

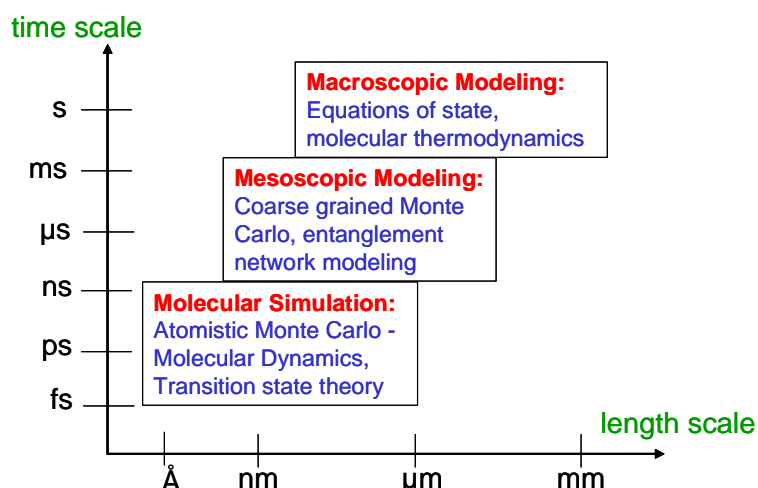
MOLECULAR THERMODYNAMICS AND MODELING OF MATERIALS

mmml.chem.demokritos.gr

Laboratory Director: Dr. Ioannis G. Economou

2007 Activities Report

I. Research work



Research work in the Molecular Thermodynamics and Modeling of Materials Laboratory (MTMML) focuses on the development and implementation of novel hierarchical methods and algorithms for the computer modelling and calculation of advanced material properties at the molecular, mesoscopic and macroscopic levels. Through this work, quantitative links are established between chemical constitution, processing conditions, and physical (thermal, mechanical, rheological, transport, interfacial, optical, dielectric) properties, which are critical for the optimal design of industrial processes and also govern the end-use performance of commercial products. In parallel, the molecular mechanisms underlying structure - property - processing - performance relations are elucidated with the objective of designing new, tailor-made materials.

The hierarchical approaches developed and implemented at MTMML start with atomistic simulations addressing length scales on the order of tens of nanometers and time scales on the order of tens of nanoseconds (e.g., Monte Carlo, molecular dynamics, transition-state theory analysis of infrequent events) and proceed with mesoscopic methods (e.g., entanglement network modelling, kinetic Monte Carlo simulation, self-consistent field theory of inhomogeneous systems) to address longer time- and length scale phenomena. Finally, for the efficient design of novel processes mainly for the chemical and polymer industry, accurate macroscopic models, mostly in the form of equations of state (eos), are developed for phase equilibria and other thermodynamic properties of multicomponent mixtures. These eos are rooted to statistical mechanics and can be safely extrapolated to conditions where limited or no experimental data exist.

Research work in 2007 focused on:

- Molecular simulation of elastomeric and glassy polymers,
- Polymer solutions and blends,
- Sorption and diffusion of small molecules in silicon-containing polymers,
- Molecular simulation of polar homo- and co-polymers,
- Mesoscopic simulation of polydisperse colloids,
- Thermodynamic properties of polar fluids in pure and in mixture,
- Ionic liquids in pure and in mixture with supercritical carbon dioxide or water.

