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EXACT CALCULATIONS OF PHASE AND MEMBRANE EQUILIBRIA FOR COMPLEX FLUIDS BY MONTE CARLO SIMULATION

Progress Report

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TABLE OF CONTENTS

1	TECHNICAL ACHIEVEMENTS	2
1.1	Highly Asymmetric Systems	2
1.2	Multisegment and Chain Molecules	4
1.3	Ionic systems	6
2	PUBLICATIONS AND PRESENTATIONS RESULTING FROM THIS WORK	8
2.1	Refereed publications	8
2.2	Publications under review	8
2.3	Conference presentations	9
2.4	Invited seminars and lectures	9
3	PERSONNEL ASSOCIATED WITH THE PROJECT	11
4	BUDGET PROJECTION TO END OF PROJECT PERIOD	12

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1 TECHNICAL ACHIEVEMENTS

The general objective of this project has been the development of novel molecular simulation techniques for the determination of phase equilibria in complex systems. One of the main areas of focus was the Gibbs ensemble Monte Carlo technique¹ originally developed in our research group and presently in widespread use throughout the world. The Gibbs ensemble methodology enables the direct determination of the properties of two coexisting fluid phases (e.g. a liquid at equilibrium with its vapor) from a single computer experiment, and is applicable to multi-component systems with arbitrary equilibrium constraints imposed. As a result of work carried out under the present DOE project, the methodology has been significantly extended and applied to obtain phase diagrams for highly asymmetric and ionic fluids. An extensive review of the Gibbs ensemble technique has been prepared (reference 2.1.5). A major limitation of conventional simulation techniques is their inability to deal with chain molecules. The modified Widom test particle technique has been developed for the calculation of chemical potentials of long polymeric molecules, and preliminary calculations of the phase behavior of simple model homopolymers have been performed. In the sections that follow, we briefly describe the progress made in each of the "task areas" of our original proposal, referring to the accompanying list of technical publications for additional details.

1.1 Highly Asymmetric Systems

Highly asymmetric mixtures have components that differ greatly in size or strength of attractive interactions. They are common in industrial practice, and often specific separation methods, such as supercritical fluid extraction processes, are based on the large degree of asymmetry between components in a mixture. Few results for the chemical potential and excess thermodynamic properties of asymmetric mixtures are available^{2,3} and the asymmetry of model systems studied covers a fairly narrow range of size ratios. However, it is precisely for these systems that the disagreement between exact simulation results and current theories of mixtures is most pronounced, since the discrepancies between theory and simulation for the excess thermodynamic properties grow rapidly with increasing asymmetry.

¹ A.Z. Panagiotopoulos, "Direct determination of phase coexistence properties of fluids by simulation in a new ensemble," *Mol. Phys.*, **61**, 813 (1987).

² K.S. Shing and K.E. Gubbins, "The chemical potential in non-ideal liquid mixtures. Computer simulation and theory," *Mol. Phys.* **49**, 1121-1138 (1983).

³ K.P. Shukla and J.M. Haile, "Computer simulation results for thermodynamic excess properties in fluid mixtures. I. Effects of atomic size in simple mixtures," *Mol. Phys.*, **62**, 617 (1987).

Our studies focused on two distinct aspects of the behavior of highly asymmetric mixtures. The first question we addressed was the behavior of mixtures as they approach the point of liquid-liquid immiscibility. The results, described in reference 2.1.2 (references are listed starting on p. 8 of this report) indicate that a reduction of the strength of unlike-pair interactions below 75% of their geometric-mean value leads to liquid-liquid demixing. The simulation results are well described by a statistical-mechanical virial equation of state⁴.

