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Toward Molecular Engineering of Polymer Glasses

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I. Introduction

Glass formation has been central to fabrication technologies since the dawn of civilization. Glasses not only encompass window panes, the insulation in our homes, the optical fibers supplying our cable TV, and vessels for eating and drinking, but they also include a vast array of ‘‘plastic’’ polymeric materials. Glasses find applications in high technology (e.g., producing microelectronic materials, etc., amorphous semiconductors), and recent advances have created ‘‘plastic metallic glasses’’ that are promising for fabricating everyday structural materials. Many commercially relevant systems, such as microemulsions and colloidal suspensions, have complex molecular structures and thus solidify by glass formation.

Despite the importance of understanding the fundamental nature of glass formation for the synthesis of new materials, a predictive molecular theory has been lacking. Much of our understanding of glass formation derives from the analysis of experimental data, a process that has uncovered a number of interesting universal behaviors, namely, relations between properties that are independent of molecular details. However, these empirically derived relations and their limitations remain to be understood on the basis of theories, and, more importantly, there is strong need for theories of the explicit variation with molecular system to enable the rational design and tailoring of new materials.

We have recently developed the generalized entropy theory, the *only analytic,* theory that enables describing the dependence of the properties of glass-formation on monomer molecular structures. These properties include the two central quantities of glass formation, the glass transition temperature and the glass fragility parameter, material dependent properties that govern how a material may be processed (e.g., by extrusion, ink jet, molding, etc.) Our recent works, which are further described below, extend the studies of glass formation in polymer systems to test the theory by directly comparing between the predictions of our generalized entropy theory with experiment and with simulations and to expand the vistas of the theory to describe a wider range of important systems (e.g. glass formation in binary blends and systems with specific interactions) and phenomena that are describable by the generalized entropy theory. In addition, we have addressed longstanding fundamental problems associated with the validity of the Adam-Gibbs theory, one of the underpinnings of the general entropy theory.

II. Theoretical advances to enable describing the properties of glass-formation over a wider class of important polymeric systems, included semi-flexible systems, the more general situation of specific interactions, and more.

Our recent work removes the simplest approximation uses the simplest model in which the interaction is approximated by a single, monomer average. Thus, the theory has been extended to allow some variations of the energy parameters between the atoms within the monomers. The theory has also been extended to include all the contributions from chain semi-flexibility. Both projects are extremely difficult, but the payback is that the process of solving the problems developed strong theoretical skills in Dr. Xu, who has recently begun a postdoc position at ORNL. The theory has also been extended to describe glass formation in partially miscible blends, with good general agreement with experiment. Again, the development of the theory presented an extremely difficult problem, but the payback is the development of a theory for a very important class of systems. Another project provides an extremely simple approximation for certain properties of glass formation in polymer melts and should make the theory more accessible to everyone.

1. Advances in the Generalized Entropy Theory of Glass-Formation in Polymer Melts.

The generalized entropy theory (GET) of polymeric glass-forming liquids is reformulated into a computationally simpler and more natural formalism than the original version of this theory. The new theoretical framework greatly facilitates the present overview of essential trends in the dependence of the segmental relaxation time τ fragility, characteristic temperatures of glass-formation, etc., on the combined influences of monomer molecular structure, chain rigidity, and cohesive interaction strength, influences that previously are only discussed independently for some properties. Special attention is placed on the estimating the parameters of the phenomenological Vogel-Fulcher-Tammann (VFT) relations for describing segmental relaxation in diverse liquids in the low temperature range of glass-formation, $T_g > T > T_c$ (or $T_g < T < T_g +$ 100 K), where T_g and T_c are, respectively, the glass transition temperature and the crossover temperature separating the high and low temperature regimes of glass-formation. Finally, we discuss how the molecular energetic interaction parameters of the GET can be estimated from experimental data. Illustrative calculations are performed for the stiffness factor σ and the cohesive energy density u as a first step in this direction.

