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FINAL

STATISTICAL MECHANICS OF POLYMER SYSTEMS

by

Jeffrey Kovac
Department of Chemistry
University of Tennessee
Knoxville, TN 37996-1600

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ABSTRACT

Work on computer simulation of polymer dynamics and the statistical mechanics of quenched systems carried out over seven years with the support of this grant is reviewed. The computer simulation work has focussed on the elucidation of the roles of the excluded volume and the nearest-neighbor attractive interactions in the dynamics of polymers. To study quenched systems we have applied the formalism suggested long ago by Mazo to two model systems and found qualitative agreement with the properties of real glasses.

INTRODUCTION

An understanding of the equilibrium and dynamic properties of polymer systems is crucial to the intelligent use of these molecules as materials. Polymeric materials are used throughout our society and the demand for increasingly sophisticated macromolecules for technological applications is growing. Despite the widespread applications, the fundamental understanding of the behavior of polymers is far from complete.

My research program in computer simulation of polymer dynamics has as its primary objective the development of simple theoretical models which elucidate some of the fundamental physical and chemical processes which govern the motions of polymers. The focus has been on dynamics, but equilibrium properties have also received some attention. We have used a number of computer simulation models to address a variety of important problems in polymer physics and chemistry. Although the individual problems have been rather diverse, there have been two major themes around which the work has been organized: the roles of excluded volume and attractive interactions in chain dynamics and the behavior of polymers near interfaces.

In addition to the work on computer simulation we have also done some work in the development of theoretical methods for the understanding of quenched or glassy systems. An understanding of the glass transition is one of the most important problems in polymer science. Although we have only examined small molecule systems we hope that the methods we are exploring will ultimately be applicable to polymers.

During the seven years of this grant we have published nineteen papers on

computer simulations and quenched systems. Some of the work initiated in the later stages of the grant period is being continued and will appear in print in the next year. The work of three doctoral students, two master's students and three postdoctoral research associates has been supported by this grant, in full or in part. In addition, seven undergraduate research participants from a variety of institutions have been involved in this research, mainly as summer research participants supported by the UTK-ORNL Science Alliance.

In the following I will summarize the results obtained during the grant period in both areas and draw some general conclusions about what we have learned. Further details can be found in the published articles.

COMPUTER SIMULATION OF POLYMER DYNAMICS

The effect of excluded volume on the equilibrium and dynamic properties of polymers is one of the outstanding unsolved problems in the field. There has been much recent progress in the development of renormalization group methods to study equilibrium properties¹, but the dynamics remain a much more difficult problem.

Computer simulation techniques offer a method to probe the basic physical processes involved in the motion of polymers with excluded volume because the position of each segment of the molecule can be followed as a function of time providing a very detailed picture of the dynamics. To study the effects of excluded volume on the dynamics it is essential that the excluded volume condition be rigorously maintained in the computer simulation model. For this reason lattice models are attractive. Both long chains and concentrated systems can be studied using lattice models because of their computational simplicity. The simplicity of lattice models also means that it is often easier to sort out the origin of the observed behavior. This means that lattice models also have great heuristic value.

There is an additional influence on the behavior of polymer chains which has not received much attention until recently, the effect of attractive pair interactions between non-bonded segments. These attractive potentials of mean force are responsible for the existence of the theta point, where they exactly compensate the repulsive excluded volume interaction. It was suggested long ago by Brochard and DeGennes² that these attractive interactions might have dramatic effects on the chain dynamics. Since attractive forces can easily be incorporated into lattice models it is possible to study the

relative effects of attractions and repulsions on the chain motions.

Over the past fifteen years my research group has made significant progress in the development of dynamic Monte Carlo computer simulation lattice models and their application to problems in chain dynamics. In particular, we have studied the effects of both the elementary motions^{3,4,5} and the lattice coordination number^{6,7} on the chain dynamics. These studies have helped to define the extent to which the properties of these simple models are independent of the specific model chosen. We have applied our models to the study of dynamics of concentrated polymer systems in an attempt to study the crossover between dilute solution dynamics and reptation^{8,9,10}. We have developed a computer simulation model which incorporates a nearest-neighbor interaction¹¹ and used it to explore the dynamics of chains in the theta region¹² and below.^{13,14} Recently, we have begun to study the dynamics of chains near interfaces^{15,16} and shape fluctuations in both linear and star polymers.^{17,18} In the following I will highlight some of the more important results obtained during the period covered by this grant.

