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Fluctuation theory of phase behavior in polymer liquid crystalline systems/

Michael S. Graff

University of Massachusetts Amherst

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FLUCTUATION THEORY OF PHASE BEHAVIOR IN POLYMER LIQUID CRYSTALLINE SYSTEMS

A Dissertation Presented
by
MICHAEL S. GRAFF

Submitted to the Graduate School of the University of Massachusetts in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

February 1992

Department of Polymer Science and Engineering
FLUCTUATION THEORY OF PHASE BEHAVIOR IN POLYMER LIQUID CRYSTALLINE SYSTEMS

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MICHAEL S. GRAFF

Approved as to style and content by:

M. Muthukumar, Chair

William J. MacKnight, Member

Scott M. Barton, Member

Jonathan L. Machta, Member

William J. MacKnight, Department Head
Polymer Science and Engineering Department
DEDICATION

This dissertation is dedicated to my father and the spirit of scientific curiosity that he instilled in me at an early age. Our conversations, recorded in pencil on the backs of a thousand lost envelopes, are still preserved in fond memories. Hopefully, all of my scientific pursuits will be motivated by desires that are consistent with the essence of these memories.
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I would like to thank Akzo Chemicals Incorporated for providing this research opportunity through their funding. Scott Cohen is credited for his indispensable assistance with some of the more theoretical aspects of this research. I appreciate several others connected with the Akzo project who have provided fresh perspectives as well as assistance with the equipment used in this research.

I would like to thank friends in the department and my research group for their friendship and assistance. Special mention goes to a few particularly supportive individuals with whom I have had considerable interaction. Specifically, I would like to thank Phil and Lee Anne White, Mahesh Kotnis, Devesh Srivastava, Molly Shoichet, Michele Maden, Todd Mansfield, Jeff Simpson, and Scott Cohen.

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significant ways. During periods of extreme difficulty, their help, in spite of the geographic distance, has many times made all the difference.
ABSTRACT

A THEORY OF BLENDS FOR LIQUID CRYSTALLINE AND FLEXIBLE COIL POLYMERS

FEBRUARY 1992

MICHAEL S. GRAFF, B.S., UNIVERSITY OF UTAH
M.S., UNIVERSITY OF MASSACHUSETTS
Ph.D., UNIVERSITY OF MASSACHUSETTS

Directed by: Professor M. Muthukumar and Professor William J. MacKnight

This research was motivated by theoretical and experimental objectives regarding blends of thermotropic liquid crystalline polymers and flexible coil polymers with specific application to in situ fiber-reinforced composites. The primary aim has been the prediction of the phase behavior of blends and diblock copolymers containing rigid (liquid crystalline) species. The objective was to first derive a free energy expression that went beyond the mean field theories by taking composition fluctuations into account. Computational procedures were then developed for the evaluation of the free energy.

The analytical derivation and the computational procedures provide the means for predicting the phase behavior of blends and diblocks as a function of molecular weight. The connectivity of the diblock molecule is shown to be responsible for a shifting of the isotropic-nematic transition in composition and a lowering of the critical \( \chi \) value. A critical examination of the theory is difficult due to the lack of experimental data required for comparison.

A secondary aim was to resolve some specific questions about a novel blend system that shows good prospects as an in situ composite. Investigation concerned the effect of blend composition on crystallization, the nucleating properties of the liquid crystalline component relative to those of more common nucleating agents, and the degree of miscibility between the blend components. The liquid crystalline component was shown to
decrease crystallinity with increasing concentration. Its nucleation properties were similar to those of more common nucleating agents. No evidence of immiscibility was found in the blend system.
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CHAPTER 1
INTRODUCTION

System of Investigation

Thermotropic liquid crystalline polymers form a unique class of materials that are of
great interest from both a theoretical and technological perspective. These materials are
particularly interesting in that they can exist in thermodynamically stable states that possess
a combination of physical properties that is neither characteristic of solids nor liquids. As
suggested by their name, thermotropic liquid crystalline polymers (referred to as TLCPs
throughout the rest of this paper), are characterized by a state that can flow like a liquid yet
maintain a relatively high degree of long-ranged order. Upon cooling from the melt, the
liquid material undergoes a first-order phase transition into the liquid-crystalline state.
Further cooling brings on a second transition into a true solid state.

Thermotropic Liquid Crystalline Polymers

A universal structural characteristic of TLCPs is molecular anisotropy. This
molecular anisotropy is most frequently a result of the incorporation of rigid mesogenic
groups into either the main chain or side groups of the polymer. Another class of TLCPs
owe their molecular anisotropy to the existence of a rigid and highly stable conformational
isomer. While being a necessary requirement for liquid crystalline behavior, molecular
anisotropy is not a sufficient requirement; many rigid molecules exist that do not show
liquid crystalline behavior.

TLCPs show three general types of structure on the level of molecular organization.
The least ordered of these is the nematic state. It is characterized by a lack of long-ranged
order in the position of the centers of mass of the molecules, and an alignment of the
molecules in the general direction of a common orientational axis. There is complete
rotational symmetry about this common axis. Smectic states are similar to the nematic
except the centers of mass of the molecules are ordered in one dimension and form layered structures of various types. The cholesteric state is the third type and it can be described as stacked nematic planes where the common orientational axis for each plane rotates as a function of position in the direction normal to the planes. The cholesteric state is the third type and it can be described as stacked nematic planes where the common orientational axis for each plane rotates as a function of position in the direction normal to the planes.4

Because of their unusual optical properties and sensitivity to external fields, TLCPs have found important application in the area of display systems. They also possess unique rheological properties, as a result of their ordered yet fluid character, and have been used as processing agents and materials for mechanical reinforcement.5 This project deals with thermodynamic and experimental aspects of using TLCPs as mechanical reinforcing agents.

**In situ** Fiber Reinforced Composites

The concept of reinforcing a material by dispersing a stronger and stiffer material into it is fundamental to composites technology. Conventionally, a molten or liquid matrix phase is compounded with a macroscopic fibrous phase material (chopped glass, carbon fibers, etc.). This produces a highly viscous mixture which is then processed. Upon processing, the fibers are oriented and the matrix phase becomes solid forming a fiber-reinforced composite. The objective is to appropriately choose materials and processing methods that allow for the synergistic combination of desirable properties. In the case of fiber reinforced composites there is a complementary combination of properties in that the fibrous phase provides strength and stiffness and the matrix phase provides toughness.

From a processing standpoint, there are many difficulties involved. Typically, the mixture is highly viscous which makes compounding difficult. The situation can be improved by using elevated temperatures and pressures; however, this can cause problems with thermal degradation. Additionally, the fibrous phase is typically very abrasive resulting in wear and drift of precision processing equipment.6

This situation is significantly improved if the reinforcing species is not actually present at the beginning of the processing, but comes into existence during the processing. This is the objective in **in situ** fiber reinforced composites. A blend of a thermoplastic
polymer with a TLCP is an example of a system with this sort of capability. Such a blend has a melt viscosity one or two orders of magnitude lower than the neat thermoplastic homopolymer.\textsuperscript{7,8} Subsequently, the compounding step is done much more easily and without the complications listed above. As the blend cools in a shear flow, the oriented, phase-separated system forms a morphology that macroscopically resembles and mechanically behaves like a conventional fiber-reinforced composite.\textsuperscript{9}

**Phase Behavior of Systems Containing Rigid Polymers**

The equilibrium phase behavior of a system indicates the most stable morphological and orientational state of a system as a function of the component molecular weights, composition, and temperature. Thermodynamics alone is an important part of an otherwise incomplete picture. This is because of the fact that most systems commonly encountered are not at equilibrium and their states are, to varying degrees, kinetically preserved. Understanding the phase behavior is of fundamental importance because it identifies the direction of the natural driving forces controlling the physical state of the system. Therefore, thermodynamics allows the representation of the natural constraints and tendencies of a system expressed in terms of the parameters within which one must work when scientifically engineering materials. Thermodynamics provides a powerful tool in discriminating between the experimentally feasible and the unfeasible. Developing statistical thermodynamic models that relate the molecular and macroscopic realms increases predictive abilities and suggests new avenues of approach towards solving technological problems.

**Technological Aspects**

Technologically speaking, the primary reason for wanting to understand the phase behavior of polymer blend components is not necessarily to produce miscible blends. More generally, the focus is on devising methods for polymer blend modification in order to obtain desirable physical and mechanical properties. Miscibility provides a simpler means to this end than alternative methods of compatibilizing.\textsuperscript{10} An ideal degree of
miscibility depends upon the desired properties of the final material. In the case of in situ fiber reinforced composites, some degree of immiscibility is expected in order to form a phase separated system; however, some degree of compatibility is required in order to have good interfacial adhesion and a high degree of dispersion of the fibrous phase within the matrix phase. On the other hand, a molecular composite, where the blending occurs on the molecular level, requires a very high degree of miscibility between the two components.

Another technological consideration is cost effectiveness. With regard to blends of polyester thermoplastics and novel thermotropic liquid crystalline polymers, it is desirable to achieve a considerable degree of enhancement of mechanical properties with a minimum of liquid crystalline component. Blends containing greater than 20% by weight of the TLCP would probably not offer a practical choice due to the cost effectiveness constraint.

Experimental Aspects

Unlike the case of solutions of rigid polymers, there is a paucity of published experimental investigations concerning the phase behavior of systems composed of blends of rigid and flexible polymers. Studies have investigated the effect of flexible polymers on the isotropic-nematic transition in a low molecular weight liquid crystalline system\textsuperscript{11,12} and the thermal behavior of blends of two polymeric liquid crystalline polymers.\textsuperscript{13} However, analogous studies have not been performed using blends of polymeric liquid crystals and flexible coil polymers.

There are a number of experimental difficulties that beset this kind of investigation. One problem is the strong dependence of experimental observation upon the processing technique used to produce the blend. Since TLCPs often have melt viscosities that are two orders of magnitude lower than their flexible coil counterparts, thorough mechanical blending is often difficult. Other difficulties such as transesterification reactions between polyester blend components, which chemically alter the materials, can occur during the high processing temperatures.
A natural way of circumventing these difficulties is by solution blending. In this case the blend components are dissolved in a common solvent at relatively low temperatures. However, by adding a third component, the solvent, the system becomes ternary. There have been several experimental investigations of ternary systems composed of mixtures of rigid polymers, flexible polymers, and a common solvent.\textsuperscript{14,15,16} All of these theories show good agreement with the Flory lattice theory for a ternary system.\textsuperscript{17}

Real systems are generally more complex than the idealistic models used to predict their behavior. Experimental investigation is made more difficult by the complexity involved in preferentially observing the essential equilibrium phase behavior over other accompanying phenomena like phase separation kinetics, semi-crystallinity, polydispersity, and interfacial properties. These are examples of problems that need to be addressed in proposing a model system that would be useful for experimentally investigating the thermodynamic behavior of blends of rigid and flexible polymers.

**Theoretical Aspects**

There are a number of different structural possibilities for systems containing rigid and flexible segments. Each type of structure is characterized by special theoretical considerations when predicting phase behavior. The structures of relevance to this research will now be presented.

**Athermal Gas of Rigid Polymers.** The phase behavior of systems that undergo isotropic-nematic transitions (orientationally disordered to ordered) offer rich problems in statistical thermodynamics. The phase behavior of the most simple system, an athermal gas of rods, is analogous in many ways to alignment in spin systems.\textsuperscript{18} In this case the transition is a function only of the concentration of the rods.

**Solutions and Blends with Rigid Polymers.** A more complex problem arises when a second component is added to the system. In this case a phase separation transition is superimposed onto the isotropic-nematic transition. The second component, either a solvent or a flexible coil polymer, will have an enthalpic interaction with the rods as well as
influencing the configurational and orientational entropy of the system. In this case the relative sizes of the two components, the interaction strength (which is a function of temperature), as well as the concentrations of the components are important in characterizing the phase behavior of the system.

The interaction strength is generally represented by the $\chi$ parameter. This parameter is a function of three different types of temperature dependent interactions: dispersion forces, free volume, and specific interactions. Phenomenologically, the $\chi$ interaction parameter has been shown to consist of both enthalpic as well as entropic terms. Generally, its temperature dependence is represented as

$$\chi = \frac{A}{T} + B.$$  

A negative $\chi$ value indicates a tendency for two polymer components to mix; whereas, a positive value generally indicates a tendency towards demixing.

Systems that undergo phase separation can be characterized by two general different types of phase behavior. The first type corresponds to a situation where the system is miscible at high temperatures and then phase separates upon cooling. A system displaying this type of behavior has an upper critical solution temperature (UCST). The second general type of phase behavior corresponds to the reverse situation where a system is immiscible at high temperatures and then forms a single homogeneous phase at low temperatures. A system displaying this type of behavior has a lower critical solution temperature (LCST). It is possible for a system to show both a UCST as well as an LCST.

The most commonly encountered type of phase behavior in polymer blends is the LCST type. This type of behavior occurs when free volume effects and specific interactions dominate over the dispersion forces in their relative contribution to the $\chi$ parameter. In systems that show both a UCST and an LCST, the dispersion forces and
free volume contributions to $\chi$ generally dominate over specific interaction contribution.

Finally, in systems showing UCST type behavior the dispersion forces are the dominant interactions influencing the $\chi$ parameter. In this research systems showing the latter type of behavior will be investigated where the dispersion interactions dominate.

Phase separation in a two component system is characterized by a miscibility gap in a plot of the free energy as a function of the composition as schematically represented in Figure 1.1. The free energy verses composition curve is strongly temperature dependent. A homogeneous system having a free energy in an unstable range of composition will spontaneously undergo phase separation in order to minimize its free energy. As shown in Figure 1.1, the chemical potential of the two components in a particular phase is given by the intercepts between a line drawn tangent to the free energy curve and the vertical lines corresponding to the pure components ($\phi=0$ and $\phi=1$). A component will selectively migrate from a phase of high chemical potential to one of a lower chemical potential. This will occur until the chemical potentials of the two components in each of the two phases are equal. At this point the system has reached equilibrium. Graphically, the equilibrium compositions are obtained by finding the line that forms a common tangent between the two parts of the free energy curve. These two equilibrium compositions can be plotted onto a phase diagram as shown in Figure 1.1. The whole phase diagram can be mapped out by repeating this procedure at different temperatures.