II. Personnel

Researchers: Dr. Ioannis G. Economou, Researcher A', Laboratory Director

Research Scientist: Dr. Niki Vergadou

Collaborating Researcher D': Dr. Nikolas Zacharopoulos (until May 2007, then part time collaborator)

Post-doctoral scientists in projects:

- ✓ Dr. Theodora Spyriouni (EU-STREP)
- ✓ Dr. Anastassia Rissanou (GSRT)
- ✓ Dr. Evangelia-Georgia Logotheti (INTAS)
- ✓ Dr. Hari Leontiadou (GSRT)
- ✓ Dr. Stelios Karanikas (GSRT – ENTER)

PhD students:

- ✓ Zoi Makrodimitri (GSRT – PENED)
- ✓ Marianna Yiannourakou

Senior undergraduate students:

- ✓ Eleni Androulaki (School of Applied Mathematics and Natural Sciences, NTUA)
- ✓ Vassilios Niotis (School of Chemical Engineering, NTUA)

Collaborating faculty:

- ✓ Professor Doros N. Theodorou, School of Chemical Engineering, NTUA

III. Publications in peer-reviewed journals

1. Z.A. Makrodimitri, R. Dohrn and I.G. Economou, "Atomistic Simulation of Poly(dimethylsiloxane): Force Field Development, Structure and Thermodynamic Properties of Polymer Melt and Solubility of *n*-Alkanes, *n*-Perfluoroalkanes, Noble and Light Gases", *Macromolecules*, **40**(5), 1720 – 1729 (2007).
2. I. Tsivintzelis, T. Spyriouni and I.G. Economou, "Modeling of Fluid Phase Equilibria with Two Thermodynamic Theories: Non-Random Hydrogen Bonding (NRHB) and Statistical Associating Fluid Theory (SAFT)", *Fluid Phase Equil.*, **253**, 19 – 28 (2007).
3. C. Panayiotou, I. Tsivintzelis and I.G. Economou, "Nonrandom Hydrogen-Bonding Model of Fluids and Their Mixtures. 2. Multicomponent Mixtures", *Ind. Eng. Chem. Res.*, **46**(8), 2628 – 2636 (2007).
4. L.D. Peristeras, A.N. Rissanou, I.G. Economou and D.N. Theodorou, "Novel Monte Carlo Molecular Simulation Scheme Using Identity-Altering Elementary Moves for the Calculation of Structure and Thermodynamic Properties of Polyolefin Blends", *Macromolecules*, **40**(8), 2904 – 2914 (2007).
5. A.N. Rissanou, M. Yiannourakou, I.G. Economou and I.A. Bitsanis, "Amorphous and Crystalline States of Ultrasoft Colloids: A Molecular Dynamics Study", *Rheol. Acta*, **46**(5), 755 – 764 (2007).
6. A.N. Rissanou, L.D. Peristeras and I.G. Economou, "Calculation of the Effect of Macromolecular Architecture on Structure and Thermodynamic Properties of Linear – Tri-arm Polyethylene Blends from Monte Carlo Simulation", *Polymer*, **48**(13), 3883 – 3892 (2007).
7. I.G. Economou, Z.A. Makrodimitri, G.M. Kontogeorgis and A. Tihic, "Solubility of Gases and Solvents in Silicon Polymers: Molecular Simulation and Equation of State Modeling", *Molec. Simul.*, **33**(9-10), 851 – 860 (2007).
8. E.K. Karakatsani, I.G. Economou, M.C. Kroon, C.J. Peters and G.-J. Witkamp, "tPC-PSAFT Modeling of Gas Solubility in Imidazolium-Based Ionic Liquids", *J. Phys. Chem. C*, **111**(43), 15487 – 15492 (2007).
9. E.K. Karakatsani and I.G. Economou, "Phase Equilibrium Calculations for Multi-Component Polar Fluid Mixtures with tPC-PSAFT", *Fluid Phase Equil.*, **261**, 265 – 271 (2007).
10. T. Spyriouni, C. Tzoumanekas, D.N. Theodorou, F. Müller-Plathe and G. Milano, "Coarse-Grained and Reverse-Mapped United-Atom Simulations of Long-Chain Atactic Polystyrene Melts: Structure,

Thermodynamic Properties, Chain Conformation, and Entanglements", *Macromolecules*, **40**(10), 3876 – 3885 (2007).