In a second study, we performed a systematic investigation of the phase behavior of mixtures of Lennard-Jones particles in which the unlike-pair interactions are described by conventional Lorentz-Berthelot combining rules. The range of parameters covered was energy ratios of up to two, and volume ratios up to eight. This range far exceeds that of previous calculations of excess thermodynamic properties for similar mixtures. Comparisons of the results with a simple theoretical model (the van der Waals 1-fluid theory of solutions) revealed surprisingly good agreement. Typical results are shown in Figure 1, taken from reference 2.1.1, in which Monte Carlo results (points) for the phase behavior of systems with size parameter ratio of $\sigma_{22}/\sigma_{11} = 1.5$ and a range of energy parameter ratios are compared with conformal solutions theory calculations (lines). Our results indicate that some simple solution theories have a much wider range of applicability in terms of their ability to predict phase equilibria than previously

Figure 1 Phase behavior of highly asymmetric systems with $\sigma_{22}/\sigma_{11} = 1.50$. (—x—) $T^* = 1.00$; (—●—) $T^* = 0.75$.

⁴ C.J. Peters, and R.N. Lichtenthaler, *Physica A* **156**, 417-435 (1989).

believed. These results provide some theoretical justification to the apparent success of semi-empirical engineering equations of state.

1.2 Multisegment and Chain Molecules

Molecules composed of a large number of segments connected by covalent bonds are of significant practical interest. The thermodynamic properties of such materials are commonly modelled using expressions for the Gibbs energy of mixing that take into account entropy of mixing effects for long chains, the best known of which is Flory-Huggins theory⁵. It is well known that the Flory-Huggins theory works well for some thermodynamic quantities and chain lengths, especially at high densities, but has shortcomings at lower densities⁶. The development of improved theoretical techniques for multisegment and polymeric systems is likely to benefit greatly from the availability of simulation results for the phase behavior of these systems. The calculation of chemical potentials for chain molecules cannot be successfully performed with small-molecule techniques such as Widom test particle insertions or grand canonical Monte Carlo because the probability of successful insertion of a molecule in a dense phase decreases exponentially with the number of segments inserted.

A new methodology for the calculation of chemical potentials in macromolecular systems was developed in the past year in a collaborative effort between our group and Prof. Sanat Kumar of Penn State. The first results were published in a *Phys. Rev. Lett.* note (reference 2.2.3). We were able to show that an exact equation for the calculation of the incremental chemical potential of a polymeric molecule is

$$\mu_{\text{segment}} = \mu_{n+1} - \mu_n = -k_B T \ln \langle \exp(-U_{\text{segment}}^* / k_B T) \rangle \quad (1)$$

where U_{segment}^* is the energy required to insert an additional segment at the end of a chain molecule. This equation is a generalization of Widom's equation for the chemical potential of small molecules to macromolecular systems, and is applicable to both polymeric melts and polymer molecules in a solvent. Using this equation and the approximation that the chemical potential dependence on chain length can be ignored in the calculation of the phase behavior, we were able to obtain the first phase diagram for a truly macromolecular continuous model (references 2.1.4 and 2.3.5). Figure 2 shows the calculated phase behavior for a simple bead-and-spring

⁵ P.J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953, Ch. 12.

⁶ R. Dickman and C.K. Hall, "Equation of state for athermal lattice chains," *J. Chem. Phys.*, **85**, 3023-6 (1986).

polymeric model for three different chain lengths, $n=20$, 50 and 100. Several aspects of the tentative results shown in Fig. 2 are in qualitative agreement with experimental data for polymer/solvent systems⁷. In particular, the critical temperature increases and the critical volume fraction decreases with increasing molecular weight. These and additional planned calculations are likely to help in the development of improved techniques the extrapolation of parameters for long molecules in engineering models⁸.

Figure 2 Calculated approximate phase diagrams for a continuous bead-and-spring polymer model. The parameter on the curves is the degree of polymerization.

The chain length and density dependence of the chemical potentials of polymeric molecules were systematically investigated in reference 2.2.1. In order to obtain the highest possible accuracy to allow validation of equation (1) and comparisons with theories, we utilized a simple cubic lattice homopolymer model for which highly accurate calculations are possible. The main conclusion from this work was that the incremental chemical potential becomes independent of chain length to an excellent approximation already for polymers of moderate length (10-15 segments).