The equilibrium compositions form a curve on a phase diagram known as the binodal. A second curve of interest denotes the region of instability in the free energy verses composition diagram. This curve is called the spinodal and it can be obtained by mapping the inflexion points from the free energy curve onto the phase diagram. The region within the spinodal line corresponds to thermodynamically unstable states that will spontaneously phase separate by a spinodal decomposition mechanism. The area between the spinodal and the binodal corresponds to a metastable region that requires an activation energy in order to phase separate by a nucleation and growth mechanism.
**Diblocks with Rigid Polymer Segments.** Another interesting problem, giving rise to even more complex possibilities than a two component blend system, is to consider a diblock or multiblock copolymer composed of two chemically different polymer segments that are physically linked together. In this single component system there is a physical constraint preventing macroscopic phase separation between the two chemically different segments. However, for chemically incompatible segments, the free energy can be lowered by a spatial segregation of the different segments. This results in a microphase separated morphology. Figure 1.2 schematically depicts four different morphologies that might be expected for a diblock composed of flexible and rigid segments. The top two schematics correspond to microphase segregated morphologies, (a) being spherical and (b) being lamellar. The bottom two morphologies are homogeneous, (c) being isotropic and (d) being nematic.

Several important differences exist between this case and the case of a polymer blend. The length scales of the structures formed in the diblock are of the order of the radius of gyration of the polymer, as opposed to the macroscopic dimensions observed in blends. The thermodynamic behavior of diblocks is often represented by a phase diagram; however, the interpretation of the diagram is slightly different from that for a blend. Typically, the phase diagram for a diblock is represented as a function of $\chi$ plotted against the fraction of one of the components in the diblock molecule. This is in contrast with the blends case where $\chi$ is plotted against the volume fraction of components in the system. Additionally, the compositions in the microphase separated system can not be directly obtained from the phase diagram by the intersection points of a horizontal line in the two phase region with the binodal, as in the case of a two component blend. The parameters $\chi$ and $f$ locate a point on the diagram that indicates a particular morphology of the microphase segregated structure, schematically represented for a flexible diblock copolymer in Figure 1.3. The sharpness of the spatial composition profile in diblocks varies as a function of $\chi$. 
This is in contrast to equilibrium, phase separated blend systems where the composition of the interface is independent of $\chi$ and is assumed to be infinitely sharp.

The diblock system composed of two flexible polymers has been investigated by several authors; the theoretical highlights are outlined in Chapter 2. In this work a modification of this problem is considered where one of the polymer segments of the diblock copolymer is a rigid rod. The subtleties of this system become richer as orientational effects are added to the problem of predicting the phase behavior.

Problems with Early Theoretical Predictions

Although the various mean field theories have met with some success in predicting the phase behavior of some systems containing rigid polymers, they generally suffer from their implicit inability to take composition fluctuations into account. This inherent weakness of a mean field approach becomes even more of a limitation in the case of copolymer systems composed of rigid and flexible segments within the same polymer molecule. For example, mean field theories are unable to make distinctions between various choices of molecular architecture with respect to the sizes and sequencing of the rigid and flexible segments within a copolymer molecule.

Research Objectives

This research project has been funded by Akzo Chemical Company. It is a part of a collective research effort that involves several polymer science and engineering faculty, graduate, and post doctoral researchers. The overall objective of the collective research is to develop in situ polyester fiber-reinforced composites (both injection molded and melt spun fibers) based on novel thermotropic liquid crystalline polymers.

The objectives of this research have been two-fold. The primary objective was to derive a free energy expression describing solutions, blends, and diblock copolymers with rigid and flexible components and then to develop a computational scheme to evaluate the free energy to predict the phase behavior of each system. The thermodynamic theory of blends proposed should provide a theoretical link between the companion research areas in
the Akzo project by relating synthetic chemistry to processing. In the processing of blends it is useful to know the thermodynamic stability of the system as a function of composition of components and temperature. This information is provided by a theory of blends through a phase diagram. Two additional parameters that govern the phase behavior of a blend are the molecular weights of the components and the interaction parameter between the two components. These parameters are directly related to the endeavors of the synthetic chemist who must chemically engineer a system that will perform within constraints dictated by the desired degree of interactions and miscibility of the blend as well as the mechanical properties and interfacial adhesion in the final composite.

**Dissertation Outline with a Brief Summary of Results**

We have developed a model for the prediction of the phase behavior of various polymeric systems containing rigid segments. The model has been derived for a general system and in such a way as to account for composition fluctuations, something inherently neglected in the mean field theories.

This model has been used specifically to predict the phase behavior for a solution of rigid molecules, a blend of rigid and flexible molecules, and a diblock composed of combined rigid and flexible portions.

Chapter 2 outlines the present theoretical understanding of the phase separation and isotropic-nematic phase transitions in polymer systems with emphasis on those containing rigid segments. A distinction is made between the mean field theories, where composition fluctuations are neglected, and the theories where composition fluctuations are taken into account. The derivation of the general free energy expression used in this research is presented within the context of the existing theoretical framework.

A major portion of the research involved computational aspects of predicting the phase behavior of the various systems of interest. Chapter 3 describes the computational methods used to obtain predictions of phase behavior from the derived free energy expression. This topic is introduced by a discussion of the computational challenges.
computational scheme is presented that outlines the step-wise procedure developed for predicting the phase diagram for a particular system. A description of the numerical methods used is also included in this chapter.

In Chapter 4 the results are presented and discussed in the form of phase diagrams for various systems as a function of molecular weight. The systems that are investigated are solutions of rod-like molecules, blends of rods and flexible coils, and diblock copolymers with rigid segments. The effect of composition fluctuations could not be included for systems with very low molecular weight components. They were observed to influence the phase diagram in a blend of rigid and flexible molecules composed of 50 segments each. The molecular weight effects are pointed out in both the blend and diblock systems. A comparison between the blend and diblock systems allows the investigation of the effects arising from connectivity between the rigid and flexible segments in the diblock. The connectivity appears to be responsible for a shifting of the isotropic-nematic transition in composition and a lowering of the critical $\chi$ value.

The conclusions and suggestions for future work are presented in Chapter 5. The future work portion of this section deals primarily with the extension of our theoretical model to the multiblock copolymer composed of rigid and flexible segments. Issues of interest in future models concern the determination of composition profiles and morphologies for block copolymer systems with rigid species.

In addition to the theoretical work, experiments were also performed on a blend system containing a liquid crystalline multiblock copolymer. The blend system under investigation has prospects for use as in a fiber reinforced composite. The experimental objectives concerned the effect of blend composition on degree of crystallinity, the nucleation properties of the TLCP relative to other nucleating agents, and the extent of miscibility between the blend components. The experimental methods, results, and conclusions are presented in Chapter 6.
The appendices comprise the final portion of the dissertation. Appendix A presents a derivation of two of the free energy terms used in this model which were previously derived by Onsager. The remaining four appendices (B through E) contain representative computer programs written to compute the phase diagrams for the various systems of interest. An effort has been made to make the computer code understandable through the use of comment statements; however, several important points related to the general strategies of the computation of phase diagrams will be discussed in Chapter 3 in conjunction with the computational methods.
Figure 1.1

Free energy verses composition diagram for a polymer blend with a miscibility gap, showing a mapping of important features onto the phase diagram.
Figure 1.2
Possible microphase separated morphologies of a diblock copolymer with rigid segments
Figure 1.3

Schematic of phase diagram for a diblock copolymer showing lamellar, cylindrical, and spherical microphase morphologies.
References

CHAPTER 2
THEORY

Molecular Theories of Two-Component Systems Containing Rigid Molecules

The molecular theories of liquid crystals, those that address the statistical mechanical details of particle interactions and correlations, fall into three general categories. The various theories are summarized in a review article by Gelbart.1

A Survey of Molecular Theories

The common feature for all of the molecular theories is the driving force towards an isotropic system. This driving force is considered to originate from the orientational entropy of the rods. There are more orientational complexions for a single rod that is not constrained to orient in a particular direction as schematically represented in Figure 2.1. This figure shows two cases of rods. Both of them have free rotation about the azimuthal angle \( \phi \). However, the polar angle \( \theta \) of rod in case (a) is constrained to an angle less than \( \pi/2 \); whereas, this same angle is not constrained in case (b). The orientational complexions are proportional to the shaded surface areas marked in the figure.

Obviously, if there is to be an isotropic-nematic transition, a second driving force favoring the formation of the nematic state is required. It is the nature of this driving force that distinguishes the various theories. Long-ranged orientational attractions were featured in the model developed by Maier and Saupe as the driving force responsible for the orientation of the rods.2 The potential experienced by a single rod was mean field averaged to give an effective one-body attraction potential.

In contrast, several theories propose that the hard body repulsions are the dominant driving force for ordering. This driving force is entirely entropic in nature and arises from the fact that in a dense system of rods the number of packing complexions increases as the excluded volume decreases.3 The excluded volume is schematically illustrated in Figure 2.2. This figure shows two space filling rods of length \( L \) and thickness \( b \). The darkened
center of mass of one of the rods traces out a parrallelepiped region in space within which it may not enter due to steric interaction. The excluded volume potential is proportional to the volume of this parrallelepiped region. This volume, in turn, is a function of the angle $\theta$ between the two rods and is, therefore, a function of the distribution of orientation and it is minimized as the rods become perfectly aligned. This approach was taken by Onsager$^4$ who computed the second virial coefficient for a system of rods in free space.

Lattice theories by Flory$^5$ are based on similar assumptions concerning the driving force for the transition. In later theories both attractive forces and steric interactions were featured. This van der Waals approach was developed by Alben,$^6$ Flory and Ronca,$^7$ and Warner$^8$ using lattice theories. Several of the representative molecular theories will now be outlined in greater detail to highlight some of their important aspects pertaining to the proposed research.

**Gas of Rods**

The earliest statistical mechanical treatment of a system of rods was done by Onsager.$^9$ His system consisted of an athermal gas of rods or a solution of rods in a noninteracting solvent. A brief derivation is included in the appendix because it has direct relevance to the free energy expression used in our approach.

The free energy has two terms and can be represented by the equation

$$A[f(u)] = A_0[f(u)] + A_1[f(u)].$$

The $A_0$ term, representing the orientational entropy, favors the randomly oriented isotropic state. The $A_1$ term, on the other hand, represents the tendency for a concentrated system of rods to align in order to minimize their excluded volume.

Both free energy terms are dependent upon the orientational distribution of the rods which is represented by a generic distribution function that is characterized by a single orientational order parameter, $\alpha$. 

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\[ f(u) = \frac{\alpha}{4\pi \sinh(\alpha)} \cosh(\alpha \cdot n) \]  

(2.2)

Where \( u \) is the unit vector in the direction of the orientation of the rods and \( n \) is the unit vector in the direction of an arbitrary reference axis. The vectors are separated by a polar angle \( \theta \) and an azimuthal angle of \( \phi \). The relationship between these vectors is schematically depicted in Figure 2.3. When \( \alpha \) is equal to zero, this distribution function is flat and corresponds to an isotropic system. As \( \alpha \) becomes increasingly large, the orientational distribution becomes strongly aligned with the reference axis \( n \) corresponding to the nematic state. At a critical concentration the value of the orientational order parameter, \( \alpha \), changes from zero to nonzero signifying a transition from an isotropic state to a nematic state.

The limitations of this approach are that it neglects long-ranged orientationally dependent attractions and that the hard-core steric repulsions are included only up to two-body interactions. Higher order interactions can be included by expanding the free energy in a virial series; however, this leads to extremely difficult calculations. Truncation of the series after the second order term means the theory is most accurate in dilute systems of rods.

Mean Field Lattice Theories

Although neglecting long-ranged attractions, early lattice theories by Flory\(^\text{10}\) are an improvement over Onsager's formulation in that they allow inclusion of higher order steric interactions. The essence of the lattice theory approach is to approximate the number of possible ways of arranging a system of rods composed of many segments on a lattice without overlapping any segments. The number of allowable complexions is a function of the probabilities of placing successive molecules on the lattice, segment by segment, until a fixed volume fraction is reached. A necessary simplifying assumption is that the
probability of placing a segment on a vacant site is equal to the number of open sites divided by the total number of sites. This is a mean-field approximation and neglects segment correlations and composition fluctuations (the composition is assumed to be uniform throughout). In contrast to the Onsager approach, lattice theories are, therefore, more accurate in concentrated systems and less accurate in dilute systems.

More recent lattice models by Flory and Ronca\textsuperscript{11} include orientation dependent attractions on a segment-to-segment level. This allowed the investigation of the isotropic-nematic transition from the athermal limit (hard-core steric interactions) to the thermotropic systems with "soft" orientation dependent attractions. Using a similar approach, Flory and Warner predicted the emergence of coexisting nematic phases in a solution of rods of sufficiently high aspect ratio and concentration.\textsuperscript{12} Later, Warner used a nonlattice theory to characterize very dense systems of short rods.\textsuperscript{13,14} In 1984 Flory used a lattice approach to include polydispersity in rod lengths, blends of rods and coils, semi-rigid chains, and ternary systems composed of rods and coils in a common solvent.\textsuperscript{15} All of these theories neglected the effect of composition fluctuations on the free energy of the system.

**Diblock Copolymers**

An entirely different statistical mechanical formalism has been utilized in the development of the theory of microphase separation in AB block copolymers. In this case polymers are composed of a block of A segments physically connected to a block of B segments. Because of this physical constraint, the system will undergo phase separation with resulting equilibrium morphologies that are altogether different from that observed in blends of two homopolymers. Whereas macroscopic phase separation is observed in homopolymer blends, diblock copolymers phase separate to form morphologies with a periodicity on the molecular length scale. This morphological constraint greatly magnifies the problem of calculating the number of copolymer configurations and renders the Flory-Huggins lattice-type calculation useless.
Mean Field Ginzberg-Landau Expansion

The Ginzberg-Landau expansion technique offers a more powerful method for addressing the complexities associated with the diblock copolymer problem. In this approach the free energy is expressed as a functional of an order parameter that characterizes the phase transitions. This general approach was first applied to polymer problems by Edwards for polymer solutions\textsuperscript{16} and then later by de Gennes for polymer blends.\textsuperscript{17} Subsequently, several theories have used this approach to investigate microphase separation in flexible diblock copolymers. These theories will be qualitatively outlined to illustrate the techniques and highlight important considerations as related to the present research.