11. Z. Kechagia, C. Kiparissides and I.G. Economou, "Determination of Liquid – Gas Partition Coefficients of BuA and MMA by Headspace-Gas Chromatography Utilizing the Phase Ratio Variation Method", *Fluid Phase Equil.*, in press.
12. I.G. Economou, E.K. Karakatsani, G.E. Logotheti, J. Ramos and A. Vanin, "Multi-scale Modeling of Structure, Dynamic and Thermodynamic Properties of Imidazolium-Based Ionic Liquids: *Ab initio* DFT Calculations, Molecular Simulation and Equation of State Predictions", *Oil & Gas Sci. Tech.*, in press.
13. A. Grenner, I. Tsvintzelis, G.M. Kontogeorgis, I.G. Economou and C. Panayiotou, "Evaluation of the Non-Random Hydrogen Bonding (NRHB) Theory and the simplified Perturbed Chain-Statistical Associating Fluid Theory (sPC-SAFT). I. Vapor – Liquid Equilibria", *Ind. Eng. Chem. Res.*, in press.
14. I. Tsvintzelis, A. Grenner, I.G. Economou and G.M. Kontogeorgis, "Evaluation of the Non-Random Hydrogen Bonding (NRHB) Theory and the simplified Perturbed Chain-Statistical Associating Fluid Theory (sPC-SAFT). II. Liquid – Liquid Equilibria and Prediction of Monomer Fraction in Hydrogen Bonding Systems", *Ind. Eng. Chem. Res.*, in press.

IV. Presentations in international conferences

1. Z.A. Makrodimitri and I.G. Economou, "Atomistic Simulation of Silicon-Containing Elastomers: Force Field Development, Structure and Thermodynamic Properties of Polymer Melt and Solubility of *n*-Alkanes, *n*-Perfluoroalkanes, Noble and Light Gases", *11th International Conference on Properties & Phase Equilibria for Product and Process Design*, Hersonissos, Crete, Greece (2007).
2. A.N. Rissanou, L.D. Peristeras and I.G. Economou, "Calculation of the Effect of Macromolecular Architecture on Structure and Thermodynamic Properties of Linear - Tri-arm Polyethylene Blends from Monte Carlo Simulation", *11th International Conference on Properties & Phase Equilibria for Product and Process Design*, Hersonissos, Crete, Greece (2007).
3. E.K. Karakatsani and I.G. Economou, "Prediction of Thermodynamic Properties and Phase Equilibria of Polar Multicomponent Mixtures from Perturbation Theory", *11th International Conference on Properties & Phase Equilibria for Product and Process Design*, Hersonissos, Crete, Greece (2007).
4. T. Spyriouni, C. Tzoumanekas, and D.N. Theodorou, "Coarse-Grained and Reverse-Mapped United-Atom Simulations of Long-Chain Atactic Polystyrene Melts: Structure, Thermodynamic Properties, Chain Conformation, and Entanglements", *11th International Conference on Properties & Phase Equilibria for Product and Process Design*, Hersonissos, Crete, Greece (2007).
5. N. Vergadou and D.N. Theodorou, "Computational Study of Permeability of Glassy Polymers to Gases", *11th International Conference on Properties & Phase Equilibria for Product and Process Design*, Hersonissos, Crete, Greece (2007).
6. M.C. Kroon, E.K. Karakatsani, M. Montero, I.G. Economou, G.-J. Witkamp and C.J. Peters, "Experimental Measurements and Modeling using tPC-PSAFT of the Phase Behavior of the Ternary Ionic Liquid System CO₂ + water + [bmim]NO₃", *11th International Conference on Properties & Phase Equilibria for Product and Process Design*, Hersonissos, Crete, Greece (2007).
7. E. Tritopoulou and I.G. Economou, "Molecular Simulation of Thermodynamic Properties of Glycols in Pure State and in Aqueous Solutions", *6th Greek Chemical Engineering Conference*, Athens, Greece (2007).
8. M. Yiannourakou, I.G. Economou and I.A. Bitsanis, "Phase Equilibria of Polydisperse Colloidal Systems", *6th Greek Chemical Engineering Conference*, Athens, Greece (2007).
9. N. Vergadou and D.N. Theodorou, "Molecular simulation towards the Prediction of Permeability of Glassy Polymers to gases", *6th Greek Chemical Engineering Conference*, Athens, Greece (2007).