2. Lattice Cluster Theory for Polymer Melts with Specific Interactions.

Despite the long-recognized fact that chemical structure and specific interactions greatly influence the thermodynamic properties of polymer systems, a predictive molecular theory that enables systematically addressing the role of chemical structure and specific interactions has been slow to develop even for polymer melts. While the lattice cluster theory (LCT) provides a powerful vehicle for understanding the influence of various molecular factors, such as monomer structure, on the thermodynamic properties of polymer melts and blends, the application of the LCT has heretofore been limited to the use of the simplest polymer model in which all united atom groups within the monomers of a species interact with a common monomer averaged van der Waals energy. Thus, the description of a compressible polymer melt involves a single van der Waals energy. As a first step towards developing more realistic descriptions to aid in the analysis of experimental data and the design of new materials, the LCT is extended here to treat models of polymer melts in which the backbone and side groups have different interaction strengths, so three energy parameters are present, namely, backbone-backbone, side group-side group, and backbone-side group interaction energies. Because of the great algebraic complexity of this extension, we retain maximal simplicity within this class of models by further specializing this initial study to models of polymer melts comprising chains with poly(*n*-*α*-olefin) structures where only the end segments on the side chains may have different, specific van der Waals interaction energies with the other united atom groups. An analytical expression for the LCT Helmholtz free energy is derived for the new model. Illustrative calculations are presented to demonstrate the degree to which the thermodynamic properties of polymer melts can be controlled by specific interactions.

3. The Simplified Generalized Entropy Theory of Glass-formation in Polymer Melts.

While a wide range of non-trivial predictions of the generalized entropy theory (GET) of glass-formation in polymer melts agree with a large number of observed universal and non-universal properties of these glass-formers and even for the dependence of these properties on monomer molecular structure, the huge mathematical complexity of the theory precludes its extension to describe, for instance, the perplexing, complex behavior observed for technologically important polymer films with thickness below ~ 100 nm and for which a fundamental molecular theory is lacking for the structural relaxation . The present communication describes a hugely simplified (SGET) version of the theory that provides one component necessary for devising a theory for the structural relaxation of thin polymer films and thereby supplements the first required ingredient, the recently developed Flory-Huggins level theory for the thermodynamic properties of thin polymer films, before the concluding third step of combining all the components into the SGET for thin polymer films. Comparisons between the predictions the SGET and the full GET for the four characteristic temperatures of glass-formation provide good agreement for highly a non-trivial model system of polymer melts with chains of the structure of poly(n-α olefins), systems where the GET has produced good agreement with experiment. The comparisons consider values of the relative backbone and side group stiffnesses such that the glass transition temperature *decreases* as the amount of excess free volume diminishes, contrary to general expectations but in accord with observations for poly(n-alkyl methacrylates). Moreover, the SGET is sufficiently concise to enable its discussion in a standard course on statistical mechanics or polymer physics.

4. Thermodynamic Scaling of Dynamics in Polymer Melts: Predictions from the Generalized Entropy Theory.

Many glass-forming fluids exhibit a remarkable thermodynamic scaling in which dynamic properties, such as the viscosity, the relaxation time, and the diffusion constant, can be described under different thermodynamic conditions in terms of a unique scaling function of the ratio ρ/T, where ρ is the density, T is the temperature, and γ is a material dependent constant. Interest in the scaling is also heightened because the exponent γ enters prominently into considerations of the relative contributions to the dynamics from pressure effects (e.g., activation barriers) vs. volume effects (e.g., free volume). Although this scaling is clearly of great practical use, a molecular understanding of the scaling remains elusive. Providing this molecular understanding would greatly enhance the utility of the empirically observed scaling in assisting the rational design of materials by describing how controllable molecular factors, such as monomer structures, interactions, flexibility, etc., influence the scaling exponent γ and, hence, the dynamics. Given the successes of the generalized entropy theory in elucidating the influence of molecular details on the universal properties of glass-forming polymers, this theory is extended here to investigate the thermodynamic scaling in polymer melts. The predictions of theory are in accord with the appearance of thermodynamic scaling for pressures not in excess of 50 MPa. (The failure at higher pressures arises due to inherent limitations of a lattice model.) In line with arguments relating the magnitude of γ to the steepness of the repulsive part of the intermolecular potential, the abrupt, square-well nature of the lattice model interactions lead, as expected, to much larger values of the scaling exponent. Nevertheless, the theory is employed to study how individual molecular parameters affect the scaling exponent in order to extract a molecular understanding of the information content contained in the exponent. The chain rigidity, cohesive energy, chain length, and the side group length are all found to significantly affect the magnitude of the scaling exponent, and the computed trends agree well with available experiments. The variations of γ with these molecular parameters are explained by establishing a correlation between the computed molecular dependence of the scaling exponent and the fragility. Thus, the efficiency of packing the polymers is established as the universal physical mechanism determining both the fragility and the scaling exponent γ.