In the general approach, the free energy density of an ordered phase is expanded in powers of an order parameter. In polymer problems the order parameter is usually defined as the average deviation from the uniform distribution of monomers at a given point in the system. It is equal to zero if the monomers are uniformly distributed and nonzero if phase separation has occurred. The objective is to calculate the coefficients of the powers of the order parameter in the free energy expansion. These coefficients can be expressed in terms of response functions which are essentially correlation functions that determine how an external potential experienced by a monomer at a point $r$ influences the monomer density at any other point $r'$ in the system. Calculation of these response functions makes use of the random phase approximation. The random phase approximation allows the calculation of the response of a system to the external potentials as if the response functions were those of the ideal chains, but the potentials acting on monomers have been corrected to take monomer interactions into account. The corrections to the external potential include an incompressibility constraint and a term to account for the fact that the enthalpic interaction between two points is a function of their average monomer densities.

A specific example of this approach as applied to the diblock copolymer problem is given by the microphase separation theory by Leibler.\textsuperscript{18} In this problem it was
demonstrated that a dominant nonzero mode of the concentration fluctuations diverges as a homogeneous disordered phase approaches conditions for phase separation. When these conditions are reached, the system spontaneously undergoes phase separation to form a microstructure with a length scale corresponding to the diverging mode in the wave vector. This type of phase transition, where the instability in $k$ occurs at a nonzero value, is also characteristic of the liquid-solid phase transition.

Leibler's theoretical objective was to formulate a theory for this microphase separation in flexible diblocks and use it to predict the phase behavior and resulting morphologies as a function of $\chi N$, the Flory-Huggins chi interaction parameter multiplied by the molecular weight of the diblock, and $f$, the fraction of A type segments in the AB diblock copolymer.

After the free energy is expressed as a function of the order parameter, the next step is to determine which of the possible microphase morphologies is the most stable in the ordered phase. To do this the order parameter is expressed as a linear combination of its dominant Fourier series elements. A different Fourier series is obtained for each microphase morphology by conjugating the spatial vector $\mathbf{r}$ with the reciprocal lattice vectors unique to that particular morphological unit cell. The most stable microphase morphology is the one that minimizes the free energy.

This procedure allows the mapping out of the phase diagram as a function of the independent parameters $\chi N$ and $f$. Using this approach, Leibler predicted that by increasing $\chi N$ a disordered system undergoes a first-order phase transition into a morphology consisting of spheres rich in the minority component arranged in a body-centered cubic lattice and embedded in a matrix rich in the majority component (except for the special case of a symmetric diblock where the transition is second-order into a lamellar domain structure). By increasing $\chi N$ other microphase morphologies are possible depending upon the value of $f$. The other morphologies predicted by Leibler are cylinders packed with hexagonal symmetry transverse to their long axes and stacked lamellar planes.
**Fluctuation Theory**

In this research the objective is to go beyond the mean field theories by taking composition fluctuations into account in predicting the phase behavior of systems containing rigid species. This has been accomplished to a level of approximation corresponding to spatial correlations in composition having a Gaussian form. The analytical methods employed to achieve this end are outlined in the next section. The general formalism is then applied to the prediction of the phase behavior of several specific systems containing rigid components.

**General Free Energy Derivation**

In equilibrium thermodynamics a system is described by its partition function

\[ Z = \sum_i \exp[-H(i)/T], \]

where the sum is over all the states \( i \) of the system, \( H \) is the Hamiltonian, and \( T \) is the temperature.

**Partition Function and Hamiltonian**

In polymer problems the states \( i \) of the system are uniquely defined by the positions of all the monomers, and so we write

\[ Z = \frac{1}{n_A! \ n_B!} \int \mathcal{D}[\mathbf{R}] \exp(-H[\mathbf{R}]/T), \]

with \( \mathcal{D}[\mathbf{R}] \) representing a functional integral over the positions \( \mathbf{R} \) of all monomers of all chains. This can be represented as

\[ \int \mathcal{D}[\mathbf{R}] = \int d\mathbf{R}_1 \int d\mathbf{R}_2 \ldots \int d\mathbf{R}_n \]
where \( n \) corresponds to number of monomers in the system whose positions are integrated over all space. The quantities \( n_A \) and \( n_B \) are the numbers of chains of A and B molecules in the system and the factorials account for the indistinguishability of the chains.

For a general, two-component system composed of A and B type homopolymers, \( H \) will have the form

\[
H = H_A + H_B + U,
\]

where \( H_A \) and \( H_B \) are the Hamiltonians for ideal, Gaussian molecules (no intermolecular interactions) of types A and B, respectively, and \( U \) represents the two-body interactions between pairs of interacting segments.

If A is a flexible chain polymer, the Gaussian part of the A component Hamiltonian in its discretized form is

\[
H_A = \frac{3}{2L^2} \sum_{\alpha=1}^{n_A} \sum_{\tau=1}^{N_A} [R_{\alpha}(\tau+1) - R_{\alpha}(\tau)]^2
\]

with \( n_A \) the number of molecules of type A, \( N_A \) their polymerization index, and \( L \) the Kuhn length. The \( R_{\alpha} \) correspond to the position vectors of segments in a single chain giving rise to a connectivity energy contribution. In the case of a rigid component this contribution is modified by a rigidity constraint

\[
\exp(-H_A/T) = \prod_{\alpha=1}^{n_A} \prod_{\tau=1}^{N_A} \delta(R_{\alpha}(\tau+1) - R_{\alpha}(\tau) - n_{\alpha} L) \exp\left(-\frac{3}{2L^2} \sum_{\alpha=1}^{n_A} \sum_{\tau=1}^{N_A} (R_{\alpha}(\tau+1) - R_{\alpha}(\tau))^2 \right)
\]

and here \( n_{\alpha} \) is a unit vector in the direction of the rod.
For $U$, we will consider here the two-body excluded volume interactions

$$U = U_{AA} + U_{BB} + U_{AB},$$

where the sums are over all monomers on all chains given by

$$U_{ij} = \sum_{\alpha=1}^{n_i} \sum_{\beta=1}^{n_j} \sum_{\tau_{\alpha}=1}^{N_i} \sum_{\tau_{\beta}=1}^{N_j} \delta(R_{\alpha}(\tau_{\alpha}) - R_{\beta}(\tau_{\beta})).$$

with $wij$ being the strength of the two-body interactions between a monomer of type $i$ ($i=A,B$) and that of type $j$ ($j=A,B$). Note that this represents the interaction between monomers rather than the full individual molecules, so that even for the case of rods, $w_{rr}$ does not depend on their orientations $\{n_{\alpha}\}$.

In order to fully represent the excluded volume effect an incompressibility constraint is used. Taking this constraint into account, the partition function becomes

$$Z = \frac{1}{n_A! n_B!} \int \mathcal{D}[R] \exp(-H[R]/T) \prod_{\mathbf{r}} \delta(\rho_0 - \rho_A(\mathbf{r}) + \rho_B(\mathbf{r})).$$

The product in the integrand is over all sites in the system (the system is discretized here, but can be readily represented in the continuous limit) and it represents an incompressibility constraint. It is assumed that the density at every point in the system is equal to a constant given by, $\rho_0 = n_T/V$, $V$ being the volume and $n_T$ being the total number of lattice sites.

Defining the order parameter for density fluctuations as

$$\psi(\mathbf{r}) = \rho_A(\mathbf{r}) - \rho_B(\mathbf{r})$$

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with

\[ \rho_i(r) = \sum_{\alpha=1}^{n_i} \sum_{\tau=1}^{N_i} \delta(r-R_i(\tau)), \]  

the partition function can be written using the definition of the order parameter as a constraint,

\[ Z = \frac{1}{n_A! n_B!} \int [D[R] D[\psi] \exp(-H[R]/T)} \prod_r \delta(\psi - \rho_A(r) + \rho_B(r)) \prod_r \delta(\rho_0 - \rho_A(r) - \rho_B(r)). \]

It is desirable to convert Equation 2.14 into continuous notation by using the identity

\[ \delta(x) = \int dK \exp(ikx). \]

A product of delta functions of a general function \( x(r) \) can be reexpressed as

\[ \prod_r \delta(x(r)) = \prod_r \int dK \exp(ikx(r)). \]

Switching from a discrete to a continuous notation, the product of integrals becomes a functional integral and the exponents can be represented by an integral

\[ \prod_r \delta(x(r)) = \int D[K] \exp[i \int dr \kappa(r) x(r)]. \]
Using this approach and letting \( k \) be conjugate to \((\rho_0 - \rho_A(r) - \rho_B(r))\) and \( k' \) be conjugate to \((\psi - \rho_A(r) + \rho_B(r))\), we can now express Equation 2.14 as

\[
Z = \frac{1}{n_A! n_B!} \exp(-C) \int D[R] D[\psi] D[k] D[k'] \exp(-H[R, \psi, k, k']/T)
\]

where

\[
H[R, \psi, k, k'] = H_A + H_B - \frac{\chi L^3}{4} \int dr \psi^2(r) - i \int dr \psi(r) \kappa'(r)
\]

\[
+ i \sum_{\alpha=1}^{n_A} \sum_{\tau=1}^{N_A} [\kappa(R_\alpha(\tau_\alpha)) + \kappa'(R_\alpha(\tau_\alpha))]
\]

\[
+ i \sum_{\beta=1}^{n_B} \sum_{\tau=1}^{N_B} [\kappa(R_\beta(\tau_\beta)) - \kappa'(R_\beta(\tau_\beta))]
\]

and

\[
C = \frac{V \rho_0 (w_{AA} \phi + w_{BB}(1-\phi))}{2L^3} + \frac{V \chi \phi(1-\phi)}{L^3}
\]

Here, \( \phi \) is the volume fraction of A, given by

\[
\phi = \frac{n_A N_A L^3}{V}
\]

\( L^3 \) being the volume occupied by a single monomer.
The R-dependent terms of the Hamiltonian in Equation 2.19 can be isolated from the rest of the Hamiltonian and the integrations over R in Equation 2.18 performed. First we simplify by making the substitutions

\[ \phi(R_\alpha(\tau_\alpha)) = \kappa(R_\alpha(\tau_\alpha)) + \kappa'(R_\alpha(\tau_\alpha)), \]

and

\[ \phi'(R_\beta(\tau_\beta)) = \kappa(R_\beta(\tau_\beta)) - \kappa'(R_\beta(\tau_\beta)). \]

Separating the Hamiltonian we have

\[ Z = \frac{\exp(-C)}{n_A! n_B!} \int D[\psi] D[\phi] D[\phi'] \exp(-H_1[\psi,\phi,\phi'/T]) \int D[R] \exp(-H_2[R,\phi,\phi'/T]) \]

where

\[ H_1[\psi,\phi,\phi'] = -\frac{\chi L^3}{4} \int dr \psi^2(r) - i \int dr \psi(r) \phi(r) - \frac{\phi'(r)}{2} \]

and

\[ H_2[R,\phi,\phi'] = H_A[R] + i \sum_{\alpha=1}^{n_A} \sum_{\tau_\alpha=1}^{N_A} \phi(R_\alpha(\tau_\alpha)) + H_B[R] + i \sum_{\beta=1}^{n_B} \sum_{\tau_\beta=1}^{N_B} \phi'(R_\beta(\tau_\beta)). \]

The R integral in Equation 2.24 can be represented as a perturbation series by expanding in powers of \( \phi \) and then averaging with respect to the ideal part of the Hamiltonian, \( H_A \) and
This procedure of expanding the exponentials, multiplying cross terms, and then averaging will lead to an exact, albeit intractable, solution for the $R$ dependent integrals.

**Gaussian Approximation**

In order to proceed beyond this point we make use of the Gaussian approximation. This approximation is based on the assumption that the only terms in the infinite series that make a significant contribution to the final solution are Gaussian in nature. Qualitatively, this means that the only contributions that are kept are those arising from the two-body correlations that occur between monomers from the same polymer chain.

A comparison can be made with the random phase approximation commonly used in dense electron gas systems\(^\text{19}\) which has also been shown to be a valid approximation in polymer systems\(^\text{20}\). After making the random phase approximation and integrating out the $R$, $\phi$, and $\phi'$ integrals, Equation 2.24 can be represented as

\[
Z = \frac{\exp(-C)}{n_A! n_B!} \int D[\psi] \exp\left[ - \sum_{n=2}^{\infty} \Gamma_n(r_1, r_2, \ldots, r_n) \psi(r_1) \ldots \psi(r_n) \right]
\]

where integrations are implied over the $r_n$ variables. In making the Gaussian approximation, we keep only the first term in the series corresponding to $n=2$. Higher order vertex terms are often kept when investigating systems composed of flexible components. In systems containing rods the $\Gamma_n$ coefficients are functions of orientation. Keeping them in the free energy expression would lead to an extremely computationally intensive numerical problem when evaluating the free energy. The higher order terms will give only minor corrections to the $\Gamma_2$ term, justifying the truncation of the series at this point.

Continuing the evaluation of Equation 2.24, we use the following identity for multivariable Gaussian integrals\(^\text{21}\)
\[
\left< \exp\left(\sum_n \xi_n x_n \right) \right> = \exp\left[ \frac{1}{2} \sum_{n \neq m} \left< x_n x_m \right> \xi_n \xi_m \right].
\] (2.28)

Making the Gaussian approximation by applying the above identity to the \(R\)-dependent part of Equation 2.24 and switching from a discrete to a continuous notation with respect to the integration over the monomers in a given chain we obtain

\[
\int \mathcal{D}[\mathbf{R}] \exp(-H_2[\mathbf{R}, \varphi, \varphi']/T) = \exp\left[ \frac{1}{2} \int_0^{\text{NA}} d\tau_\alpha \int_0^{\text{NA}} d\tau_\alpha' \left< (\varphi(\mathbf{R}_\alpha(\tau_\alpha)) \varphi(\mathbf{R}_\alpha(\tau_\alpha'))) \right> \right.
\]
\[
+ \frac{1}{2} \int_0^{\text{NB}} d\tau_\beta \int_0^{\text{NB}} d\tau_\beta' \left< (\varphi'(\mathbf{R}_\beta(\tau_\beta)) \varphi'(\mathbf{R}_\beta(\tau_\beta'))) \right> \].
\] (2.29)

**Translational Invariance**

At this point it is helpful to make use of an assumption of the translational invariance of the system. Qualitatively, this assumes that an interaction between two bodies is a function of the distance between them and that the interaction is not affected by spatial translation of the bodies as long as the vector separating them remains the same.

