, 2001). Mr. Hehmeyer joined our group in January 2002, working on tethered and confined chain systems. He was the recipient of a Krell Fellowship that covers most of his stipend and tuition, with a supplement provided by the DOE grant. He received his PhD in the fall of 2006 and is presently a researcher with ExxonMobil in Houston, TX.

Philip J. Lenart (B.S., U. Pittsburgh, 2001). Mr. Lenart joined our group in January 2002 and worked on polarizable models and effective interactions in electrolytes. He was the recipient of a National Science Foundation Fellowship that covered most of his stipend and tuition in his first four years, with a supplement and the last year’s support provided by the DOE grant. He received his PhD in the fall of 2006 and is presently a researcher with ExxonMobil in Fairfax, VA.

Jonathan R. Davis (B.S., U. Delaware, 2003). Mr. Davis joined our group in January 2004 and works on model surfactants. He was the recipient of a National Science Foundation Fellowship that covered most of his stipend and tuition in his first three years, with a supplement and the last year’s support provided by the DOE grant. He is expected to receive his PhD in the fall of 2009.

Andrew L. Ferguson (B.S., Imperial College, 2005). Mr. Ferguson joined our group in January 2006 and works on novel sampling methods and water / hydrocarbon systems. He is expected to receive his PhD in the fall of 2010.