Dynamics of Chain Molecules in the Theta Region

Following the work of J. Naghizadeh, James Patton Downey studied the dynamics of polymer chains near the theta point. In the model the excluded volume condition was rigorously maintained and the chain was shrunk to its ideal conformation by means of a nearest neighbor attractive interaction. The surprising result was that, at the theta point, the relaxation times of the higher order normal modes were significantly slower than predicted by the Rouse model for ideal chains. The qualitative effect was independent

of the lattice coordination number of the model, although some lattice dependent effects were observed. The lattice dependence was successfully explained in terms of the different types of elementary motions used in the different models. These effects were similar to those seen in concentrated systems. The major slowing-down of the higher order modes, however, is independent of lattice coordination number.

There are three possible explanations for this behavior. The simplest is the larger segment concentration at the theta point. Based on previous work on concentrated systems this effect is too small to explain the observed slowing. The second is local chain stiffness. The dynamic scaling hypothesis relates the relaxation time of the chain to its equilibrium dimensions.¹⁹ If the internal dimensions of the chain were relatively expanded compared to the end-to-end distance this would explain the slowing of the higher order modes. Calculations by a current graduate student, Charlene Carpenter Sorensen, show that the internal dimensions of the chains are somewhat expanded, but not enough to explain the dramatic chain slowing seen in our simulations.²⁰ The third possible explanation is the most likely and the most interesting. Brochard and DeGennes have suggested that in the presence of a nearest neighbor attractive interaction the lifetime of pair contacts might be long enough to significantly affect the chain dynamics. In the semidilute regime the long lived contacts will turn the system into a gel giving rise to certain fast relaxation modes. In the dilute region, however, we hypothesize that the lifetime of the pair contacts will slow certain of the relaxation modes as the chain unwinds.

Charlene Sorensen has completed the task of determining the distribution of the

lifetimes of the pair contacts as a function of the attractive potential. We find that the distribution broadens significantly in the theta region and below and that the longest lived pair contacts have a lifetime comparable to the relaxation of the $k = 3$ mode. It seems quite clear that the lifetime of pair contacts can have a significant effect on the intermediate length scale chain dynamics in the theta region and below. Experimental results which are consistent with our computer simulations have recently been obtained at the University of Wisconsin by the research group of Mark Ediger.^{21,22}

The slowing of the intermediate range modes in the theta region is a very interesting effect, which may have important theoretical and experimental consequences.

Dynamics of Chains Near Interfaces

In recent years we have begun to study the dynamics of polymer chains near interfaces. The early work involves very simple systems. In his M.S. thesis, Thomas D. Hahn studied the dynamics of a tethered chain using a face-centered cubic lattice simulation model.^{23,24} He studied the effect of the interface on the end-to-end vector relaxation of the chain and showed that the impenetrable barrier slowed the relaxation much more than would be predicted by the dynamic scaling hypothesis which relates the relaxation time to the chain dimensions. The static properties of the chain were consistent with the recent renormalization group (RG) calculations done by Karl Freed and co-workers.²⁵ After conversations with Professor Freed we are now doing simulations corresponding to other cases which is group is studying using RG techniques. We have recently completed a study of the properties of a single chain trapped in a

reflecting wedge.²⁶ The results for the equilibrium properties agree quite well with the RG calculations.²⁷ The results for the dynamic properties show that the dynamic scaling hypothesis holds for sufficiently long chains.

As a first step toward the understanding of chain-chain interactions near the interface we are currently studying the dynamics of two tethered chains as a function of the distance between them. In addition to the usual static and dynamic properties we are also looking at the radius-of-gyration both parallel and perpendicular to the surface. As described below, we already have some experience in interpreting radius of gyration data in the context of star polymers. This work should appear within the next year.

The chains studied by Hahn were rigidly attached to the surface. Using the nearest-neighbor interaction model we can study adsorbed chains which retain some mobility along the surface as well as chains which adsorb at points other than the end. All of these cases correspond to important experimental situations where polymers are used as surfactants, adhesives, and lubricants, among other applications. For some of these cases the equilibrium properties can also be studied using RG methods and the comparison with simulations would be illuminating.

As part of her Ph.D. thesis Charlene Carpenter Sorensen is studying single chains which are rigidly attached to the surface, but which also have attractive intrachain interactions as well as an attractive or repulsive chain-surface interaction. These results are currently being interpreted. We have also begun to study the system in which the chain is untethered and only attached to the surface by an attractive chain-surface interaction.