5. Concentration Fluctuations in Miscible Polymer Blends: Influence of Temperature and Chain Rigidity.

In contrast to binary mixtures of small molecule fluids, homogeneous polymer blends exhibit relatively large concentration fluctuations that can strongly affect the transport properties of these complex fluids over wide ranges of temperatures and compositions. The spatial scale and intensity of these compositional fluctuations are studied by applying Kirkwood-Buff theory to model blends of linear semiflexible polymer chains with upper critical solution temperatures. The requisite quantities for determining the Kirkwood-Buff integrals are generated from the lattice cluster theory for the thermodynamics of the blend and from the generalization of the random phase approximation to compressible polymer mixtures. We explore how the scale and intensity of composition fluctuations in binary blends vary with the reduced temperature $\tau \equiv (T - T_c)/T$ (where T_c is the critical temperature) and with the asymmetry in the rigidities of the components. Knowledge of these variations is crucial for understanding the dynamics of materials fabricated from polymer blends, and evidence supporting these expectations is briefly discussed.

6. Influence of Cohesive Energy on the Thermodynamic Properties of a Model Glass-Forming Polymer Melt

Monomer chemical structure and architecture represent the most important characteristics of polymers that affect basic molecular parameters (such as the microscopic cohesive energy parameter χ and chain persistence length) and that correspondingly govern the bulk physical properties of polymer materials. Here, we focus on elucidating how the microscopic parameter χ influences the bulk thermodynamic properties of polymer melts by using molecular dynamics simulations for a standard coarse-grained bead-spring model of unentangled polymer melts under both constant volume and constant pressure conditions. Basic dimensionless thermodynamic properties, such as the cohesive energy density, thermal expansion coefficient, isothermal compressibility, and surface tension, are found to be universal functions of the temperature scaled by χ, and thermodynamic signatures for the onset and end of glass-formation are identified based on observable features from the static structure factor. We also find that general trends in the thermodynamics and the characteristic temperatures of glass-formation determined from our simulations qualitatively accord with the predictions of the generalized entropy theory of polymer glass-formation.

7. Influence of Cohesive Energy on Relaxation in a Model Glass-Forming Polymer Melt.

The wide range of chemical compositions exhibited by polymers enables the fabrication of materials having highly tunable cohesive energy strength χ, and many of the properties that make polymers so useful as structural and responsive materials in both manufacturing and living systems derive from the variability of this basic property. The design and characterization of polymer materials then inevitably leads to a consideration of how ϙ impacts the thermodynamic and relaxation properties of polymer liquids. Our prior paper uses molecular dynamics simulations of a model coarse-grained polymer melt to systematically investigate the dependence of commonly measured thermodynamic properties on χ, while the present work focuses on the relaxation dynamics of the same molecular model. After demonstrating, as expected, that χ greatly influences the segmental relaxation time, we obtain a universal reduction of all our data for relaxation in terms of an activated transport model in which the activation free energy is increased from its high temperature value by a factor precisely determined by the average extent of the cooperative motion of monomers in the polymer liquid. This data reduction is consistent with the recently developed string model of glass-formation, as well as with the assumptions of the generalized entropy theory of glass-formation derived from a combination of the classical Adam-Gibbs model with a statistical mechanical model of polymer melts. In addition to providing firm observational data facilitating the development of improved theories of polymer glass-formation, our results also yield insights into the molecular origin of particular thermodynamic and relaxation properties of polymers, insights that should aid in the design of polymer materials.

8. Two Glass Transitions in Miscible Polymer Blends?

In contrast to mixtures of two small molecule fluids, miscible binary polymer blends often exhibit two structural relaxation times and two glass transition temperatures. Qualitative explanations postulate phenomenological models of local concentration enhancements due to chain connectivity in ideal, fully miscible systems. We develop a quantitative theory that explains these observations for partially miscible polymer blends. The theory is a synthesis of the lattice cluster theory of blend thermodynamics, the generalized entropy theory for glass-formation in polymer materials, and the Kirkwood-Buff theory for concentration fluctuations in binary mixtures.