10. I.G. Economou, A. Grenner, I. Tsvintzelis, C. Panayiotou and G.M. Kontogeorgis, "Evaluation of Statistical Mechanics-Based Equations of State for Complex Fluid Mixtures", *6th European Congress of Chemical Engineering*, Copenhagen, Denmark (2007).
11. I.G. Economou, E.K. Karakatsani, M.C. Kroon, C.J. Peters and G.-J. Witkamp, "Modeling of Ionic Liquid Binary and Ternary Mixture Phase Equilibria at Low and High Pressure With the tPC-PSAFT", *6th European Congress of Chemical Engineering*, Copenhagen, Denmark (2007).
12. I.G. Economou, Z.A. Makrodimitri, A. Tihic and G.M. Kontogeorgis, "Molecular Simulation and Macroscopic Modeling of Thermodynamic and Transport Properties of Silicon-Containing Rubbery Polymer – Solvent Mixtures", *6th European Congress of Chemical Engineering*, Copenhagen, Denmark (2007).
13. H. Leontiadou and I.G. Economou, "Structure and Thermodynamic Properties of Poly(ethylene oxide) from Molecular Dynamics Simulations", *Thermodynamics 2007*, Paris, France (2007).
14. G.-E. Logotheti, F.J. Ramos-Díaz and I.G. Economou, "Molecular Modelling of 1-n-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide Ionic Liquid", *Thermodynamics 2007*, Paris, France (2007).
15. Z.A. Makrodimitri and I.G. Economou, "Molecular Modeling of Polydimethylsiloxane Mixtures", *International Conference on Computational Methods in Science and Engineering 2007*, Corfu, Greece (2007).
16. M. Yiannourakou, I.A. Bitsanis and I.G. Economou, "Phase Equilibrium of Colloid Systems with Particle Size Dispersion: A Molecular Dynamics Study", *International Conference on Computational Methods in Science and Engineering 2007*, Corfu, Greece (2007).
17. M. Yiannourakou, L. Marsella, F. de Meyer, B. Smit, "Clustering of Proteins Embedded in Lipid Bilayers: a Monte Carlo Study", *International Conference on Computational Methods in Science and Engineering 2007*, Corfu, Greece (2007).
18. F. de Meyer, M. Venturoli, M. Yiannourakou, L. Marsella, B. Smit, "Mesoscopic Simulation Study of Lipid-Mediated Interactions Between Intrinsic Membrane Proteins", *AIChE Annual Meeting*, Salt Lake City, Utah, USA (2007).
19. I.A. Bitsanis, M. Yiannourakou and I.G. Economou, "Amorphous and Crystalline States of Ultrasoft Colloids: A Molecular Dynamics Study", *APS Spring Meeting*, Denver, Colorado, USA (2007).
20. A.N. Rissanou, M. Yiannourakou, I.A. Bitsanis, I.G. Economou, "Thermal Vitrification and Crystallization in Concentrated Suspensions of Ultrasoft Colloids", *Soft, Complex, and Biological Matter Conference*, Città del Mare, Terrasini, Sicily (2007).