Dynamics of Non-linear Polymers

In the past several years we have made significant progress in the study of shape fluctuations in linear and star polymers. While the average shape of a macromolecule in solution is spherical its instantaneous shape is ellipsoidal as was shown long ago by Solc and Stockmayer²⁸ who studied the radius-of-gyration tensor of random walk polymers. A non-rigid ellipsoid has two different modes of motion. The ellipsoid can rotate in space without changing shape and the extensions along the principle axes can change, a motion we call the "breathing motion." The breathing motions of linear polymers were studied by computer simulation by Kranbuehl, Verdier and co-workers using the original Stockmayer-Verdier algorithm.²⁹ In his master's thesis, Thomas Hahn studied both the breathing motions and the rigid body rotations using the Crabb-Kovac cubic lattice model and found results which differ from those of Kranbuehl, Verdier and co-workers in ways that reflect the differences in the two simulation models.

For linear chains shape relaxation as measured by fluctuations in the radius-of-gyration tensor is not particularly interesting because the Rouse normal coordinates give a good picture of the chain motions. For non-linear polymers, such as stars, the situation is different. In the non-linear case there are no agreed-upon probes which give a picture of the motions of the molecule. Shape fluctuations are an attractive choice. Shape fluctuations are currently being used to probe the motions of spherical micelles by dynamic neutron scattering. Even if they turn out not to be experimentally accessible in polymers shape fluctuations should provide a graphic picture of the molecular motions and, therefore, should have important heuristic value. They may also provide a model

system for the study of the relaxation of tensor variables in fluids.

Our approach to the problem is to calculate the instantaneous radius-of-gyration tensor of the molecule using the expression given by Solc and Stockmayer. This three-by-three tensor is then numerically diagonalized. The eigenvalues represent the extensions of the molecule along the three principal axes and, therefore, are a measure of the instantaneous shape. The autocorrelation functions of these eigenvalues then measure the principle shape fluctuations or breathing motions of the molecule. From the eigenvectors it is possible to calculate the angles that the principle axes make with respect to the laboratory coordinate system. The rotation of the principle axes can then be monitored by computing the autocorrelation functions of the squares of the second order spherical harmonics of the two rotational angles. It is necessary to use the squares of the spherical harmonics because the numerical diagonalization procedure can switch the plus and minus directions of the principle axes. This will change the sign of the trigonometric functions and introduce non-physical jumps into the rotational trajectory. Use of the square eliminates this problem quite neatly.

We have studied the shape relaxation of two different systems using these ideas. The first system studied was linear cubic lattice model chains. The results have recently been reported in *Macromolecules*.³⁰ Hahn found that the relaxations times of the eigenvalues, the breathing motions, obeyed the dynamic scaling relationship and that the three relaxation times seemed to be proportional to the first three Rouse relaxation times for chains with and without excluded volume. The angular relaxations, however, did not decay exponentially, even at long times, so it was not possible to extract a simple

relaxation time from the decay of the autocorrelation functions. Some comparisons were made using the time at which the autocorrelation function had decayed to a value of e^{-1} , but this is a rather crude measure of the chain motion so detailed conclusions could not be drawn.

A more interesting system is uniform star polymers which have been studied by Shu-Jun Su over the past several years. His results on shape fluctuations in isolated three- and four-arm stars have recently appeared in *Macromolecules*.³¹ In the case of stars it was not possible to use the fixed bond lattice algorithms that we have developed over the past years because there are no obvious elementary motions of the branch point in the excluded volume case. Therefore, we have implemented the bond fluctuation model introduced by Carmesin and Kremer³² in three dimensions and extended it to the study of stars.

Su has studied isolated three- and four-arm stars with excluded volume and compared them to linear chains of the same degree of polymerization. He calculated the relaxation times of the eigenvalues of the radius-of-gyration tensor. He also studied the rotation of the molecules using the autocorrelation functions of the squared of the spherical harmonics of the angles that the molecular principle axes make with respect to a fixed laboratory coordinate system. As in the linear chain case these autocorrelation functions were found to be non-exponential and were therefore analyzed using the Kolrausch-Williams-Watts (KWW) or stretched exponential function. This function contains two parameters: a relaxation time and a width parameter usually taken to be characteristic of the width of the actual distribution of relaxation times of the system. Su

was able to extract the two KWW parameters for the rotational relaxations.