9. The Meaning of the "Universal" WLF Parameters of Glass-forming Polymer Liquids.

Although the Williams-Landell-Ferry (WLF) equation for the segmental relaxation time τ(T) of glass-forming materials is one of most commonly encountered relations in polymer physics, its molecular basis is not well understood. The WLF equation is often claimed to be equivalent to the Vogel-Fulcher-Tammann (VFT) equation, even though the WLF expression for τ(T) contains no explicit dependence on the fragility parameter D of the VFT equation, while the VFT equation lacks any explicit reference to the glass transition temperature T_g, the traditionally chosen reference temperature in the WLF equation. The observed approximate universality of the WLF parameters $C_{(g)1}$ and $C_{(g)2}$ implies that τ(T) depends only on $T-T_g$, a conclusion that seems difficult to reconcile with the VFT equation where the fragility parameter D largely governs the magnitude of _ (T). The current paper addresses these apparent inconsistencies by first evaluating the macroscopic WLF parameters $C_{(g)1}$ and $C_{(g)2}$ from the generalized entropy theory (GET) of glass-formation and then by determining the dependence of $C_{(g)1}$ and $C_{(g)2}$ on the microscopic molecular parameters (including the strength of the cohesive molecular interactions and the degree of chain stiffness) and on the molar mass of the polymer. Attention in these calculations is restricted to the temperature range ($T_g < T < T_g + 100$ K), where both the WLF and VFT equations apply.

10. Generalized Entropy Theory of Glass Formation in Polymer Melts with Specific Interactions.

Chemical structure has been long recognized to greatly influence polymer glass formation, but a general molecular theory that predicts how chemical structure determines the properties of glass-forming polymers has been slow to develop. While the generalized entropy theory (GET) explains the influence of various molecular details on polymer glass formation, the application of the GET has heretofore been limited to the use of the simplest polymer model in which all united atom groups within the monomers of a species interact with a common monomer averaged van der Waals energy. However, energetic heterogeneities are ubiquitous within the monomers of real polymers, and their implications for polymer glass formation remain to be investigated theoretically. This paper uses an extension of the GET to explore the influence of energetic heterogeneities within monomers upon the nature of polymer glass formation. This extension of the GET is achieved by combining the Adam-Gibbs theory relating the structural relaxation time to the configurational entropy with a recent significant extension of the lattice cluster theory for polymer melts with specific interactions, in particular, for melts where three distinct van der Waals interaction energies are required to describe the energetic heterogeneities within monomers. The present paper focuses on establishing general trends for the variation of characteristic properties of glass formation, such as the isobaric fragility parameter m_P and the glass transition temperature T_g, with molecular details, such as the specific interactions and chain stiffness. Our computations confirm that the previously used model with monomer averaged interactions correctly captures general trends in the variation of m_P and T_g with various molecular parameters. More importantly, adjustment of the energetic heterogeneities within monomers alone are shown to provide an efficient mechanism for tailoring the properties of glass-forming polymers. The variations of polymer properties along iso-fragility and iso-T_g lines are illustrated as important design tools for exhibiting the combined influence of specific interactions and chain stiffness.

11. Influence of Cohesive Energy and Chain Stiffness on Polymer Glass Formation.

The generalized entropy theory is applied to assess the joint influence of the microscopic cohesive energy and chain stiffness on glass formation in polymer melts using a minimal model containing a single bending energy and a single (monomer averaged) nearest neighbor van der Waals energy. The analysis focuses on the combined impact of the microscopic cohesive energy and chain stiffness on the magnitudes of the isobaric fragility parameter m_P and the glass transition temperature Tg. The computations imply that polymers with rigid structures and weak nearest neighbor interactions are the most fragile, while Tg becomes larger when the chains are stiffer and/or nearest neighbor interactions are stronger. Two simple fitting formulas summarize the computations describing the dependence of m_P and Tg on the microscopic cohesive and bending energies. The consideration of the combined influence of the microscopic cohesive and bending energies leads to the identification of some important design concepts, such as iso-fragility and iso-Tg lines, where, for instance, iso-fragility lines are contours with constant m_P but variable Tg. Several thermodynamic properties are found to remain invariant along the iso-fragility lines, while no special characteristics are detected along the iso-Tg lines. Our analysis supports the widely held view that fragility provides more fundamental insight for the description of glass formation than Tg.