By taking the Fourier transform the pair correlation function for \(\varphi(r)\) can be expressed as

\[
\left< \varphi(r) \varphi(r') \right> = \frac{1}{(2\pi)^6} \int dk \int dk' \varphi(k) \varphi(k') \left< \exp(-ik\cdot r) \exp(-ik'\cdot r') \right>
\] (2.30)

with

\[
\left< \exp(-ik\cdot r) \exp(-ik'\cdot r') \right> = \int dr \int dr' G(r-r') \exp(-ik\cdot r) \exp(-ik'\cdot r')
\] (2.31)

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where $G(r-r')$ gives the normalized probability of finding a segment at $r'$ given that there is a segment at $r$. Note that this distribution function is only dependent upon the distance between $r$ and $r'$.

Using the idea of the translational invariance of the system, it is possible to express the integration over $r$ and $r'$ as integrals over the midpoint $R$ between $r$ and $r'$ and the vector $(r-r')$ as shown in Figure 2.4. This is accomplished by making the following substitutions:

\begin{equation}
\begin{aligned}
r' &= R - \frac{\nu}{2} \quad \text{and} \quad r = R + \frac{\nu}{2},
\end{aligned}
\end{equation}

so that $r-r' = \nu$.

After substituting we have

\begin{equation}
\langle \exp(-i k \cdot r) \exp(-i k' \cdot r') \rangle = \int dR \exp[-i R \cdot (k+k')] \int d\nu \ G(\nu) \exp[-\frac{i}{2} \nu \cdot (k-k')].
\end{equation}

Performing the $R$ integral in Equation 2.33 gives the delta function $\delta(k+k')$.

Taking this into account and substituting Equation 2.33 back into Equation 2.30 we have

\begin{equation}
\langle \varphi(r) \varphi(r') \rangle = -\frac{1}{(2\pi)^6} \int dk \int dk' \varphi(k) \varphi(k') \delta(k+k') \int d\nu \ G(\nu) \exp[-\frac{i}{2} \nu \cdot (k-k')].
\end{equation}

Performing the $k'$ integral gives

\begin{equation}
\langle \varphi(r) \varphi(r') \rangle = \frac{1}{(2\pi)^3} \int dk \varphi(k) \varphi(-k) \int d\nu \ G(\nu) \exp[-i(\nu \cdot k)].
\end{equation}
By applying the result of the translational invariance assumption expressed in Equation 2.35 to Equation 2.29 we get

\[ \int D[R] \exp(-H_2[R,\varphi,\varphi']/T) = \exp \left[ \frac{1}{(2\pi)^3} \int dk \varphi(k) \varphi(-k) \phi_A S_A(k) \right. \]

\[ \left. + \frac{1}{(2\pi)^3} \int dk \varphi'(k) \varphi'(-k) \phi_B S_B(k) \right] \]

(2.36)

where \( S_A(k) \) and \( S_A(k) \) are the single chain structure factors for components A and B respectively. They are given by

\[ S_A(k) = \frac{1}{N_A} \int d\tau_\alpha \int d\tau_\alpha' \int dR \ G_A(R) \exp[-i (R \cdot k)] \]

(2.37)

and

\[ S_B(k) = \frac{1}{N_B} \int d\tau_\beta \int d\tau_\beta' \int dR \ G_B(R) \exp[-i (R \cdot k)] \]

(2.38)

where \( R = R(\tau_i) - R(\tau_i') \), letting \( i = \alpha, \beta \).

Substituting Equation 2.36 into Equation 2.24 we now have

\[ Z = \exp(-C) \frac{1}{n_A! n_B!} \int D[\psi] \int \int \frac{1}{(2\pi)^3} \int dk \exp \left[ \frac{\chi L^3}{4} \psi^2(k) \right] \int D[\varphi] \exp \left[ \varphi(k)\varphi(-k) \phi_A S_A(k) + i \psi(k) \frac{\varphi(k)}{2} \right] \]

\[ \int D[\varphi'] \exp \left[ \varphi'(k)\varphi'(-k) \phi_B S_B(k) - i \psi(k) \frac{\varphi'(k)}{2} \right]. \]

(2.39)
The $\phi$ and $\phi'$ integrals are of a Gaussian form and are easily done to give

$$Z = \frac{\exp(-C)}{n_A! n_B!} \int D[\psi] \frac{1}{(2\pi)^3} \int dk \exp[-2\chi]$$

where

$$\Gamma_2(k) = \frac{1}{\phi_A S_A(k)} + \frac{1}{\phi_B S_B(k)} - 2\chi.$$  \hspace{1cm} (2.41)

Now the $\psi$ integrals are done similarly. Taking the negative logarithm and using Stirling's approximation for the factorials, the free energy per volume is

$$\frac{F}{kTV} = \frac{\phi \ln \phi}{N_A} + \frac{(1-\phi) \ln (1-\phi)}{N_B} + \chi \phi (1-\phi)$$

$$+ \frac{1}{16\pi^3} \int dk \ln \left[ \frac{\phi(1-\phi) S_A(k) S_B(k)}{S(k)} \right].$$  \hspace{1cm} (2.42)

For the most part we have ignored constants which are irrelevant for our purposes, such as those which depend solely on the volume of the system but not upon $\phi$ and those terms which are linear in $\phi$. The exception to this is the $\chi \phi$ term which was kept in order to make the first three terms of the equation identifiable as the familiar Flory-Huggins equation for polymer blends. The inclusion of this term will not influence the phase behavior.

The $\phi \ln \phi$ and $(1-\phi) \ln (1-\phi)$ terms correspond to the entropy of mixing for a two-component system. They are recovered from the combinatorial prefactor terms in the partition function in Equation 2.18. These terms would not be present in the case of a
single-component diblock copolymer system. The enthalpic part of the Flory-Huggins expression comes from the C term in Equation 2.20. The last term is new and represents the contribution of the composition fluctuations to the free energy within the Gaussian approximation.

**Application to Blends of Rigid and Flexible Polymers**

The inverse of the structure factor, $S(k)$, for the entire system is equal to $\Gamma_2(k)$ and is given by

$$\frac{1}{S(k)} = \frac{1}{\phi S_A(k)} + \frac{1}{(1-\phi) S_B(k)} - 2\chi$$

where the volume fraction of component A is represented by $\phi$ and that for component B by $(1-\phi)$.

We have thus derived a free energy for a general two-component mixture, including density fluctuations. Given the single chain structure factors for the two components, $S_A(k)$ and $S_B(k)$, the free energy can be computed.

For the specific case where the system is composed of rigid molecules blended with flexible polymers, the structure factor for the polymeric molecule, $S_A(k) = S_f(k)$, is equal to the Debye structure factor for a Gaussian polymer chain. When the length of the flexible molecule is composed of only a single segment ($N_f = 1$), the structure factor used is $S_A(k)=1$. The structure factor for the rod, $S_B(k) = S_R(k)$, is given by

$$S_R(k) = \frac{1}{N_r} \sum_{\alpha=1}^{n_r} s_r(k \cdot n \alpha) = \int d^2n \ f(n \cdot u) \ s_r(k \cdot n)$$

with
\[ s_r(k) = \frac{\sin^2((N_r k \cdot n)/2)}{N_r \sin^2(k \cdot n/2)} \]

and \( f(n \cdot u) \) is the orientational distribution function for the rods given in Equation 2.2.

The structure factors for rigid and flexible molecules of length \( N_f = N_r = 20 \) is given in Figure 2.5. Case (a) represents the flexible case. Two structure factors are plotted for the rigid case, case (b) corresponding to the case where \( \alpha = 0.0 \) and case (c) for \( \alpha = 100.0 \). The structure factor for an ordered system of rigid molecules has an oscillatory nature. The figure shows a maximum in the structure factors for \( k = 0.0 \). This indicates that the dominant correlations within the system have an infinite length scale \( (r=2\pi/k) \). This is consistent with the fact that the system undergoes macroscopic phase separation when the critical point is reached.

The sum over states also includes integration over the orientations of the rods to account for their orientational entropy and orientation-dependent, excluded volume interactions. See Appendix A for the derivation of these terms.

Following Onsager, we assume a generic expression for the orientational distribution of rods that is characterized by a single orientational order parameter, \( \alpha \) (see Equation 2.2). Note that this orientational order parameter is not directly related to the compositional order parameter represented by \( \psi \). Hence, the free energy for a blend of rods is

\[ F = \frac{\phi \ln \phi}{N_A} + \frac{(1-\phi) \ln(1-\phi)}{N_B} + \chi \phi (1-\phi) \]

\[ + \frac{\phi}{N_r} \int d^2 n \ f(n) \ln(f(n)) \]
\[ + \phi 2 \int d^2 n \, d^2 n' \, f(n) \, f(n') \, [n x n'] \]

\[ + \frac{1}{16 \pi^3} \int d^3 k \, \ln \left[ \frac{\phi(1-\phi) S_A(k) S_B(k)}{S(k)} \right]. \]

The free energy expression with the exception of the last term will be henceforth referred to as the mean field free energy for the various systems considered.

**Simplification by Analytic Solution of One of the Free Energy Integrals**

The integrals in Equation 2.44 are surface integrals over the orientational axis \( n \).

These integrals are also parts of the integrand in Equation 2.42 where the integration is over the three dimensions of \( k \)-space. The integrations over the \( k \) vectors and \( n \) vectors are independent of each other; however, the equations can be simplified by making an appropriate choice for the relative orientations of the two coordinate systems.

If the coordinate system is chosen such that \( u \) is in the \( z \) direction, then \( u \cdot n = \cos \theta \) where \( \theta \) is the polar angle that \( n \) makes with respect to the \( z \) axis. The vector \( k \) is independent of both \( u \) and \( n \); however, the coordinate system can be chosen such that it lies somewhere within the \( xz \) plane. This original coordinate system is schematically represented without primes in Figure 2.6.

At this point the integral in Equation 2.42 is five-dimensional with three dimensions corresponding to the \( k \) integration and two dimensions corresponding to the \( n \) integration. The azimuthal integration of the \( k \) integral is trivial and after it is performed the resulting integral is four-dimensional. By making the appropriate coordinate system transformation, one of the integrals can be solved analytically. The new coordinate system after the transformation is also schematically represented in Figure 2.6 using primed unit vectors. The transformation consists of a rotation about the \( y \) axis until the new \( z \) vector is in the
same direction as the \( \mathbf{k} \) vector. The orientation distribution function in Equation 2.2 now becomes

\[
f(\mathbf{u} \cdot \mathbf{n}) = f(\mathbf{z} \cdot \mathbf{n}) = \eta(\alpha) \cosh(\alpha \cos \theta)
\] (2.47)

where \( \eta(\alpha) \) is a normalization parameter for the orientational distribution function and is equal to \( \frac{\alpha}{4\pi \sinh(\alpha)} \). The quantity \( \cos \theta \) can be expressed in terms of the new coordinate system using the identity

\[
\cos \theta = \cos \beta \cos \gamma + \sin \beta \sin \gamma \cos(\delta - \varphi)
\] (2.48)

where the various angles are defined in Figure 2.6. As a result of this choice of transformation, we have the following relationships which can also be seen from Figure 2.6

\[
\cos \beta = \frac{z}{k} \cos \gamma
\] (2.49)

and

\[
\sin \beta = \frac{p}{k}
\]

as well as

\[
\mathbf{u} \cdot \mathbf{n} = \frac{z}{k} \cos \theta + \frac{p}{k} \sin \theta \cos(\delta - \varphi).
\] (2.50)
The variable ($\delta - \phi$) is renamed $\phi$ and the variable $\gamma$ renamed $- \theta$ to express $S(k)$ in Equation 2.44 as

\begin{equation}
S_R(k) = \int d^2 n \ f(u \cdot n) \ s_r(k \cdot n)
\end{equation}

or more explicitly as

\begin{equation}
S_R(k) = \eta(\alpha) \int_0^\pi \ \int_0^{2\pi} d\phi \ \sin \theta \ \cosh[ \ \frac{\alpha z}{k} \ \cos \theta + \frac{\alpha p}{k} \ \sin \theta \ \cos(\phi) ] \ s_r(k \cos \theta).
\end{equation}

We make use of the following identity to perform the integration\(^23\)

\begin{equation}
2\pi \ \int_0^{2\pi} d\phi \ \exp[ \pm \ \frac{\alpha p}{k} \ \sin \theta \ \cos(\phi) ] = 2\pi \ I_0(\frac{\alpha p}{k} \ \sin \theta)
\end{equation}

where $I_0$ is the zeroth-order modified Bessel function of the first kind. The $\phi$ integral can now be performed to give

\begin{equation}
S_R(\rho, z) = \pi \ \eta(\alpha) \int_0^\pi \ \sin \theta \ s_r(k \cos \theta) \ I_0(\frac{\alpha p}{k} \ \sin \theta) \ [ \ \exp(\frac{\alpha z}{k} \ \cos \theta) + \ \exp(\frac{-\alpha z}{k} \ \cos \theta) ]
\end{equation}

which simplifies to

\begin{equation}
S_R(\rho, z) = \eta(\alpha) \ 2\pi \ \int_{-1}^{+1} dx \ s_r(kx) \ \cosh(\frac{\alpha z x}{k}) \ I_0(\frac{\alpha p}{k} \ \sqrt{1 - x^2}).
\end{equation}
Note that one of the integrals has been performed leaving a three-dimensional integral. The variables to be integrated over are $x$, within the logarithm argument, and $\rho$ and $z$ from the remaining $k$ integrations. The dependence of the magnitude of $k$ on $\rho$ and $z$ is given by the equation, $k = \rho^2 + z^2$.

The final free energy expression is given by

$$\frac{F}{kTV} = \frac{\phi \ln \phi}{NA} + \frac{(1-\phi) \ln(1-\phi)}{NB} + \chi \phi(1-\phi)$$

$$+ \frac{\phi}{N_r} \int d^2 n \ f(n) \ln(f(n))$$

$$+ \phi^2 \int d^2 n \ d^2 n' \ f(n) \ f(n') [n x n']$$

$$+ \frac{1}{16\pi^3} \int d\rho \int d\zeta \ln[(1-\phi)S_P(\rho, \zeta) + (\phi - 2\chi) \phi(1-\phi)S_P(\rho, \zeta)] S_R(\rho, \zeta)$$

where $\phi$ is the volume fraction of rods and the structure factor of rods is given by Equation 2.55.