V. Invited lectures

1. I.G. Economou, "Prediction of Structure and Physical Properties of Complex Fluids Using Molecular Simulation", Department of Chemical Engineering, Technical University of Denmark, Lyngby, January 2007.
2. I.G. Economou, "Structural and Physical Properties of Complex Fluids via Molecular Simulation Methods", Department of Materials Science and Technology, University of Crete, Heraklion, Crete, Greece, April 2007.
3. I.G. Economou, "Solubility of Gases and Solvents in Silicon Polymers: Molecular Simulation and Equation of State Modeling", IVC-SEP Discussion Meeting, Department of Chemical Engineering, Technical University of Denmark, Helsingør, Denmark, June 2007.
4. I.G. Economou, "Materials Property Predictions Using Equation of State Theories", 2nd Innovative Modeling Technology Consortium Meeting and Seminar, National Technical University of Athens, Greece, June 2007.

5. I.G. Economou, "Molecular Simulation of Ionic Liquids: Structure, Thermodynamic and Dynamic Properties", Department of Chemical Engineering, IVC-SEP, Technical University of Denmark, Lyngby, November 2007.

VI. Educational work

A. Teaching

A. Undergraduate courses

1. Ioannis G. Economou, "Physical Chemistry", 2nd year course in *Studies in Natural Sciences*, Open University of Greece, 2007 – 08.
2. Ioannis G. Economou, "Corrosion and Selection of Materials", Department of Chemical Engineering, Technical University of Denmark, Lyngby, Denmark, Fall 2007
3. Nikolas Zacharopoulos, "Simulation", 7th Semester, Department of Product and Systems Design, University of the Aegean, 2006 – 2007.
4. Nikolas Zacharopoulos, "Introduction to Probability and Statistics", 4th Semester, Department of Product and Systems Design, University of the Aegean, 2006 – 2007.
5. Nikolas Zacharopoulos, "Material Science Laboratory", 4th Semester, Department of Product and Systems Design, University of the Aegean, 2006 – 2007.
6. Nikolas Zacharopoulos, "Material Selection for Design", 9th Semester, Department of Product and Systems Design, University of the Aegean, 2006 – 2007.

B. Post-graduate courses

1. Ioannis G. Economou, "Molecular Simulation of Complex Chemical Systems with Emphasis to Practical Applications", PhD Program in *Chemical Engineering*, Technical University of Denmark, Lyngby, Denmark, January - February 2007.
2. Ioannis G. Economou, «Polymer Physics I». Post-graduate program in *Polymer Science and Its Applications*, Department of Chemistry, University of Athens, October – November 2007.

B. Post-graduate degree awarded

PhD degrees

Eirini Karakatsani, «Development and Evaluation of a New Equation of State for Polar Fluids: Pure Components and Mixtures», School of Chemical Engineering, NTUA, May 2007.

VII. Current external funding

1. "Computer Aided Molecular Design of Multifunctional Materials with Controlled Permeability Properties" [MULTIMAT], *European Union, STREP FP6, Priority 3, NMP*. Scientific director: Doros N. Theodorou. Total funding for Institute of Physical Chemistry: 173,117 €, funding for MTMML: 86,308 €. Co-funding is provided by GSRT. Duration: 1 / 3 / 2005 – 28 / 2 / 2008.
2. "Reorganization of the Liaison Office of NCSR "Demokritos"", *Greek Secretariat of Research and Technology, Program for Support of Liaison Offices in Universities and Research Centers*. Scientific director: Ioannis G. Economou. Total funding: 300,000 €. Duration: January 1, 2005 – July 30, 2008.
3. "Development of New Molecular Simulation Methods and Macroscopic Models for the Calculation of Microscopic Structure and of Thermodynamic Properties of Complex Polymer Systems", *Greek Secretariat of Research and Technology, Program for Research Support (PENED)*. Scientific director: Ioannis G. Economou. Total funding: 60,000 €. Duration: December 1, 2005 – November 30, 2008.
4. "Development of Sustainable Industrial Processes: Experimental, Theoretical and Computational Investigation of Thermodynamic Properties and Phase Equilibria of Ionic Liquid Mixtures", *INTAS*.

Scientific director: Ioannis G. Economou. Total funding: 150,000 €. Funding for I.G. Economou: 12,500 €. Duration: September 1, 2006 – May 30, 2009.