Su's results showed that a generalized dynamic scaling relation holds for the relaxations of the eigenvalues of the radius-of-gyration tensor for the stars. The rotational motions are not exponential and there seems to be no clear time scale separation between the rotations and the breathing motions. There has been very little computer simulation or theoretical work on the dynamics of stars, a recent paper by Grest, Kremer, Milner and Witten³³ being a notable exception. Our work adds to the available simulation data on isolated stars and will help to provide insight for future theories of the motions of non-linear polymers.

The first extension this work that we pursued was the study of a uniform star immersed in a bath of uniform linear chains.³⁴ This is a system that can be studied by means of dynamic light scattering using index of refraction matching techniques. Experimental results on such systems have been recently obtained by Lodge and co-workers.³⁵ We studied the motion of a single two-, three-, or four-arm star immersed in a bath of linear molecules as a function of the bath concentration. Since this was a preliminary study, only a single arm length, 20 monomers was used. For simplicity, the linear bath molecules had the same length as the arms. As expected, the bath molecule slowed the various motions of the stars. We also observed that the overall size of the stars, as measured by $\langle R_G^2 \rangle$, decreased slightly as the concentration of bath molecules increased. More surprising was the observation that the shape of the stars, as measured by the eigenvalues of the radius-of-gyration tensor, changed with concentration, becoming more plate-like at the higher concentration. The changes were quite small, however, and

may not be significant. We hope to follow up on this study in the future.

Conclusions

Our work on computer simulations has resulted in the development of versatile simulation codes which can be applied to a wide variety of problems. We have gained considerable insight into the roles of the two important parameters in the behavior of problems: the excluded volume and the nearest neighbor attractive energy. Questions still remain which we plan to study in succeeding years.

STATISTICAL MECHANICS OF QUENCHED SYSTEMS

Understanding the glass transition and the glassy state is a classic problem in physical chemistry. Glasses are technologically important materials and, consequently, have been studied in great detail.³⁶ In spite of this widespread interest it is generally agreed that our understanding of the fundamental physics of glasses is incomplete. This is due, in large part, to the fact that glasses are a metastable form of matter and, hence, cannot be completely understood in terms of the usual equilibrium theories of thermodynamics and statistical mechanics. Some, particularly Gibbs and DiMarzio, have argued that considerable progress toward the understanding of glasses can be made using ordinary equilibrium statistical mechanics.^{37,38} In fact, the classic Gibbs-DiMarzio theory of polymeric glasses has been widely and successfully used to study a variety of systems.³⁹

There are others, however, who would suggest that an understanding of the glass transition can only come as a by-product of a molecular theory of the viscosity of complex liquids.^{40,41} In this view, the glass transition is a dynamic phenomenon and equilibrium theories are irrelevant to its understanding. The classic dynamic explanation of the glass transition is the free volume theory of Cohen and Turnbull.⁴² A more sophisticated free volume approach has recently been developed by Cohen and Grest.⁴³ Recent theoretical developments in the understanding of the dynamic aspects of the glass transition have been reviewed by Fredrickson.⁴⁴

My view has always been that there must be an appropriate quasi-equilibrium theory of glasses. Though technically metastable materials, the properties of glasses are

stable over long periods of time (i.e., years) and can be measured using standard "equilibrium" techniques. The important question, then, is what is the appropriate statistical mechanical theory of glasses? Can one simply use ordinary equilibrium ensemble theory, perhaps with minor modifications, or, must a different formalism be employed? This is still an open question. For example, Gibbs and DiMarzio² have used ordinary equilibrium statistical mechanics to study polymeric glasses and predicted the existence of an underlying equilibrium second order phase transition. More recently, Stillinger has suggested that one can calculate the properties of glasses by employing the usual canonical ensemble but excluding that part of phase space which includes crystallites larger than a certain size.⁴⁵

A third view suggests that the properties of glasses should be calculated using the quenched system formalism introduced long ago by Mazo⁴⁶ and used extensively in the theory of spin glasses.⁴⁷ This method has been used, or at least advocated, in recent papers on glasses by Edwards⁴⁸, Roe⁴⁹ and, Wolynes and co-workers,⁵⁰ as well as in two of my own papers.^{51,52} This formalism takes into account the non-equilibrium, quenched nature of the system in the calculation of nominally equilibrium quantities such as the free energy. The quenched system formalism differs from ordinary equilibrium statistical mechanics in that the free energy is averaged over an a priori probability that certain structural constraints are incorporated into the system during the quenching process. This probability is determined by the kinetics of the quenching process.