**Application to Diblocks Composed of Rigid and Flexible Segments**

Although the diblock problem is a single component system, this general approach to deriving the free energy including composition fluctuations is virtually the same as that outlined for the two component system. The inverse system structure factor, which is identical to the $\Gamma_2$ coefficient, for a diblock composed of a rigid and flexible segment is given by

$$\frac{1}{S(k)} = \Gamma_2 = \frac{h_{rr} + h_{ff} + h_{rf}}{h_{rr} h_{ff} - h_{rf}^2} - 2\chi$$  
(2.57)
Where the $h$ terms correspond to form factors for the coherent scattering from the different parts of the diblock molecule. The $h_{rr}$ term corresponds to scattering between two centers located within the rigid part of the molecule. The $h_{pp}$ term corresponds to scattering between centers within the flexible part of the molecule. The $h_{rp}$ term is a cross term that represents scattering between the rigid and the flexible segments. All of the form factors are computed from the same general formula

$$h_{ab} = \int d\tau_a \int d\tau_b' \langle \exp[ik \cdot (\mathbf{R}(\tau_a) - \mathbf{R}(\tau_b'))] \rangle$$

where the ranges of integration correspond to the regions of each type of segment $a$ and $b$. The averages are with respect to the distribution function appropriate for each type of segment. The derivations are straightforward and will not be detailed here. The values derived are the following:

$$h_{ff} = \frac{8}{k^4} \left[ \frac{k^2 N_f}{2} - 1 + \exp\left(\frac{-k^2 N_f}{2}\right)\right],$$

$$h_{rr} = \frac{4\alpha}{k^2 \sinh(\alpha)} \int_0^1 dx \cosh(\alpha x) \frac{\sin^2 N_f k x}{x^2},$$

$$h_{rf} = \left[1 - \exp\left(\frac{-k^2 N_f}{6}\right)\right] \frac{6\alpha}{k^3 \sinh(\alpha)} \int_0^1 dz \frac{\sin(N_f k z)}{z} \cosh(\alpha z),$$

where $N_f$ is the number of flexible segments per chain and $N_r$ is the number of rigid segments per chain.
A plot of the structure factor for various diblock molecules is shown in Figure 2.7. The diblocks are composed of two halves, each with a molecular weight of 20 segments. Case (a) corresponds to two flexible halves. Case (b) corresponds to a flexible half joined to a rigid half with an isotropic orientation ($\alpha = 0.0$); whereas, case (c) corresponds to the same molecule with a nematic orientation ($\alpha = 10.0$). In contrast to the structure factors of the homopolymers in the blend case (Figure 2.5), all of the diblock structure factors show a maximum at a $k$ value that is nonzero. This is an indication of an inherent degree of correlation on a finite length scale in the disordered system. As the system approaches the critical point, the structure factor will diverge at this maximum value in $k$-space corresponding to the length scale of the resulting microphase morphology in $r$-space. From Figure 2.7 it is clear that the presence of the rigid segment in the diblock molecule results in a microphase morphology with a larger length scale. The length scale increases as the degree of orientational ordering increases.

The final free energy for the diblock system is given by

$$\frac{F}{kTV} = \frac{f}{N_r} \int d^2 n \, f(n) \ln(f(n)) + f^2 \int d^2 n \, d^2 n' \, f(n) \, f(n') \, [nxn']$$

$$+ \frac{1}{16\pi^3} \int \rho \, dp \int dz \, \ln \left[ \frac{h_{rr} + h_{ff} + h_{rf}}{h_{rr}h_{ff} - h_{rf}^2} - 2\chi \right]$$

where $f$ is the fraction of rigid monomers per chain and the form factors, given in Equations 2.59-2.61, are functions of $k$ through $\rho$ and $z$ as in the polymer blend case.
Figure 2.1
Schematic representing orientational entropy of a constrained rod (a) and an unconstrained rod (b). Orientational complexions are proportional to the surface area traced by the ends of the rods.
Figure 2.2

Schematic showing excluded volume effect between two rods with orientations given by unit vectors $u$ and $u'$. Excluded volume potential is proportional to parallelepiped volume given by $V = 2bL^2 \langle uu' \rangle$. 
Figure 2.3

Schematic showing the orientation of the rod unit vector $\mathbf{u}$ with respect to that of the reference axis $\mathbf{n}$. 
Figure 2.4
Schematic showing integration vectors $\mathbf{R}$ and $\nu/2$ in relationship to the particle position vectors $\mathbf{r}$ and $\mathbf{r}'$ used in assumption of translational invariance.
Figure 2.5

Structure factors of (a) flexible polymer, (b) isotropic rigid polymer ($\alpha=0.0$), and (c) nematic rigid polymer ($\alpha=100.0$). All molecules have a molecular weight of 20 segments.
Figure 2.6

Diagram of original, unprimed coordinate system and transformed, primed coordinate system used to analytically perform one integral in the free energy expression.
Figure 2.7

Structure factors for diblocks (a) flexible/flexible, (b) rigid/flexible ($\alpha=0.0$), and (c) rigid/flexible ($\alpha=10.0$). Each molecule has a molecular weight of 40 segments.
References


CHAPTER 3
METHODS

Computation of Phase Diagrams

Numerical evaluation of the free energy expression derived in the previous section is fairly difficult and computationally intensive. This section outlines the numerical approach for evaluating the free energy expression and mapping out the phase diagram for various systems.

The fluctuation term in the free energy expression in Equation 2.56 contains a one-dimensional integral within the logarithm in the integrand of a two-dimensional integral. A Gauss Quadrature integration technique was used to evaluate the three-dimensional integral in the free energy equation.

It is important to note that the $k$ integral diverges at the upper limit (at infinitesimally small length scales) and that it is necessary to introduce an appropriate cutoff that is consistent with the smallest relevant length scale for the system. The cutoff value used was computed from the radii of gyration of the molecules in their ideal state.

In this model there are four independent parameters in the free energy expression: the volume fraction of solvent $\phi$, the Flory interaction parameter $\chi$, the degree of polymerization of the rods $N_r$, and the degree of polymerization of the second component $N_p$. The orientational order parameter $\alpha$ is dependent upon the other parameters. It is important to note that the temperature does not enter the expression for the free energy directly, rather, it enters through the $\chi$ parameter. The phase diagram will be expressed in terms of $\chi$ and composition. By assuming some temperature dependence of $\chi$, the phase diagram could be alternatively expressed in terms of temperature and composition.

Computational Scheme

Figure 3.1 shows a flow chart of the computational scheme used to compute the phase diagrams. A particular phase diagram is computed for constant values of $N_p$ and $N_r$. 

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The basic structure consists of three loops. The two outer loops correspond to the independent parameters \(\chi\) and \(\phi\) while the inner loop corresponds to the dependent parameter \(\alpha\). For each set of the three parameters, the free energy is computed using a three-dimensional Gaussian quadrature numerical integration routine. The free energy is minimized with respect to \(\alpha\) to give free energy as a function of \(\phi\). A Lagrangian undetermined multipliers routine was written to locate the common tangent points to be mapped onto the phase diagram.

**Orientational Distribution and Order Parameter**

In characterizing phase transitions in systems of rods it is necessary to quantify the degree of orientational ordering of a system at equilibrium. The orientation of a single rod can be represented by a unit vector \(\mathbf{u}\). In the case considered here there is a reflection symmetry for each rod. That is \(\mathbf{u}\) is equal to \(-\mathbf{u}\) or, in other words, the two ends of a rod are indistinguishable from each other. A system of rods can be characterized by an orientational distribution function, \(f(\mathbf{u})\), which gives the fraction of rods having an orientation unit vector of \(\mathbf{u}\).

The most general description of the orientational distribution function of a collection of rods requires a second rank tensor. A convenient second order tensor can easily be constructed to have the property that its components are zero for an isotropic distribution of rods and nonzero for an anisotropic (nematic) distribution. The components of such a tensor are given by

\[
S_{ij} = \langle u_i u_j - \frac{1}{3} \delta_{ij} \rangle
\] (3.1)

These properties are a result of the fact that the vector average \(\langle \mathbf{u} \rangle\) vanishes due to the reflection symmetry. Additionally, the tensor is symmetric \((S_{ij} = S_{ji})\) and traceless \((S_{ii} = 0)\).
Alternatively, the same tensor can be represented without taking the average as in Equation 3.1. For a given distribution of rods, the only essential vector quantity is the orientation of the rods about an arbitrary reference axis denoted by \( n \). The vector components can, therefore, be represented as

\[
S_{ij} = \eta (n_in_j - \frac{1}{3} \delta_{ij})
\]

(3.2)

where \( \eta \) is a scalar coefficient. Using the two definitions of the tensor components given in Equations 3.1 and 3.2, the coefficient \( \eta \) can be derived

\[
\left( \frac{3}{2} n_in_j \right) S_{ij} = \left( \frac{3}{2} n_in_j \right) \eta (n_in_j - \frac{1}{3} \delta_{ij})
\]

\[
= \frac{3}{2} \eta (n_i^2n_j^2 - \frac{1}{3} n_in_j \delta_{ij})
\]

\[
= \frac{3}{2} \eta (1 - \frac{1}{3})
\]

\[
= \eta.
\]

Substituting Equation 3.3 into Equation 3.1 gives

\[
\eta = \left( \frac{3}{2} n_in_j \right) \left< u_iu_j - \frac{1}{3} \delta_{ij} \right>
\]

\[
= \frac{3}{2} \left< (n \cdot u)^2 - \frac{1}{3} \right>
\]

(3.4)

The dot product in Equation 3.4 can be expressed as a function of the angle, \( \theta \), between the unit vector of a given rod and the reference axis, giving
The average in Equation 3.5 corresponds to a spherical averaging weighted by the orientational distribution function. Assuming azimuthal symmetry and letting \( x = \cos \theta \),

\[
\eta = \frac{3}{2} \left\langle \cos^2 \theta - \frac{1}{3} \right\rangle. \tag{3.5}
\]

The quantity in the brackets is the second Legendre polynomial. The coefficient \( \eta \) can be used to characterize the degree of orientational order in the system. It has a value of 0 if the distribution function is isotropic and a value of +1 if the distribution is perfectly aligned with respect to the reference axis. The order parameter can have a value of -1/2 if the rods are aligned perpendicular to the reference axis.

It is important to realize that the orientational order parameter defined here does not give a unique characterization of the orientational order. That is to say that different orientational distributions can be characterized by the same value of the order parameter. This can be easily demonstrated by considering the representation of the orientational distribution function as a series expansion of Legendre polynomials.

\[
f(x) = \sum_{n=0}^{\infty} a_n P_n(x) \tag{3.7}
\]
It is natural to represent \( f(x) \) this way since the Legendre polynomials form a complete, orthogonal set over the interval represented by the distribution function \([-1, 1]\). By multiplying both sides of Equation 3.7 by \( P_n(x) \) and integrating over the interval we obtain as a result of orthogonality,

\[
\int_{-1}^{+1} dx \, f(x) \, P_2(x) = \frac{2a_n}{2n+1}.
\]

Equation 3.8 is equal to zero for all odd \( n \) values since the integral corresponds to integrating over a symmetric interval. The integral for \( n = 0 \) leads to a trivial result. Since \( P_0(x) = 1 \), the coefficient for the case \( n = 0 \) is the same for any distribution function. The first nontrivial, nonzero coefficient corresponds to the case \( n = 2 \), where the integral in Equation 3.8 is equal to \( \eta \). Using \( P_2(x) \), the quadrupole term, gives rise to the order parameter most commonly encountered when characterizing orientational order in systems of rods. Higher even multipoles can be used to obtain the other coefficients. An infinite number of coefficients is required to uniquely characterize a particular distribution. In practice, only the coefficient corresponding to the quadrupole term is generally used.

The orientational order parameter defined here is the one most commonly referred to in the context of nematic ordering of liquid crystals. Other orientational order parameters can be defined and, depending upon the situation, are sometimes more directly useful. Following Onsager\(^2\), the free energy of the systems considered in this research are dependent upon the orientational distribution function. It is, therefore, desirable to define a generic orientational distribution function that is characterizable by a single orientational order parameter. By minimizing the free energy with respect to the order parameter, one can determine the orientation distribution function. The distribution function used in this case is given by
\[ f(\theta) = \frac{\alpha}{4\pi \sinh(\alpha)} \cosh(\alpha \cos \theta) \]  

(3.9)

where \( \theta \) is the angle the rods of a particular orientation make with the reference axis as shown in Figure 2.3. In this case \( \alpha \) is an orientational order parameter that is equal to zero for an isotropic distribution and nonzero for a nematic distribution. It has an infinite magnitude when the rods are perfectly aligned. This function is plotted in Figure 3.2 for several values of \( \alpha \).

By substituting Equation 3.9 into Equation 3.6 it is easy to derive the relationship between the order parameter \( \alpha \) defined by this particular choice of generic distribution function and the more familiar order parameter \( \eta \). Substituting and solving for \( \eta \) gives

\[
\eta = 1 - \frac{3 \coth(\alpha)}{\alpha} + \frac{3}{\alpha^2}
\]

(3.10)

Figure 3.3 shows the dependence of \( \eta \) on \( \alpha \).

Minimization of Free Energy with Respect to Alpha

There are two main steps to mapping out the phase diagram for a given system of fixed \( Np \) and \( Nr \). First, we must calculate the equilibrium value of \( \alpha \) for given values of \( \chi \) and \( \phi \). Ideally, the free energy expression could be differentiated with respect to the \( \alpha \) parameter to determine the free energy minima. However, due to the complexity of the expression, the \( \alpha \) minimizing the free energy must be determined numerically by computing the free energy at several \( \alpha \) values with all other parameters held constant.

In this way a free energy versus \( \alpha \) curve can be generated. This curve characteristically has at least one local minimum at \( \alpha = 0.0 \) corresponding to an isotropic state. A second or third local minimum, corresponding to nematic states, may be observed as well at nonzero \( \alpha \). One of these local minima will also be the global minimum and will
indicate the degree of orientation that minimizes the free energy for a homogeneous system for the particular fixed values of the parameter settings. Figure 3.4 shows free energy as a function of $\alpha$ at constant $\chi$ for two different compositions corresponding to an isotropic state (a) and a nematic state (b).