5. "Investigation of Structure, Thermodynamic and Transport Properties of Poly(styrene-*co*-acrylonitrile) in High Temperatures", *Greek Secretariat of Research and Technology, ENTER 2003 Program*. Scientific director: Ioannis G. Economou. Total funding: 78,000 €. Duration: October 1, 2006 – September 30, 2008.
6. "Polymer Surfaces Responsive to Thermal and Chemical Stimuli: Towards the Micro-design of 'Intelligent' Materials", *Greek Secretariat of Research and Technology, Greece – USA Research and Technology Cooperation in Materials Research*. Scientific director: Ioannis G. Economou. Total funding: 50,000 €. Funding for I.G. Economou: 25,000 €. Duration: June 1, 2006 – May 31, 2008.

VIII. Current collaborations

1. Professor Georgios Kontogeorgis, Department of Chemical Engineering, Technical University of Denmark. Development of thermodynamic models for non-ideal polymer systems.
2. Dr. Ioannis Bitsanis, Institute of Electronic Structure and Laser, Foundation of Research and Technology, Hellas, Heraklion, Crete, Greece. Mesoscopic simulation of colloids and polymers.
3. Professor Athanassios Z. Panagiotopoulos, Department of Chemical Engineering, Princeton University, USA. Molecular simulation of dendrimers.
4. Professor Costas Panayiotou. Department of Chemical Engineering, Aristotle University of Thessaloniki, Greece. Development of a lattice equation of state for non-ideal fluids.
5. Professor Cor Peters, Department of Chemical Engineering, Delft University of Technology, The Netherlands. Modeling thermodynamic properties of ionic liquids.
6. Professor Ralf Dohrn, Bayer Technology Services, Leverkusen, Germany. Physical properties of polymer membranes.
7. Dr. J. Ramos-Díaz, Department of Macromolecular Physics, Instituto de Estructura de la Materia - CSIC, Madrid, Spain. Quantum-mechanics calculations for ionic liquids.

IX. Other activities

Ioannis G. Economou

1. Scientific Director of Technology Transfer Office, NCSR "Demokritos".
2. Visiting Professor, Department of Chemical and Biochemical Engineering, Technical University of Denmark, Lyngby, Denmark.
3. Visiting Professor, American College of Greece, Graduate School, Athens, Greece.
4. Adjunct Professor, Open University of Greece.
5. Chairman, Working Group on Thermodynamics and Transport Properties, *European Federation of Chemical Engineering*.
6. Vice-chairman, International Organizing Committee, *11th International Conference on Properties & Phase Equilibria for Product and Process Design*, 20 – 25 May 2007, Hersonissos, Heraklion, Crete.
7. Referee for the following international scientific journals: *AIChE Journal*, *Chemical Engineering Research and Design*, *European Polymer Journal*, *Fluid Phase Equilibria*, *Industrial and Engineering Chemistry Research*, *Journal of the American Chemical Society*, *Journal of Chemical and Engineering Data*, *Journal of Chemical Physics*, *Journal of Computational Chemistry*, *Journal of Physical Chemistry B*, *Macromolecular Rapid Communications*, *Macromolecules*.
8. Evaluation of research proposals for funding from the agencies: *Secretariat of Research and Technology, Greece*; *INTAS, Belgium*.
9. External examiner for PhD thesis at Department of Physical Chemistry, Université Paris-Sud 11, Orsay, France.
10. Guest Editor, *Fluid Phase Equilibria*, **261**, 2007.
11. Consultant, Scienomics SARL, Paris, France.

Nikolas Zacharopoulos

Non-tenure teacher 407/80, Department of Product and Systems Design, University of the Aegean.

Marianna Yiannourakou

Visiting PhD fellow of Marie Curie EuroSim Programme, CECAM, Lyon, December 2006 – December 2007.