An important problem for polymeric systems is attaining equilibrium for the configurational degrees of freedom. To address this problem, we have developed a new method for efficiently sampling conformations of macromolecules (reference 2.2.2). The technique is based on the Rosenbluth and Rosenbluth⁹ segment-by-segment growth algorithm and has also been used to study the thermodynamics of

⁷ T. Dobashi, M. Nakata and M. Kaneko, "Coexistence curve of polystyrene in methylcyclohexane. II. Comparison of coexistence curves observed and calculated from classical theory," *J. Chem. Phys.*, **72**, 6692-7 (1980).

⁸ C. Tsonopoulos, "Critical constants of normal alkanes from methane to polyethylene," *Amer. Inst. Chem. Eng. J.*, **33**, 2080- 3 (1987).

⁹ M.N. Rosenbluth and A.W. Rosenbluth, "Monte Carlo calculations of the average extension of molecular chains", *J. Chem. Phys.* **23**, 356-359 (1955).

folding/denaturation transitions of model proteins (reference 2.2.3).

An additional methodological development achieved during the present project reporting period was the solution of the phase coexistence determination problem for filled lattice systems. Such systems are important for comparisons with common theories (Flory-Huggins theory was originally developed from a lattice description). The study of microstructured fluids (for example surfactant solutions) is often performed on lattices because of computational time constraints. The Gibbs ensemble technique is not applicable for lattice models because the volume change step fails. In references 2.3.8 and 2.2.3 we present a new technique for determination of phase coexistence in lattice systems that involves the introduction of a small concentration of a non-interacting species. We are presently using this technique for the study of equilibria in lattice models of simple block copolymeric systems, as detailed in the plan of proposed research accompanying this progress report.

1.3 Ionic systems

Electrolyte solutions, molten salts, and certain colloidal systems are all examples of systems in which the dominant interparticle forces are coulombic interactions. Coulombic interactions are of infinite range, since the potential decays only with the first power of interionic distance in an unshielded system. Because of the long-range nature of the coulombic forces, accurate statistical-mechanical descriptions of these systems are difficult to obtain, especially at low temperatures. A class of simple models for ionic systems are charged hard sphere models, a special case of which is the restricted primitive model (charged hard spheres of equal diameter). It has been postulated on theoretical grounds for some time now that charged hard sphere systems exhibit vapor-liquid coexistence. There are, however, significant disagreements among results of previous investigations; an attempt to resolve these differences using the Gibbs ensemble technique was made as part of this project. Application of the Gibbs methodology to ionic systems is, in principle, identical to calculations for simple molecular systems. In practice, however, two important issues need to be addressed before successful application of the methodology, namely handling of the infinite-ranged coulombic forces and the development of an efficient algorithm for particle transfers. After extensive tests of many alternatives, it was concluded that it is necessary to use a full summation of the long-range forces (Ewald sum) to achieve results that are approximately independent of simulation system size. In previous simulations of chemical potentials for electrolyte systems¹⁰, the electroneutrality requirement imposed the need for simultaneous

¹⁰ J.P. Valleau and L.K. Cohen, "Primitive model electrolytes. I. Grand Canonical Monte Carlo computations," *J. Chem. Phys.*, **72**, 5935-5941 (1980).

insertions of pairs of ions. At low temperatures which is the regime of interest for phase equilibrium calculations, this approach becomes impractical. One way to address this problem is to satisfy electroneutrality during single particle transfers by introducing uniform neutralizing backgrounds. However, this approach modifies the original system, and may have some effect on the observed phase behavior. Independent calculations from Prof. J. Valleau's group at the University of Toronto¹¹ have obtained a slightly different estimate for the location of the critical point than our Gibbs ensemble calculations. The difference might be due to the use of minimum image periodic conditions in Valleau's calculations versus Ewald sum in ours, or in the use of neutralizing backgrounds. We plan to pursue this issue further in the coming project period.