**Free Energy Verses Composition Diagrams**

The next step is to determine the curve of coexistence between the nematic and isotropic states. The free energy versus composition computations produce two curves, one corresponding to the nematic state and the other corresponding to the isotropic state as shown in Figure 3.5. These curves are obtained by plotting the free energies of the local minima (from the free energy versus alpha curve) as a function of composition for constant $\chi$. The point of intersection between the isotropic and nematic curves indicates the composition corresponding to the isotropic-nematic transition. A line drawn tangent to both curves identifies a composition range where the system can lower its free energy by separating into two phases with different compositions and degrees of orientation. In this two-phase composition range a given component has the same chemical potential in both phases. A routine was written to compute the common tangent points between the two curves. The computational scheme was to first fit two curves to the two sets of data points and then compute a common tangent using a method based on Lagrange’s method of undetermined multipliers (see Appendix E). The iterative routine first fixed a point on the isotropic curve and then extremized the slope of a line subject to the constraint that it must pass through that point and the nematic curve. This procedure was repeated but this time the nematic curve contained the fixed point and the isotropic curve served as the constraint. Using this iterative method, convergence onto the two common tangent points occurred rapidly.

As stated above, the free energy versus composition curve near an isotropic-nematic transition shows a miscibility gap that is associated with the slope discontinuity between the curves corresponding to the isotropic and nematic states. Additionally, just as in the case
of a blend of two flexible homopolymers, miscibility gaps arise that do not necessarily correspond to an isotropic-nematic transition. The compositions and orientation distributions for the coexisting phases are computed in the same way and by using the same routines outlined above.

**Phase Diagrams**

The computation of the free energy versus composition curve and subsequent computation of the common tangent points is repeated for several values of $\chi$ and the two-phase composition ranges for each $\chi$ are plotted on a single phase diagram.

**Gauss Quadrature Numerical Integration**

The final free energies resulting form composition fluctuations in the various systems considered can be expressed in the form of multiple integrals for which there are no known analytical solutions. Therefore, the prediction of phase behavior requires the numerical evaluation of definite integrals with finite integration limits. Several interpolary approaches to numerical integration exist, the Gaussian quadrature technique being the most efficient. The theoretical basis for the various interpolary formulas will be outlined below with special emphasis on the Gaussian quadrature method including its distinctive features, important assumptions, and limitations.

The objective is to approximate a definite integral by an appropriate summation.\(^3\)

$$\int_{a}^{b} f(x)w(x)dx \approx \sum_{k=1}^{n} A_k f(x_k)$$

This is accomplished by approximating the function by a polynomial $P(x)$ of degree (n-1)

$$f(x) = P(x) = \sum_{k=1}^{n} \frac{\alpha(x)}{(x-x_k) \alpha'(x_k)} f(x_k)$$
This form of $P(x)$ is chosen so that $P(x_k) = f(x_k)$ for each of the $n$ roots of the polynomial $\alpha(x)$ given by

$$\alpha(x) = (x-x_1)(x-x_2)\ldots(x-x_n).$$

(3.13)

The desired condition $P(x_k) = f(x_k)$ is met since

$$\lim_{x \to x_k} \frac{a(x)}{(x-x_k) a'(x_k)} = 1.$$ 

(3.14)

The integral in Equation 3.11 can, therefore, be approximated by substituting Equation 3.12

$$\int_a^b f(x) w(x) dx = \int_a^b w(x) \sum_{k=1}^n \frac{\alpha(x)}{(x-x_k) \alpha'(x_k)} f(x_k).$$

(3.15)

By rearranging we obtain

$$\int_a^b f(x) w(x) dx = \sum_{k=1}^n f(x_k) A_k(x_k)$$

(3.16)

where

$$A_k(x_k) = \int_a^b \frac{\alpha(x)}{(x-x_k) \alpha'(x_k)} w(x) dx.$$ 

(3.17)
Equations 3.16 and 3.17 represent all of the interpolary forms of numerical integration. Several different possibilities exist. The Newton-Cotes formulas are applicable when the zeros of \( \alpha(x) \), specified by \( x_k \), are taken to be equally spaced. Of these methods, Simpson's rule, based on a sum of three-point fits, is the most accurate. This is the preferred method if the values of the integrand is only known for a finite number of evenly spaced points.

It can be shown that a much higher degree of precision exists if the \( x_k \) are not taken to be evenly spaced, but rather equal to the zeros of an \( n \)th-degree polynomial that is orthogonal to all lower degree polynomials over the integration interval. The orthogonal polynomial set should be chosen so that its interval and weighting function correspond with the interval and weighting function of the integral to be numerically approximated. The Legendre polynomials are commonly used for integrals with finite limits since the integration limits can always be linearly transformed to the interval \([-1,1]\) and because they have a weighting function if \( w(x) = 1 \). Extensive tables list the \( A_k \) coefficients and the \( x_k \) zeros of the \( n \)th-degree orthogonal polynomial set chosen.\(^4,5\)

A fundamental assumption in all Gaussian quadrature approaches is that the integrand can be represented by a \((2n-1)\)-degree polynomial. If the integrand is characterized by a very sharp slope or is highly oscillatory this approximation can be a poor one resulting in a low degree of numerical accuracy.

The relative accuracy of a Gaussian quadrature routine can be assessed by comparing the results from a series of numerical integrations using an increasing number of quadrature points, the routine should converge with increasing accuracy on a solution. The level of acceptable tolerance in the approximated value of the integral determines the appropriate choice for the number of quadrature points. It may also be worthwhile to perform an absolute check of the Gaussian quadrature routine by comparing the results obtained with those obtained by a completely different numerical integration method. In this work, both relative and absolute checks were made. The alternative method used for
the absolute check was a Monte Carlo integration routine. The Monte Carlo method was not used as the primary routine because it was considerably slower. The integrals performed were three-dimensional. It is expected that the Monte Carlo method would have been more efficient, and the preferred integration routine, if the integrals to be solved would have had greater than four dimensions.
Choose values for Nr and Np

Chi loop

Composition loop

Alpha loop

Compute free energy for fixed Nr, Np, chi, volume fractions, and alpha using a three-dimensional Gauss quadrature integration routine.

Minimize free energy with respect to alpha.

Find common tangents on free energy verses composition curves using an undetermined multipliers routine.

Plot phase diagram (chi verses composition).

Figure 3.1

Flow chart showing the computational scheme used to generate the phase diagrams.
Figure 3.2

Orientational distribution function as a function of the angle $\theta$ as defined in Figure 2.3.

Distribution function is plotted for three values of $\alpha$. 

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Figure 3.3
Relationship between the two orientational order parameters, \( \eta \) and \( \alpha \).
Figure 3.4

Free energy verses $\alpha$ for two different volume fractions of rods. The most stable distribution is (a) isotropic for $\phi=0.1$, and (b) nematic for $\phi=0.8$. 
Figure 3.5

Free energy as a function of volume fraction of rods showing a close-up of miscibility gap corresponding to the isotropic-nematic transition.
References


CHAPTER 4
RESULTS AND DISCUSSION

Solutions of Rods

The free energy term associated with the composition fluctuations in Equation 2.46 contains a logarithmic argument that may take on values less than zero for certain parameter choices, resulting in an undefined quantity. This corresponds to the physical situation where the system is in a thermodynamically unstable region, i.e., the $\chi$ value is greater than $\chi_s$. The curve for which $\chi$ is equal to or greater than $\chi_s$ outlines the spinodal region. Computationally speaking, for this reason an upper bound in $\chi$ exists, corresponding to the point of instability with respect to the fluctuation free energy term, above which the free energy of the system cannot be computed. This effectively limits the extent of the phase diagram that may be computed when composition fluctuations are taken into account. This problem is not encountered in the case where only the mean field free energy is computed. The phase diagrams presented here show both predictions based strictly on a mean field calculation, represented by closed circles, as well as predictions that include the effect of composition fluctuations, represented by open circles.

Figure 4.1 shows the phase diagram for a system composed of a solution of rods of 10 segments length in a monomeric solvent. The main qualitative feature of this phase diagram is the biphasic region that is narrow at low $\chi$ values and then broadens with increasing $\chi$. The binodal curve on the lower end of the volume fraction scale gives the composition of the isotropic component in the phase separated region; whereas, the other binodal gives the composition of the nematic phase. Additionally, there is a homogeneous isotropic phase at low rod volume fractions and low $\chi$ values. At low $\chi$ values and high volume fractions, there exists a homogeneous nematic phase. These predictions are in qualitative agreement with mean field lattice theory. Since the predictions in the literature
are expressed in reciprocal reduced temperature rather than $\chi$, it is difficult to make a direct quantitative comparison. The precise relationship between these two parameters is not well defined.

As the length of the rods in solution is increased from 10 to 50 segments (see Figure 4.2), the isotropic-nematic transition occurs at a lower concentration and there is a narrowing of the two-phase chimney region that separates the homogeneous isotropic and nematic phases. This behavior is consistent with the theoretical predictions made by Flory and Warner. Additionally, a biphasic region corresponding to coexisting nematic phases is present that was not observed in solutions with smaller aspect ratios. This occurs at a rod volume fraction of approximately 0.9. The two nematic phases in this region are of slightly different composition and degree of orientational ordering. The more concentrated phase with respect to the rod component is also more highly aligned. Coexisting nematic phases have been observed experimentally in solutions of rigid polymers. Flory and Warner have theoretically predicted the existence of coexisting nematic phases in solutions of rods of sufficiently large aspect ratio. They predict coexisting nematic phases that show a critical point behavior in $\chi$. This means that coexisting nematic phases do not form below a critical $\chi$ value. No critical point in $\chi$ has been observed in our model.

**Blends of Rods and Flexible Coils**

Figure 4.3 shows the phase behavior for a system composed of a blend of rods of 10 segments in length and coils of 50 segments in length. By comparing Figures 4.1 and 4.3 it is evident that the increasing the length of the solvent molecule in a solution of short rods causes a shifting of the isotropic-nematic transition to higher volume fractions of rods. There is also a rescaling of the binodal curve with respect to the $\chi$ axis as would be expected as the two component system begins to take on more blend character.

A important point illustrated by the phase diagram in Figure 4.3 is the extreme degree to which the flexible polymer molecules are excluded form the nematic phase. It has been previously predicted for a ternary system consisting of flexible and rigid polymers
dissolved in a common solvent that the flexible polymers will be virtually excluded from the phase rich in rigid polymer. This point is made more apparent by contrasting Figure 4.1 with Figure 4.3. The nematic phase in Figure 4.3 is made up of pure rigid polymer for \( \chi \) values greater than about 0.25. This is not observed in Figure 4.1 where the diluent is a monomeric solvent. The nematic phase contains a nonzero amount of solvent even at higher \( \chi \) values.

Figure 4.4 shows the phase diagram for a blend of flexible coils with rigid rods. The length of both the rods and flexible coils is 50 segments. This diagram shows three possible homogeneous phases for the mean field case, one of them is isotropic and two of them are nematic. Two narrow biphasic regions separate these three homogeneous phase regions. Including composition fluctuations modifies the phase diagram by the broadening of the coexisting nematic phase region.

One of the primary motivations of this project is to model the phase behavior of systems that are likely candidates for use as \textit{in situ} fiber reinforced composite blends. From an empirical standpoint, this implies studying block copolymer systems that are composed of both rigid and flexible segments. In this context the polymer blend case just presented can be considered to be a first approximation to this end: a system composed of relatively short polymer blocks. The next step towards a better approximation of the desired system is make larger molecules by connecting the blocks. This is done in the next section for the diblock copolymer. The realistic possibility of taking this further to investigate a true multiblock copolymer system is outlined in the Future Work section of Chapter 5.

**Diblocks Composed of Rigid and Flexible Segments**

As shown in the theory section, in order to account for fluctuations in composition, our approach was to perform the functional integral over the compositional order parameter in the derivation of the partition function. An alternative mean field approach, which would necessarily neglect composition fluctuations, would be to impose various composition
profiles and, by comparison of free energies, determine the stability regions for each type
of profile. These two approaches have mutually exclusive advantages and disadvantages.
The former approach, the one used in this research, has the advantage that it takes
composition fluctuations into account, but does not allow differentiation between various
microphase morphologies. On the other hand, the latter approach has an advantage in that
it allows the prediction of various microphase morphologies while failing to take
composition fluctuations fully into account.

As a direct consequence of the above considerations, the phase diagrams for the
diblock system will not include differentiation between the various possible microphase
morphologies. The phase diagrams reported here will identify three regions: a
homogeneous isotropic region, a homogeneous nematic region, and a microphase separated
region.

The phase diagrams are shown as a function of the $\chi$ interaction parameter and $f$,
the fraction of rods in each molecule of the diblock. Each diagram is computed for a total
molecular weight. Figure 4.5 shows a phase diagram for a diblock with a total molecular
weight of 20 segments. It shows an isotropic-nematic transition at a rod fraction of 0.65.

If the molecular weight of the diblock is increased from 20 to 40 segments, as
shown in Figure 4.6, the position of the isotropic-nematic transition is shifted from 0.65 to
0.61 in rod fraction. The spinodal curve is also shifted downward in $\chi$. These trends
continue as the molecular weight of the diblock is increased. Figures 4.7 and 4.8 show
diblocks for molecular weights of 60 and 100 segments, respectively.

The shifting of the spinodal downward as a function of increasing molecular weight
is observed in the case of flexible diblocks. Moreover, when composition fluctuations are
neglected the amount of shift is directly proportional to the molecular weight. In this case
the variable $\chi N$ is usually plotted against the rod fraction in order to obtain a universal
curve.\textsuperscript{5} This universal behavior is not observed in our case when composition fluctuations
are taken into account. This is consistent with the result of Helfand for the case of flexible diblocks with composition fluctuations taken into account.6

**Comparison of Corresponding Diblocks and Blends**

Comparison can be made between the phase behavior of a polymer blend and a diblock with a molecular weight equal to the sum of the molecular weights of the blend components. Two sets of comparisons will be made: the diblock and blend composed of 10 rigid units and 50 flexible units (identified hereafter as the 10/50 case), and the diblock and blend composed of 50 rigid units and 50 flexible units (identified hereafter as the 50/50 case).