III. Basic theory of glass-formation

12. Towards First Principles Theory of Relaxation in Supercooled Liquids Formulated in Terms of Cooperative Motion.

A general theory of the long time, low temperature dynamics of glass-forming fluids remains elusive despite the almost 20 years since the famous pronouncement by the Nobel Laureate P. W. Anderson, "The deepest and most interesting unsolved problem in solid state theory is probably the theory of the nature of glass and the glass transition." While recent work indicates that Adam-Gibbs theory (AGT) provides a framework for computing the structural relaxation time of supercooled fluids and for analyzing the properties of the cooperatively rearranging dynamical strings observed in low temperature molecular dynamics simulations, the heuristic nature of AGT has impeded general acceptance due to the lack of a first principles derivation. This deficiency is rectified here by a statistical mechanical derivation of AGT that uses transition state theory and the assumption that the transition state is composed of elementary excitations of a string-like form. The strings are assumed to form in equilibrium with the mobile particles in the fluid. Hence, transition state theory requires the strings to be in mutual equilibrium and thus have the size distribution of a self-assembling system in accord with the simulations and analyses of Douglas and coworkers. The average relaxation rate is computed as a grand canonical ensemble average over all string sizes, and use of the previously determined relation between configurational entropy and the average cluster size in several model equilibrium self-associating systems produces the AGT expression in a manner enabling further extensions and more fundamental tests of the assumptions.

13. Entropy Theory of Polymer Glass-Formation in Variable Spatial Dimension. The importance of packing frustration is broadly appreciated to be an important aspect of glass-formation. Recently, great interest has focused on using spatial dimensionality d as a theoretical tool for exploring this and other aspects of glass-forming liquids. We approach this problem analytically based on the generalized entropy theory (GET), a synthesis of the Adam-Gibbs model with direct computation of the configurational entropy s_c of polymer fluids using an established statistical mechanical model. This predictive model for the segmental relaxation time τ_α of polymeric glass-forming liquids is investigated for $d > 2$ where a fluid state with finite viscosity exists in the thermodynamic limit. As a primary result, we find that the structural relaxation time τ_α in the fluid state becomes asymptotically Arrhenius in the limit of infinite d, and upon cooling, we find a first-order "glass-transition" into an amorphous state of finite positive residual configurational entropy. In this low temperature thermodynamic "glass" state with astronomical relaxation times, the activation energy for Arrhenius relaxation is formally much larger than its high temperature counterpart, but the physical significance of this quantity is unclear given the long relaxation times involved. The GET also predicts the variation with d of measures of fragility and of the characteristic temperatures of glass-formation demarking the onset T_A, middle T_c and end T_0 of the broad glass transition. The "ideal" glass transition temperature, at which the configurational entropy s_c formally vanishes in the GET, fails to exist above a critical dimensionality d_c that lies

for the polymer model we study in the vicinity of d = 8. A generalization of the Williams-Landel-Ferry expression for τ_α is introduced based on the thermodynamically well-defined crossover temperature T_c (i.e., inflection point in s_cT) rather than the glass transition temperature T_g. The ultimate trend indicated is rather obvious physically, namely, as d becomes large, fluctuation effects associated with packing fluctuations diminish (consistent with the "decorrelation principle" emphasized by Torquato and Stillinger) so that Arrhenius relaxation applies over the entire fluid range. Direct computations of the isothermal compressibility and the thermal expansion coefficient, taken to be physical measures of packing frustration, indicate that these fluid properties quantitatively correlate with the observed d dependence of the fragility of glass-formation for the family of molecular models investigated. On the other hand, our analysis reveals that both fragility and T_g are not really fundamental measures of the dynamics of glass-formation given the sensitivity of Taking the lessons of our calculations in d dimensions back to the physically important case of d = 3, we deduce apparently universal relationships between T_0/T_A, a measure of the "breadth" of the glass-formation and thus transition "cooperativity" (abandoning the concept of fragility in everything but the spirit of this concept as a measure of the "sharpness" of the transition), and both the isothermal compressibility and thermal expansion coefficient of polymer melts at T_g. These relationships apply independently of chain stiffness, cohesive interaction energy, and chain length for the family of polymer models studied, although the universality of these relationships requires further tests for polymers with different monomer structures. Further studies are also needed to establish fundamental metrologies of the cooperativity of glass-formation based on theoretical considerations rather than empirical correlation. Such concepts should be useful in engineering the properties of polymer materials.