Results of our calculations for the restricted primitive model of electrolyte solutions are shown in Figure 3. Reference 2.1.4 describes these results in detail and discusses the pronounced clustering behavior of this fluid. These results were also presented at an invited talks at the Gordon conferences on Molten Salts and Liquid Metals (presentation 2.4.12) and Liquids (2.4.13). Our simulation results differ substantially from previous theoretical estimates for the phase coexistence envelope for this simple model.

The difficulties in obtaining reliable results for the strongly interacting coulombic systems at low temperatures which is to a large extent due to ion clustering prompted us to investigate the use of a distance-biased algorithm for particle transfer. The results are described in reference 2.2.4, and indicate that simple distance-biasing does not achieve efficient transfers of pairs of particles or accurate determinations of chemical potentials. We concluded that there is a need

Figure 3 Phase diagram for the restricted primitive model. (· · O · ·) Gibbs ensemble MC; (— · · —) lower limit for ρ_G^* of Gillan (1983); (- · -) Stell, Wu and Larsen (1976); (- -) Chasovskikh and Vorontsov-Vel'yaminov (1976); (—) modified Bjerrum theory as reported by Friedman and Larsen (1979). Lines are arbitrarily drawn through the points for visual clarity.

¹¹ J.P. Valleau, "The coulombic phase transition: density-scaling Monte Carlo", *J. Chem. Phys.*, **95**, 584-9 (1991).

for unphysical sampling methods (temperature- and density- scaling Monte Carlo¹²) to achieve ergodic sampling of phase space for these systems. We plan to pursue these methods in the coming project period.

2 PUBLICATIONS AND PRESENTATIONS RESULTING FROM THIS WORK

2.1 *Refereed publications*

1. V.I. Harismiadis, K.K. Koutras, D.P. Tassios and A.Z. Panagiotopoulos, "How good is conformal solutions theory for phase equilibrium predictions?" *Fluid Phase Equil.*, **65**, 1-18 (1991).
2. M.E. van Leeuwen, C.J. Peters, J. de Swaan Arons and A.Z. Panagiotopoulos, "Investigation of the transition to liquid-liquid immiscibility for Lennard-Jones (12,6) systems using Gibbs-ensemble molecular simulations," *Fluid Phase Equilibria*, **66**, 41-55 (1991).
3. S.K. Kumar, I. Szleifer and A.Z. Panagiotopoulos, "Determination of chemical potentials in polymeric systems from Monte Carlo simulations," *Phys. Rev. Lett.*, **66**, 2935-2938 (1991).
4. A.Z. Panagiotopoulos, "Molecular simulation of fluid-phase equilibria: simple, polymeric and ionic fluids," *Fluid Phase Equil.*, in press (1992).
5. A.Z. Panagiotopoulos, "Direct determination of fluid phase equilibria by simulation in the Gibbs ensemble: a review," *Mol. Simulation*, in press, (1992).

2.2 *Publications under review*

1. I. Szleifer and A.Z. Panagiotopoulos, "Chain length and density dependence of the chemical potential of lattice polymers", submitted for publication, *J. Chem. Phys.* (1992).
2. I. Szleifer, E.M. O'Toole and A.Z. Panagiotopoulos, "Monte Carlo Simulation of the Collapse-Coil Transition in Homopolymers", submitted for publication, *J. Chem. Phys.* (1992).
3. A.D. Mackie, E.M. O' Toole, D.A. Hammer and A.Z. Panagiotopoulos, "Molecular simulation of self-assembly in surfactant and protein solutions", submitted for publication, *Fluid Phase Equil.* (1992).
4. G. Orkoulas and A.Z. Panagiotopoulos, "Chemical potentials in ionic systems from Monte Carlo simulations with distance-biased test particle insertions", submitted for publication, *Fluid Phase Equil.* (1992).

¹² G.M. Torrie and J.P. Valleau, *J. Chem. Phys.*, **66**, 1402 (1977).