The 10/50 case corresponds to a comparison between Figure 4.3 and Figure 4.7. The isotropic-nematic transition occurs at a rod volume fraction of 0.59 for the diblock as opposed to the range 0.45 to 0.51 for the blend. This result is consistent with the expectation that the extra orientational constraint of the flexible segments inhibits the ordering of the rigid segments, requiring a greater abundance of rigid segments in order to induce the orientational transition through an increased contribution from the excluded volume effect. This is even more pronounced in the 50/50 case involving larger rigid segments as observed by comparing Figures 4.4 and 4.8.

The connectivity between the rigid and flexible segments in a diblock is also observed to have a large effect on the value of $\chi_s$ corresponding to the point of instability. In the 10/50 case (Figures 4.3 and 4.7) the corresponding rod volume fraction is 0.17. The $\chi$ values corresponding to segregation of components are 0.01 and 0.6 for the diblock and blend, respectively. Similarly, in the 50/50 case (Figures 4.4 and 4.8) the corresponding rod volume fraction is 0.5. The $\chi$ values corresponding to segregation are 0.0008 and 0.076 for the diblock and the blend, respectively. These differences are consistent with the explanation that the diblock, due to its connectivity, has a lower entropic barrier to overcome in undergoing microphase separation than does the blend in undergoing
phase separation. Because of this reduced entropic barrier, the corresponding enthalpic contribution required to induce segregation in the diblock is also reduced.

As previously pointed out, the blend system shows a strong tendency to exclude the polymeric component from the nematic phase. It would be an interesting to make a comparison of the extent of this effect in the blend and the corresponding diblock. However, using this method of approach where the composition fluctuations have been included, the composition profile and the microphase morphologies within the spinodal region cannot be determined.
Figure 4.1

Phase diagram showing mean field prediction with (o) and without (+) composition fluctuations taken into account. System is a solution of rods with a length of 10 segments in a monomeric solvent.
Figure 4.2
Phase diagram showing mean field prediction with (o) and without (•) composition fluctuations taken into account. System is a solution of rods with a length of 50 segments in a monomeric solvent.
Figure 4.3
Phase diagram showing mean field prediction with (o) and without (*) composition fluctuations taken into account. System is a blend of rods and coils with lengths of 10 and 50 segments, respectively.
Figure 4.4
Phase diagram showing mean field prediction with (o) and without (•) composition fluctuations taken into account. System is a blend of rods and coils, each with a length of 50 segments.
Figure 4.5

Phase diagram for a diblock composed of a rigid and a flexible section. The total molecular weight is 20 segments.
Figure 4.6

Phase diagram for a diblock composed of a rigid and a flexible section. The total molecular weight is 40 segments.
Figure 4.7

Phase diagram for a diblock composed of a rigid and a flexible section. The total molecular weight is 60 segments.
Figure 4.8

Phase diagram for a diblock composed of a rigid and a flexible section. The total molecular weight is 100 segments.
References


CHAPTER 5
CONCLUSIONS AND FUTURE WORK

Conclusions

We have derived a general statistical mechanical model for a one or two component system that takes rigidity and composition fluctuations into account. The model has been used to investigate blends and diblock copolymer systems with rigid and flexible components of various molecular weights. It is readily adaptable to other systems.

The Model

Using only the mean field terms from our free energy derivation, we are able to make predictions of the phase behavior of a blend with components having a range of molecular weights. Due to computational difficulties, the inclusion of composition fluctuations was restricted to a limited range of application in the two-component systems with low molecular weight components. Composition fluctuations were observed to have an effect on the phase diagram of the blend of rigid and flexible molecules of 50 segments each, particularly for systems with a high concentration of rods. Using our approach, the inclusion of the composition fluctuation terms, therefore, seems the most useful for systems of an intermediate to high molecular weight. It is expected that the effect of composition fluctuations becomes less important as the molecular weight of the components increases.\textsuperscript{1,2}

For the diblock composed of a rigid and flexible segment, our method is well-suited for determining the regions of isotropic and nematic stability and the region of homogeneous instability when composition fluctuations are taken into account. This approach does not provide a means for the differentiation between the various possible microphase separated morphologies and the determination of their respective concentration profiles.
The question as to the degree of accuracy with which this model predicts the phase behavior of blends and diblocks containing rigid polymers is inconclusive at this point. The primary reason for this is the paucity of experimentally determined phase diagrams for these systems. To date no such phase diagrams have been found in the literature. The best comparisons can be made with other theories as discussed in Chapter 4.

**Applications**

In *in situ* fiber reinforced composite systems it is desirable to have phase separation in the blend system with the formation of a load bearing phase that is highly oriented and concentrated in the rigid component. The data clearly show that the thermodynamic favorability for phase separation and the formation of a strongly aligned nematic phase that is concentrated in the rigid component is dependent upon the molecular weights of both components. The formation of this desired state becomes increasingly thermodynamically favorable as the molecular weights of the rigid and flexible components increase.

Experience with real systems indicates that the more common problems encountered with *in situ* composites concerns the interfacial adhesion and the dispersion between the reinforcing phase and the matrix phase. This is precisely the reason for the interest in block copolymer systems where the compatibilizing properties of the system are a function of the connectivity of the dissimilar blocks. At present our model does not address these important issues. The Future Work section of this chapter outlines suggestions as to how the present model for block copolymers can be extended to include these important considerations.

It is important to keep in mind that thermodynamic stability is only a small part, albeit a very important one, of the larger picture in making applications to a real system. For example, none of the anticipated equilibrium microphase separated morphologies for a diblock suggested in Figure 1.3 or for an equilibrated blend system, is particularly well-suited for possibilities as an *in situ* composite. What is desired is a structure that contains an oriented fibrous phase, capable of bearing a load, embedded in a matrix. However, it is
important that these morphologies represent equilibrium structures and that upon processing they may be frozen into a structure that has an oriented fibrous phase capable of bearing a load.

**Future Work**

One of the strengths of our approach is that, in principle, its application can be extended to any one-component or two-component system where the system structure factor is known. The structure factor could be analytically derived, as done in this research, or, for more difficult systems, it could be obtained from computer simulations or scattering experiments. The structure factor data could be stored in the form of a table which would be called by the computational program in evaluating the free energy.

A natural extension of this research would be to consider a multiblock copolymer composed of a sequence of rigid and flexible segments. In this problem both the distribution and the length of the rigid and flexible segments could be adjustable parameters in the model. By taking this one step further the case of blend of a multiblock copolymer and a flexible coil polymer could be considered. This would model a system like the real system experimentally investigated in Chapter 6 and would be more akin to systems likely to find application as *in situ* fiber reinforced composites.

An interesting and slightly different theoretical approach would be to derive the free energy as a function of the composition profile. This would allow the mapping of the unstable region with the various microphase separated morphologies. Additionally, the composition of the segregated domains and the degree of sharpness of the domain interfaces could be determined. This would have implications concerning the optimization between interfacial adhesion and surface tension, which would be a function of interfacial thickness, verses the extent of segregation and orientation in the rigid domains.
References


CHAPTER 6
EXPERIMENTAL INVESTIGATIONS

Objectives

The objective of this part of the research is an investigation of the nucleation properties and extent of molecular interaction in a blend system that has prospects for use in an in situ fiber-reinforced composite. The blend under investigation is that formed from poly(butylene terephthalate), or PBT, and poly(tetramethylene 4,4'-terephthaloyldioxydibenzoate)-b-PBT, a TLCP synthesized by Caxia Lu at the University of Massachusetts. This multiblock copolymer will be henceforth referred to as TR4-b-PBT (5:8) and it has the following chemical structure:

\[
\begin{align*}
\text{O} & \quad \text{O} & \quad \text{O} & \quad \text{O} \\
\text{[O-C-Ph-O-C-Ph-C-O-Ph-C-O-(CH}_2\text{)}_4-]\text{]}_5\text{--[O-C-Ph-C-O-(CH}_2\text{)}_4-]}_8
\end{align*}
\]

It has been observed that this TLCP gives a higher degree of reinforcement to PBT than other multiblock copolymers synthesized that were based on combinations of the same rigid and flexible segments with variations in block lengths.\(^1\) The particular structure of this TLCP was chosen in an effort to increase its compatibility with the PBT component. One of the objectives of this research is to examine the extent of molecular interactions in this blend system.

It has also been observed that the TR4-b-PBT (5:8) multiblock copolymer behaves as a nucleating agent for both PBT and poly(ethylene terephthalate).\(^2\) The specific objectives of the nucleation study concern the effect of the TLCP concentration on the total...
degree of crystallinity in the blend and whether the nucleating properties of the TLCP on PBT are substantially different from other, less exotic nucleating agents.

While relating to the theory of blends work under the global objective of developing \textit{in situ} fiber reinforced composites, the experimental investigations are not intended to represent an experimental check of the theoretical portion of the project.

**Introduction**

A brief theoretical background for the physical phenomena under investigation and the experimental techniques employed is outlined below.

**Crystallization and Nucleation**

Two important considerations in the technological application of polymeric materials is the degree of crystallinity and rate of crystallization. Crystalline homopolymers can be thought of as quasi-biphasic materials with crystalline domains embedded within an amorphous matrix. The dense, ordered crystallites typically have mechanical and physical properties that are different from the amorphous regions. Because of these differences, the degree of crystallinity of a polymer can strongly influence such physical and mechanical properties as gas permeability, dimensional stability, optical transparency, tensile strength, and modulus.\(^4\) The rate of crystallization often determines the residence time required for molding plastics.

Nucleating agents are additives that promote the formation of the initial crystalline nuclei and can, thereby, increase the rate of crystallization and degree of crystallinity. Also affected are the crystalline structure and spherulitic size. The mechanistic details of heterogeneous nucleation are not well understood. Experiments suggest that different mechanisms are operative in different systems.\(^5\) Some important factors are the size, concentration, and surface energy of the particles.\(^6,7\)

The technique used for the nucleation study was differential scanning calorimetry. In this technique a reference cell is heated or cooled so that its temperature changes from one predetermined temperature to another at a constant rate. A second cell containing the
sample is heated or cooled so as to keep its temperature equal to the changing temperature of the reference cell. As the sample undergoes a thermodynamic transition, there is a change in the power required to maintain the sample cell at the same rate of temperature change. The power differential between the two cells is measured and it is directly related to the enthalpy associated with the transition. By knowing the enthalpy of crystallization and the sample weight, it is easy to determine its degree of crystallinity.

**Blend Miscibility**

Complete miscibility of the blend components is neither required for *in situ* processing nor is it commonly encountered in practice. An extreme example, the molecular composite, deserves particular mention because of its exceptionally high degree of miscibility.

Mechanical reinforcement tends towards its theoretical ideal as the aspect ratio (ratio of length to width) of the reinforcing phase increases. The limiting case is obtained by maximizing the length and minimizing the diameter of the reinforcing phase to the molecular dimensions of a single liquid crystalline polymer molecule. In other words, the mixing between the two components occurs on the molecular level. Experimental observations agree with theoretical reasoning that the formation of such an ideal, known as a molecular composite, is very unlikely due to its thermodynamic instability. However, several examples (or close approximations) have been reported in the literature based on a technique where a dilute solution of the rigid and flexible components are solution spun. During the processing step, the dilute, isotropic system is oriented and quenched as the solvent is removed leaving a composite with an unusually high degree of phase dispersion and superior mechanical properties.

Miscibility of the blend components, which is a function of their molecular interactions, strongly influences the shape, degree of dispersion and adhesion of the reinforcing phase within the matrix. A high degree of miscibility indicates a low surface tension between the two phases which allows for a higher surface area to volume ratio.
manifesting in the formation of smaller and more elongated droplets with good interfacial strength.10,11 A common way of enhancing miscibility is through specific interactions between blend components, e.g., hydrogen bonding, acid-base interactions, dipole-dipole interactions, and aromatic ring complexing. A second approach, which is used in the present example of the PBT and TR4-b-PBT blend system, is to increase compatibility by synthesizing multiblock copolymer TLCPs that are composed of blocks of the flexible component interspersed with blocks of the rigid component.7,8,12

**Dynamic Mechanical Analysis.** There are a number of ways of measuring the extent of molecular interactions in a blend system. One of the methods that is used here is dynamic mechanical thermal analysis. Dynamic mechanical spectroscopy measures two components of the complex modulus of a material, one component corresponds to the storage of elastic energy and the other corresponds to the loss of energy due to viscous damping. These moduli are measured as a function of temperature and frequency of oscillatory loading. The moduli of a polymer at a given temperature are directly related to the molecular mobility or the available modes of molecular motion which are limited by the thermal energy. The storage moduli typically changes dramatically over relatively short temperature ranges corresponding to molecular relaxation processes, e.g., the glass transition. These relaxation processes provide a key to measuring the extent of molecular interaction. If a polymer blend is immiscible there is segregation between the two components and each of their molecular environments will not be substantially altered by the presence of the other. In this case, two different glass transitions will be observed, one for each component. On the other hand, if the two components are miscible, then the blend will show a single glass transition somewhere between the glass transitions of the neat homopolymers. Miscibility can be probed on even shorter length scales by considering the effect of blending on sub-glass relaxations.

**Hoffman-Weeks Analysis.** The colligative properties of ideal solutions are based on the thermodynamic concept that the chemical potential of a solvent in a liquid solution is
lower than that of the pure solvent. In an ideal solution this is purely a result of the entropy of mixing between the two components. A result of this is that the equilibrium temperature for the pure crystalline solvent in a liquid solution will be lower than that for the pure crystalline solvent in a pure liquid solvent. This is a statement of the phenomena of melting point depression.

The same principle applies to polymer solutions. In this case a semi-crystalline polymer is in solution with an amorphous diluent. By equating the chemical potential difference between the pure crystalline polymer and the pure liquid polymer with the chemical potential difference between the polymer in solution and the pure liquid polymer, an expression can be obtained for the thermodynamic equilibrium. This equation gives an expression for the degree of melting point depression

\[
\frac{1}{T_m} - \frac{1}{T_m^o} = -\frac{R}{\Delta H^2} \frac{V_2}{V_1} \chi (1 - \phi_2)^2.\tag{6.1}
\]

In this expression component 1 is the amorphous diluent polymer and component 2 is the semi-crystalline polymer. The \(V\) terms are molar volumes, \(\phi\) is volume fraction, \(\Delta H\) is the enthalpy of fusion per mole of repeat unit, \(\chi\) is the Flory-Huggins interaction parameter, \(T_m\) is the depressed melt temperature, and \(T_m^o\) is the equilibrium melt temperature.