Since the dynamics of the glass transition are poorly understood, the usual procedure has been to make a reasonable physical assumption concerning the form of

the probability distribution and then compare the thermodynamic properties of the system to those of real glasses. In spin glass systems an additional mathematical approximation known as the replica trick has also been used. While extensive work has been done on spin glass systems,⁵³ much less attention has been paid to the so-called structural glasses which, of course, are considerably more important technologically.

The motivation of my research program has been to explore the use of the quenched system formalism in the description of structural glasses in an attempt to assess whether it is the proper way in which to approach the problem. Our initial approach has been to find simple, usually one-dimensional, models for which we can calculate the thermodynamic properties exactly using a reasonable guess for the nature of the quenched-in constraint and for the probability distribution of that constraint. These initial efforts have been quite encouraging. We have qualitatively reproduced some of the important properties of real glasses. In the succeeding pages we will review the Mazo formalism in some detail and highlight our previous results on model systems.

The focus of my research on the glass transition over the past several years has been the calculation of the quasi-equilibrium properties of quenched systems. In particular we have been applying the formalism introduced by Mazo, which has previously been applied to spin glasses and elastomers,⁵⁴ to the calculation of the properties of structural glasses. Our approach has been to find simple, usually one-dimensional models in which we can calculate the quenched system free energy exactly without the use of the so-called replica trick which is ordinarily used in spin glass calculations. Two systems have been studied in detail. In the next few paragraphs I will

review the formalism and our results to date.

Statistical mechanical calculations of equilibrium systems begin with the partition function which is the sum over the Boltzmann factors of all distinguishable accessible microscopic states. The feature which characterizes a glass or a quenched system is that not all molecular states are accessible due to some sort of constraint which is kinetically frozen-in. The static or quasi-equilibrium properties of glasses can be measured as long as the experimental time scale is short enough. Therefore, there ought to be a method for calculating these properties from the principles of statistical mechanics. There is not universal agreement as to what this procedure is, however.

A formal method was described long ago by Mazo. One first identifies the nature of the constraint on the system, say m . Next, the free energy $A(m)$ is calculated as a function of this constraint. In this calculation the constraint is assumed to have a fixed value. Last, one calculates the free energy of the quenched or glassy system by averaging the constrained free energy $A(m)$ over the probability $P(m)$ that the particular value of the constraint is realized in the quenching procedure according to the equation

$$A = \sum_m A(m)P(m)$$

This procedure can only be properly applied when the dynamics of the quenching procedure are completely understood so that both the constraint and the probability distribution can be specified. Our knowledge of quenched systems certainly does not go that far at this time. Therefore we have taken the following approach. We look at very simple model systems, usually in one-dimension, in which we can make a physically sensible a priori choice of both the quenched-in constraint and its probability

distribution. We then calculate both the quenched and equilibrium free energies of the systems and obtain the thermodynamic observables for the two cases. We then compare the thermodynamic properties of the quenched systems to the known properties of glassy systems to see which ones can be successfully reproduced. No attempt at quantitative comparison is made. The model systems are too simple for that. Our goal is to see if the Mazo formalism can give the correct qualitative behavior for structural glasses and to try to learn what kinds of glassy behavior are the result of particular types of constraints and probability distributions.

Over the past several years we have studied two different model systems. All of this work has been done in collaboration with Dr. Rajiv Singh who spent a year as a postdoctoral research associate in my group and is currently employed by Allied Signal Corporation in Buffalo, N. Y. The first system that we studied was a one-dimensional bonded fluid model which was intended to be a simple model for a network glass.⁵⁵ The quenched-in constraint was the bond energy which was assumed to have a Poisson distribution. The Poisson distribution was chosen so as to insure that the bond energy was always positive and also because it made the problem exactly soluble. The calculated behavior of the quenched system was qualitatively similar to that of a real glassy system.

The second system studied was a one dimensional van der Waals fluid with a hard shoulder in the repulsive part of the potential.⁵⁶ The width of the shoulder was taken to be a quenched-in constraint in an attempt to model the random packing or extra free volume in the glass. For simplicity, the probability distribution of the constraint was

taken to be a Gaussian. Since the equilibrium fluid has a first order liquid-solid transition it was possible to study the competition between freezing and glass formation. What we found was that as the width of the Gaussian distribution was increased the first order transition of the equilibrium fluid was transformed into a second order glass-like transition which exhibited thermodynamic behavior qualitatively similar to that of a real glass former.