IV. Polarization Effects in Polyelectrolytes and Granular Materials

In order to provide optimal training of the members of my group, my group seminars have been combined with those of Juan de Pablo (ANL and University of Chicago) where I have learned about the interest in understanding the influence of polarization on properties of systems containing polyelectrolytes, electrolytic properties involving electrostatic double layers, and the influence of polarization on the processing of granular particles (including avalanches).

14. Perturbative Many-body Expansion for Electrostatic Energy and Field for System of Polarizable Charged Spherical Ions in a Dielectric Medium.

An analytical solution for the electrostatic energy and potential for a system of charged, polarizable spheres in a dielectric medium is developed from a multiple scattering expansion that is equivalent to a formal solution to Poisson's equation for the system. The leading contributions emerge in the form of effective two-, three-, and four-body interactions that are explicit analytical functions of the sphere positions, charges, and internal dielectric constants and the external dielectric constant, thereby also enabling analytical computation of the electrostatic forces on the ions. Tests of successive terms demonstrate their rapid convergence. Similar methods can be used to evaluate higher order contributions and he expansion for the electrostatic field. The results will prove far more efficient for MD and MC simulations than current approximate methods that require the computation of surface polarization charge distributions.

15. A Theory of Interactions between Polarizable Dielectric Spheres.

Surface charging or polarization can strongly affect the nature of interactions between charged dielectric objects, particularly when sharp dielectric discontinuities are involved. By relying on a generalized image method, we derive an analytical, perturbative theory of the polarization and the interactions between charged particles in many-body systems. The validity and accuracy of the theory are established by comparing its predictions to full-blown numerical solutions. The importance of polarizability is then demonstrated for clusters of dielectric spheres, as well as a periodic crystal of charged dielectric spheres arranged into a NaCl-type lattice. The analytical framework for understanding the consequences of polarization will enable molecular simulations of large systems of polarizable particles.

16. Image Method for Induced Surface Charge from Many-body System of Dielectric Spheres.

Charged dielectric spheres embedded in a dielectric medium provide the simplest model for many-body systems of polarizable ions and charged colloidal particles. We provide a multiple scattering formulation for the total electrostatic energy for such a system and demonstrate that the polarization energy can be rapidly evaluated by an image method that generalizes the image methods for conducting spheres. Individual contributions to the total electrostatic energy are ordered according to the number of polarized surfaces involved, and each additional surface polarization reduces the energy by a factor of $(a/R)^3\,\epsilon$, where a is the sphere radius, R the average inter-sphere separation, and ϵ the relevant dielectric mismatch at the interface. Explicit expressions are provided for both the energy and the forces acting on individual spheres, which can be readily implemented in Monte Carlo and molecular dynamics simulations of polarizable charged spheres, thereby avoiding costly computational techniques that introduce a surface charge distribution that requires numerical solution.

List of publications acknowledging DE-SC0008631

Title	Authors	Contributor Organization(s)	Report/Product Number	Keywords
Thermodynamic scaling of dynamics in polymer melts: Predictions from the generalized entropy theory	Wen-Sheng Xu, Karl F. Freed	University of Chicago	DOE-UCHICAGO-0008631-02 DOI 10.1063/1.4809991	glass formation, free volume, entropic barriers, enthalpic barriers, thermodynamic scaling
Concentration fluctuations in miscible polymer blends: Influence of temperature and chain rigidity	Jacek Dudowicz, Karl F. Freed, and Jack F. Douglas	University of Chicago, National Institute of Standards and Technology	DOE-UCHICAGO-0008631-03 DOI 10.1063/1.4875345	polymer blends, miscibility, concentration fluctuations, glassy dynamics, phase transitions
Two Glass Transitions in Miscible Polymer Blends?	Jacek Dudowicz, Jack F. Douglas, and Karl F. Freed	University of Chicago, National Institute of Standards and Technology	DOE-UCHICAGO-0008631-04 DOI 10.1063/1.4884123	polymer blends, miscibility, concentration fluctuations, glassy dynamics, phase transitions
Perturbative Many-body Expansion for Electrostatic Energy and Field For System of Polarizable Charged Spherical Ions in a Dielectric Medium	Karl F. Freed	University of Chicago	DOE-UCHICAGO-0008631-05 DOI 10.1063/1.4890077	electrostatic polarization, aggregation, multiple scattering theory, surface charges
Lattice cluster theory for polymer melts with specific interactions	Wen-Sheng Xu, Karl F. Freed	University of Chicago	DOE-UCHICAGO-0008631-06 DOI 10.1063/1.4890959	specific interactions, polymer melts, glass=formation
Influence of Cohesive Energy and Chain Stiffness on Polymer Glass Formation	Wen-Sheng Xu, Karl F. Freed	University of Chicago	DOE-UCHICAGO-0008631-07 DOI 10.1021/ma501581u	glass-formation, cohesive energy, chain stiffness, glass transition temperature, fragility parameter