2.3 Conference presentations

1. "Gibbs-ensemble simulations of ionic systems," presented at the Annual AIChE meeting, Chicago, Illinois, Nov. 11-16, 1990.
2. "Determination of chemical potentials of polymer systems from Monte Carlo simulations" American Physical Society 1991 March meeting, Cincinnati, OH, March 18-22, 1991 (with Sanat Kumar).
3. "Determination of chemical potentials of polymeric systems from Monte Carlo simulations," presented at the Annual AIChE meeting, Los Angeles, CA, Nov. 1991 (with Sanat Kumar and Igal Szleifer).
4. "Determination of the chemical potential of polymeric fluids from Monte Carlo simulations", paper number B32:3, presented at the 1992 March Meeting of the American Physical Society, March 16-20, 1992 (with I. Szleifer).
5. "Molecular Simulation of phase equilibria in polymer systems," presented at the ACS Spring National meeting, San Francisco, CA, Apr. 5-10, 1992 (with I. Szleifer). Also in *Polymer Preprints*, **33**(1), 547-548.
6. "Monte Carlo simulation of phase equilibria in solutions of block copolymers," poster presented at the ACS Spring National meeting, San Francisco, CA, Apr. 5-10, 1992 (with Allan Mackie and Dan Hammer). Also in *Polymer Preprints*, **33**(1), 677-678.
7. "Chemical potentials in ionic systems from Monte Carlo simulations with distance-biased test particle insertions" to be presented at the 6th Inter. Conference on Fluid Properties and Phase Equil. for Chem. Process Design, Cortina d' Ampezzo, Italy, July 19-24, 1992 (with G. Orkoulas - based on 2.2.3).
8. "Molecular simulation of self-assembly in surfactant and protein solutions," to be presented at the 6th Inter. Conference on Fluid Properties and Phase Equil. for Chemical Process Design, Cortina d' Ampezzo, Italy, July 19-24, 1992 (with A.D. Mackie, E.M. O' Toole and D.A. Hammer - based on 2.2.4).

2.4 Invited seminars and lectures

1. "Molecular Simulation of Phase Equilibria", Univ. of Houston (Chem. Eng. Dept. seminar speaker), March 16, 1990.
2. "Molecular Simulation of Phase Equilibria", Princeton Univ. (Chem. Eng. Dept. seminar speaker), May 2, 1990.
3. "Gibbs Ensemble Simulations of Fluid Phase Equilibria", plenary lecture at the Third Liblice conference on Liquids, Bechyně, Czechoslovakia, May 28-June 1, 1990.

4. "The Gibbs Method for Calculating Phase Equilibria by Simulation", seminar presented at Shell Laboratories, Amsterdam, the Netherlands, June 3, 1990.
5. "Phase equilibria of ionic fluids", seminar presented at the Chemical Engineering Department, University of Karlsruhe, W. Germany, June 4, 1990.
6. "Molecular Simulation of Phase Equilibria", Univ. of California, Santa Barbara (Chem. Eng. Dept. seminar speaker), Oct. 4, 1990.
7. "Molecular Simulation of Phase Equilibria", Univ. of California, Berkeley (Chem. Eng. Dept. seminar speaker), Oct. 8, 1990.
8. "Determination of chemical potentials of polymeric systems from Monte Carlo simulations," Chemical Physics Seminar Series, Cornell Univ., Dec. 14, 1990.
9. "Monte Carlo simulations of polymeric systems," Chemical Engineering Department, National Technical University of Athens, Greece, Dec. 28, 1990.
10. "Molecular simulation of fluid-phase equilibria," invited lecture at the workshop on phase separation in multicomponent fluids, Taormina, Italy, February 25-28, 1991.
11. "Molecular simulation of phase equilibria: Simple, Ionic and Polymeric Fluids," invited lecture at the 11th Symposium on Thermophysical Properties in Boulder, Colorado, June 23-27, 1991 (based on 2.1.4).
12. "Gibbs-ensemble simulations of phase equilibria in ionic systems," invited lecture at the Gordon Research Conference on Molten Salts and Liquid Metals, Aug. 5-9, 1991.
13. "Molecular simulation of phase equilibria: simple, ionic and polymeric fluids," invited lecture at the Gordon Research Conference on the Chemistry and Physics of Liquids, Aug. 12-16, 1991.
14. "Monte Carlo simulations of phase equilibria and conformational transitions in polymeric systems", University of Akron, (Chem. Eng. Dept. seminar speaker), Dec. 5, 1991.
15. "Monte Carlo simulations of phase equilibria and conformational transitions in polymeric systems", National Center for Research in the Physical Sciences "Demokritos", Athens, Greece, March 16, 1992.
16. "Monte Carlo simulations of phase equilibria and conformational transitions in polymeric systems", Chemical Engineering Department. Univ. of Patras, Greece, March 18, 1992.
17. "Monte Carlo simulations of phase equilibria and conformational transitions in polymeric systems", Department of Chemistry, Univ. of Toronto, Canada, March 30, 1992.