This is admittedly a crude single particle approximation to a complicated many particle problem. The shouldered Hamiltonian is an attempt to model effects of imperfect packing. While this cannot be considered a general solution to the glass transition problem it does seem a sensible first step in evaluating the ability to the Mazo formalism to calculate the properties of glassy systems.

Conclusions

These initial results show that the Mazo formalism is a promising alternative for the study of quenched systems. The challenge for the future is in applying the formalism to realistic models which can be compared directly to experiment.

PERSONNEL INVOLVED WITH THIS PROJECT

Principal Investigator:

Jeffrey Kovac, Professor of Chemistry

Postdoctoral Research Associates:

J. Naghizadeh, Ph.D., University of Chicago

Rajiv R. Singh, Ph.D., University of Tennessee

Shu-Jun Su, Ph.D., University of New Hampshire

Ph.D. Students:

J. Patton Downey, Ph.D., 1989

Charlene Carpenter Sorensen, Ph.D., expected 1993

Frank L. Somer, Jr., Ph.D., expected 1994

M.S. Students:

Michelle Dial, worked on the project for one year and transferred to another research group

David F. Hoffman, Jr. left school without a degree

Thomas D. Hahn, M.S., 1989

Undergraduate Students:

Celeste Stokely, University of Tennessee

Thomas D. Hahn, Penn State University

E. Todd Ryan, Marshall University

Melinda S. Denny, St. Andrews Presbyterian College

Lisa C. Hill, Pfeiffer College

Heather Curry, Ball State University

James Ianni, Cheyney University

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1. "Normal Coordinate Analysis of the Dynamics of Cubic Lattice Models for Polymer Chains," Poster presentation, Gordon Research Conference on Liquids, August 19-23, 1985.
2. "Computer Simulation of Polymer Dynamics," Invited presentation, University of California Statistical Mechanics Conference, Davis, CA, March 26-29, 1986.
3. "Computer Simulation of Polymer Dynamics," 41st NW Regional ACS Meeting, Portland, OR, June 18, 1986.
4. "Temperature Dependent Cubic Lattice Model Stimulation of Chain Dynamics," Invited Poster, Gordon Research Conference on Polymer Physics, July 14-18, 1986.
5. "Temperature Dependent Cubic Lattice Model Stimulation of Chain Dynamics," Statphys 16, Boston University, August 10-15, 1986.
6. "Normal Mode Analysis of Lattice Model Polymer Chains at High Concentrations," Poster presentation 1987 MMI International Symposium on Polymer Melt Dynamics, August 16-18, 1987.
7. "Computer Simulation of Polymer Dynamics," East Tennessee Section, American Chemical Society, January 19, 1988.
8. "Statistical Mechanics of a Quenched Bonded Fluid," Invited Poster, Gordon Research Conference on Polymer Physics, July 18-22, 1988.
9. "Thermodynamics and Statistical Mechanics of Glasses," Invited Seminar, Department of Chemistry, University of Detroit, October 19, 1988.
10. "Computer Simulation of Polymer Dynamics," Invited Seminar, Research Laboratories, Tennessee Eastman Company, October 27, 1988.
11. "Computer Simulation of Polymer Dynamics," Invited Seminar, Department of Mathematics and Computer Science, Royal Military College of Canada, February 16, 1989.
12. "Dynamics of Lattice Models of Polymer Chains Near the Theta Point," Poster presentation, Gordon Conference on Liquids, August 1989.
13. "Statistical Mechanics of Quenched Systems," Invited presentation, Symposium on Continuous Thermodynamics for Complex Mixtures, AIChE National Meeting,

March 19, 1990, Orlando, FL.

14. "The Puzzle of the Theta Point," Invited Presentation, Fixman Symposium, Colorado State University, October 5-6, 1990.
15. "The Puzzle of the Theta Point," Invited Seminar, Department of Chemistry, University of Oregon, January 28, 1991.
16. "The Puzzle of the Theta Point," Invited Seminar, Department of Chemistry, Oregon State University, January 29, 1991.
17. "The Puzzle of the Theta Point," Arthur F. Scott Lecture, Reed College, January 31, 1991.
18. "The Puzzle of the Theta Point," Invited Horizons Lecture, Kimberly-Clark Corporation, November 15, 1991.

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