Towards first principles theory of relaxation in supercooled liquids formulated in terms of cooperative motion	Karl F. Freed	University of Chicago	DOE-UCHICAGO-0008631-08 DOI 10.1063/1.4897973	Adam-Gibbs theory, generalized entropy theory, transition state theory, grand canonical ensemble, structural relaxation
Advances in the generalized entropy theory of glass-formation in polymer melts	Jacek Dudowicz, Jack F. Douglas, and Karl F. Freed	University of Chicago, National Institute of Standards and Technology	DOE-UCHICAGO-0008631-09 DOI 10.1063/1.4903842	generalized entropy, polymer melts, glass formation, structural relaxation time
The meaning of the “universal” WLF parameters of glass-forming polymer liquids	Jacek Dudowicz, Jack F. Douglas, and Karl F. Freed	University of Chicago, National Institute of Standards and Technology	DOE-UCHICAGO-0008631-10 DOI 10.1063/1.4905216	mechanical response, dynamic moduli, time-temperature superposition, dielectric response
Generalized Entropy Theory of Glass Formation in Polymer Melts with Specific Interactions	Wen-Sheng Xu, Karl F. Freed	University of Chicago	DOE-UCHICAGO-0008631-11 DOI 10.1021/acs.macromol.5b00144	specific interactions, polymer melts, glass, formation
The Simplified Generalized Entropy Theory of Glass-formation in Polymer Melts	Karl F. Freed	University of Chicago	DOE-UCHICAGO-0008631-12 DOI 10.1063/1.4927766	generalized entropy theory, glass formation, monomer molecular structure
Entropy Theory of Polymer Glass-Formation in Variable Spatial Dimension	Wen-Sheng Xu, Jack F. Douglas, Karl F. Freed	University of Chicago, National Institute of Standards and Technology	DOE-UCHICAGO-0008631-13 DOI 10.1002/9781119290971.ch6	generalized entropy theory, glass formation, polymer melts, glass transition temperature, fragility parameter, polymer packing

A theory of interactions between polarizable dielectric spheres	Jian Qin, Jiyuan Li, Victor Lee, Heinrich Jaeger, Juan J. de Pablo, Karl F. Freed	University of Chicago, Argonne National Laboratory, Stanford University,	DOE-UCHICAGO-0008631-14 DOI 10.1016/j.jcis.2016.02.033	electrostatic polarization, aggregation, multiple scattering theory, comparison with experiments for granular materials, surface charges
Image method for induced surface charge from many-body system of dielectric spheres	Jian Qin, Juan J. de Pablo, and Karl F. Freed	Stanford University, University of Chicago, Argonne National Laboratory	DOE-UCHICAGO-0008631-15 DOI 10.1063/1.4962832	electrostatic polarization, aggregation, multiple scattering theory, image method for spheres, surface charges
Influence of Cohesive Energy on the Thermodynamic Properties of a Model Glass-Forming Polymer Melt	Wen-Sheng Xu, Jack F. Douglas, Karl F. Freed	University of Chicago, National Institute of Standards and Technology	DOE-UCHICAGO-0008631-16 DOI 10.1021/acs.macromol.6b01503	thermodynamical properties, polymer, melts, glasses, molecular dynamics simulations, generalized entropy theory
Influence of Cohesive Energy on Relaxation in a Model Glass-Forming Polymer Melt	Wen-Sheng Xu, Jack F. Douglas, Karl F. Freed	University of Chicago, National Institute of Standards and Technology	DOE-UCHICAGO-0008631-17 DOI 10.1021/acs.macromol.6b01504	image method, electrostatics, induced charge, aggregation, Poisson’s equation