3 PERSONNEL ASSOCIATED WITH THE PROJECT

The following researchers have been associated with various stages of the present project.

A. Principal Investigator: Athanassios Z. Panagiotopoulos

B. Post-doctoral Associates

Igal Szleifer (Ph.D, Technion U., 1987). Dr. Szleifer came to Cornell in 1989 as a post-doctoral associate in the Department of Chemistry (with Prof. B. Widom). In the period June, 1990 to June, 1991, he has collaborated with our group on methods to obtain chemical potentials for polymeric systems. Dr. Szleifer is presently an assistant professor in the Chemistry department at Purdue University.

C. Graduate Students

Alan Mackie (B.S., U. of Edinburgh, 1989). Mr. Mackie came to Cornell as a first-year graduate student in September 1989. He is co-supervised by Profs. D. Hammer and the PI of this project. His thesis topic is molecular simulation studies of surfactant solutions and biological membranes. He has been supported at a 25% level by the present project.

Germonda Mooij (B.S., U. of Amsterdam, 1989). Ms. Mooij is a doctoral candidate in the group of Prof. Daan Frenkel at FOM-Amsterdam. She visited Cornell for the period 1/92 to 4/92. Her research is in the area of phase equilibria of polymeric systems. She received a travel fellowship from Shell Research, and thus no direct financial support from the present grant.

Gerassimos Orkoulas (B.S., U. of Patras, 1989). Mr. Orkoulas joined our group in June 1990. His doctoral thesis project is simulations of phase equilibria of ionic systems. He has been fully supported by the present project.

Joel Recht (B.S. Chemistry, Rutgers University, 1990). Mr. Recht joined our group in January 1991. His doctoral research is on studies of phase equilibria for continuous models of surfactant solutions. He has been the recipient of a Department of Education "National Needs" fellowship which expires in 8/92. After that time it is anticipated that he will be supported at a 50% level by funds from this project.

Jane Sheng (B.S. and M.S., National Taiwan University, 1990). Ms. Sheng joined our group in January 1991. Her thesis topic is studies of phase equilibria in polymeric systems. She is fully supported by funds from the present project.

D. Undergraduate Students

Monica van Leeuwen
Vassilis Harismiadis
Nikos Koutras
Karen Millane

4 BUDGET PROJECTION TO END OF PROJECT PERIOD

The table below gives a summary of the financial status of the grant. As can be determined from the table, our original budget projections were followed closely, except for a slightly higher expenditure on equipment and a slightly lower expenditure on PI and student salaries and benefits. It is anticipated that the grant funds will be fully utilized by the end of the current project period.

	Original Budget ('000)	Expenditures to 5/31/92 ('000)	Projection to 12/31/92 ('000)
Principal Investigator	38	25	32
Graduate and Postdoctoral Students	158	124	153
Fringe Benefits	6	4.1	4.7
Equipment	44.2	54	57
Travel	3.5	2.2	3.5
Supplies	2.7	3.9	4.5
Indirect Costs	78.5	60.0	76.2
TOTAL	330.9	273.2	330.9

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