The above relationship provides a relatively simple way to measure \(\chi\), which is an assessment of the degree of miscibility, for a system composed of a blend of a semi-crystalline polymer and an amorphous polymer diluent. The indirect experimental objective is the determination of the equilibrium melting temperature so that \(\chi\) can be computed. A definition for the equilibrium melt temperature is the melting temperature for a polymer crystal in which crystalline perfection is maximized and that is large enough that surface effects are negligible. In practice this would take an inordinate amount of time so this value must be extrapolated from experimentally measurable data.
The procedure is to isothermally crystallize the blend from the melt at different degrees of undercoolings. Smaller undercoolings produce the largest and most perfect crystals. Upon remelting, the melt temperature is recorded. At very small undercoolings, crystallization no longer occurs on a reasonable time scale. By plotting $T_m$ verses $T_c$, the data are extrapolated linearly to the point of intersection with the line $T_m=T_c$ which corresponds to zero undercooling and gives the value of the thermodynamic melt temperature. From this the $\chi$ value can be easily calculated.\textsuperscript{15}

**Polarized Optical Microscopy.** The third technique used to assess the degree of miscibility is polarized optical microscopy. The concept is simply one of optically observing the system above the crystalline melt temperature using crossed polarizers to provide contrast between the disordered matrix phase and ordered liquid crystalline domains.

**Experimental Methods and Results**

Since the same blend components were processed using similar sample preparation procedures for all of the experiments, this information will be presented in a single section. The unique experimental methods and results will presented in a separate section for each type of experiment.

**Blend Components and Sample Preparation**

The inherent viscosity of the TR4-b-PBT (5:8) multiblock copolymer was 0.3 (0.2g/dL in trifluoroacetic acid). This low viscosity and the inability to draw substantial fibers indicated that the molecular weight of the TLCP was not particularly high. DSC analysis showed a melting transition at 216°C and an isotropic-nematic transition centered around 265°C that occurred over a range of about 25°C. The poly(butylene terephthalate) was received from Akzo Chemical Company denoted by the trade name "Armitel" (Mn=10,500, and Mw:Mn=3:1). It had a melt transition at 221°C and $\Delta H$ of crystallization of 140J/gm. for a 100% crystalline sample.\textsuperscript{16}
Four nucleation agents were considered in this study: the TR4-b-PBT (5:8) multiblock copolymer, the oligomeric TR4 mesogen, Vectra, and amorphous fumed silica. The vectra used was denoted as A-900 and was obtained from Celanese. The amorphous fumed silica "Cab-O-Sil M5" had a particle size of 12nm and was 99.8% pure. The oligomeric TR4 was believed to consist, on the average, of eight repeat units of the mesogenic monomer and showed an isotropic-nematic transition at 270°C.

Blends were prepared in two steps. First, the components were cooled with liquid nitrogen and then powdered using a pellet grinder. The powdered components were then weighed and mixed together dry. The powdered mixture was then melt blended using a Mini-max melt blending apparatus. This extra dry-blending step was to facilitate the mixing and dispersion of the two components. The mixing time in the melt blender was approximately 60 seconds and the temperature was kept at approximately 280°C. It has been shown that a transesterification reaction can occur between the two blend components; however, the processing times and temperatures were kept sufficiently low to avoid these reactions.17

Blends of PBT with the TLCP were prepared in the following range of compositions with respect to the weight percent of the TLCP component: 0%, 1%, 5%, 10%, and 20%. The PBT samples in the nucleation study were prepared similar to the above procedure and all compositions were 1% with respect to the weight percent of the nucleating agents.

In addition to the above melt blending procedure the samples for the DMTA experiments were melt pressed at 270°C under vacuum. The DMTA sample dimensions were 1.0cm. x 1.5cm. x 0.1cm.

Differential Scanning Calorimetry

The first experiment utilized differential scanning calorimetry in a comparison of the effect of the various nucleating agents on the overall degree of crystallinity, crystallization temperature, and relative rates of crystallization in the PBT. The temperature ramp used
was the following: heat from 100°C to 325°C at 20 C/minute, hold temperature at 325°C for 5 minutes, cool to 100°C at 20°C/ minute. This procedure was done twice and the data were taken during the first cooling and second heating (the first heating erases the thermal history of the sample and allows the sample to melt and establish good contact with the sample pan).

A second DSC study investigated the effect of TLCP concentration on the degree of crystallinity in the blend. Samples were prepared as outlined above using the same temperature ramp as that used in the nucleation study.

A comparison of data obtained for various nucleating agents for PBT is made in Tables 6.1 and 6.2. The cooling data in Table 6.1 show a shift in the crystallization temperature of a few degrees for all nucleating agents. The peak width also becomes substantially narrowed in the samples with nucleating agents. This is an indication of an increase in the overall rate of crystallization. It does not, however, distinguish between the rate of nucleation and the rate of crystal growth, both of which contribute to the overall rate of crystallization. The TR4 oligomer had a slightly higher degree of crystallinity, the others being about the same as pure PBT.

The enthalpy of crystallization does not always provide the most accurate measure of the degree of crystallinity since the cooling sample may continue to gradually crystallize over a very broad range in temperature. The enthalpy of melting data shown in Table 2 provide a more reliable measurement of the degree of crystallinity since the melting generally occurs over a much shorter temperature range. This data indicates that the total degree of crystallinity is the same for pure PBT and the sample nucleated with TR4 oligomer. The other nucleating agents actually decreased the degree of crystallinity slightly.

A composition study was also conducted using the DSC. In this study blends of PBT were prepared with various compositions of the TR4-b-PBT multiblock copolymer. The results are shown in Table 6.3. The data show a decrease in overall degree of
crystallinity as the composition of the multiblock copolymer is increased. This is somewhat surprising considering that the rate of crystallization of PBT has already been shown to increase in the presence of the copolymer.

A similar effect has been reported where a silica nucleating agent was mixed with poly(ethylene terephthalate). At higher concentrations of the nucleating agent, the crystallization rate and the degree of crystallinity decreased with increasing silica content. These results were attributed to an increase in the melt viscosity due to the adsorption of the polymer chains onto the particle surfaces.\(^\text{18}\)

The final DSC experiment consisted of a Hoffman-Weeks analysis of the blend system. Encouraged by the data in Table 6.3, which show a decrease in the melt temperatures of the blend with increasing concentration of the TLCP, it was conjectured that it might be possible to observe the depression of the PBT melting point by the TLCP diluent and, thereby, obtain a value for $\chi$.

The experiments were conducted by heating the sample above the melt temperature to 275°C and holding it there for 5 minutes. The sample was then quenched at 200°C per minute to the crystallization temperature $T_c$. The sample was isothermally crystallized at this temperature for 30 minutes. At this point the samples were heated at 20°C per minute to 275°C and the melt transition observed.

The data are shown in Table 6.4. Rather than showing a linear increase in the $T_m$ with increasing $T_c$, the data show rather complex, erratic behavior. As the value of $T_c$ approaches $T_m$, the melt transition should become smaller yet more sharply defined. At $T_c=205^\circ\text{C}$ two broad melt transitions are observed at 219°C and 222°C. The melting points for the pure TLCP and PBT are 216°C and 221°C, respectively. Single peaks were observed at all other crystallization temperatures except at 215°C where no detectable crystallization occurred.
Dynamic Mechanical Thermal Analysis

The DMTA experiments involved a compositional study of the glass relaxation process in the blend system. All experiments consisted of a thermal scan from -30°C to 150°C at a rate of 3°C per minute conducted at 1 hz. oscillation frequency.

The results of the experiments are displayed in Table 6.5. The peak in tangent $\delta$ was used to indicate the glass transitions of the samples. The glass transitions of the pure PBT and the pure multiblock copolymer were measured at 56.0°C and 52.0°C, respectively. As shown in the table, the glass transitions for blends of all intermediate compositions were slightly higher than either of the pure components. The tangent $\delta$ curves were slightly broader for the blends than for the pure homopolymers. There was no evidence of multiple glass transitions for any of the blends.

Polarized Optical Microscopy

The blends with compositions of 10% and 20% TLCP by weight were observed using polarized optical microscopy. The temperature was cycled through the melting and crystallization transitions. At 100X magnification both blends showed a small number of tiny birefringent specks against a dark background when heated above the melt temperature of the PBT. These birefringent specks remained as the material began to flow. They were still present at a temperature of 350°C, well above the isotropic-nematic transition temperature. The birefringent specks were concluded to be impurities rather than domains of nematic TLCP. No evidence of phase separation was observed.

Conclusions

The conclusion drawn from this study was that all of the nucleating agents increased the rate of crystallization and raised the crystallization temperature to approximately the same degree. The presence of the nucleating agents lowered the degree of crystallinity except in the case of the TR4 oligomer in which case the degree of crystallinity was the same as pure PBT. It was also concluded that neither the TR4-b-PBT
multiblock nor the TR4 oligomer showed nucleation properties that were substantially different from other, less exotic nucleating agents.

There was no substantial difference in the crystallization rates, as measured by comparing crystallization peak widths, for any of the samples containing the multiblock copolymer. A possible explanation for these observations is that the multiblock copolymer, in addition to seeding nuclei, gets incorporated into the PBT crystalline structure. If this is the case the mesogenic segments may disrupt the crystalline structure and thereby lower the overall degree of crystallization without dramatically affecting the nucleation rate.

The Hoffman-Weeks analysis showed complex, erratic crystallization behavior that did not fit the theoretical expectations upon which the usual method for the determination of the equilibrium melting point is based. Isothermal crystallization at 205°C appeared to produce a melting peak for both components; however, similar behavior was not observed at the other temperatures.

The DMTA experiments revealed that the two blend components have glass transitions that are only 4°C apart from each other. The closeness of the two transitions makes it impossible to resolve any evidence for miscibility.

No evidence of phase separation was observed using polarized optical microscopy.
Table 6.1  First cooling data from nucleation study using DSC.

<table>
<thead>
<tr>
<th>Nucleating Agent</th>
<th>Tcryst (peak, °C)</th>
<th>% Crystallinity</th>
<th>Peak Width*</th>
</tr>
</thead>
<tbody>
<tr>
<td>(absent)</td>
<td>184</td>
<td>43</td>
<td>12.5</td>
</tr>
<tr>
<td>TR4-b-PBT (5:8)</td>
<td>187</td>
<td>44</td>
<td>6.2</td>
</tr>
<tr>
<td>vectra</td>
<td>189</td>
<td>44</td>
<td>6.2</td>
</tr>
<tr>
<td>silica</td>
<td>188</td>
<td>44</td>
<td>5.7</td>
</tr>
<tr>
<td>TR4 oligomer</td>
<td>187</td>
<td>46</td>
<td>5.7</td>
</tr>
</tbody>
</table>

*Peak width is defined as the width of the peak in degrees Celsius at one-half peak height.

Table 6.2  Second heating data from nucleation study using DSC.

<table>
<thead>
<tr>
<th>Nucleating Agent</th>
<th>Tmelt (peak, °C)</th>
<th>% Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>(absent)</td>
<td>221</td>
<td>51</td>
</tr>
<tr>
<td>TR4-b-PBT (5:8)</td>
<td>220</td>
<td>49</td>
</tr>
<tr>
<td>vectra</td>
<td>220</td>
<td>46</td>
</tr>
<tr>
<td>silica</td>
<td>221</td>
<td>46</td>
</tr>
<tr>
<td>TR4 oligomer</td>
<td>220</td>
<td>51</td>
</tr>
</tbody>
</table>

Table 6.3  Second heating data from composition study using DSC.

<table>
<thead>
<tr>
<th>Composition TR4-b-PBT (wt %)</th>
<th>Tmelt (peak, °C)</th>
<th>% Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>221</td>
<td>51</td>
</tr>
<tr>
<td>1.0</td>
<td>220</td>
<td>49</td>
</tr>
<tr>
<td>5.0</td>
<td>216</td>
<td>44</td>
</tr>
<tr>
<td>10.0</td>
<td>215</td>
<td>40</td>
</tr>
<tr>
<td>20.0</td>
<td>213</td>
<td>37</td>
</tr>
</tbody>
</table>
Table 6.4 Dynamic mechanical thermal analysis.

<table>
<thead>
<tr>
<th>% TLCP</th>
<th>Tg °C (from Tangent δ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>56.0</td>
</tr>
<tr>
<td>1.0</td>
<td>57.5</td>
</tr>
<tr>
<td>5.0</td>
<td>60.0</td>
</tr>
<tr>
<td>10.0</td>
<td>58.5</td>
</tr>
<tr>
<td>20.0</td>
<td>58.5</td>
</tr>
<tr>
<td>100.0</td>
<td>52.0</td>
</tr>
</tbody>
</table>

Table 6.5 Hoffman-Weeks analysis using DSC.

<table>
<thead>
<tr>
<th>Tc</th>
<th>ΔH</th>
<th>Tm</th>
</tr>
</thead>
<tbody>
<tr>
<td>175</td>
<td>53.0</td>
<td>223.0</td>
</tr>
<tr>
<td>185</td>
<td>54.7</td>
<td>222.5</td>
</tr>
<tr>
<td>195</td>
<td>44.6</td>
<td>224.4</td>
</tr>
<tr>
<td>205</td>
<td>49.8</td>
<td>219.3 / 222.2*</td>
</tr>
<tr>
<td>210</td>
<td>31.1</td>
<td>221.2</td>
</tr>
<tr>
<td>215</td>
<td>0.0</td>
<td>(absent)</td>
</tr>
</tbody>
</table>

* Two melt transitions observed
References

1. B. Jo, C. Pehlert, and R. Farris, "Processing and Mechanical Properties of Polymer Blends and Molecular Composites" (to be published).

2. B. Jo, and R. Farris, "Thermoplastic Composites Containing a Thermotropic Liquid Crystalline Block Copolymer" (to be published).

3. B. Jo, and R. Farris, "Crystallization Behavior of Blends of Poly(Butylene Terephthalate) and Thermotropic Liquid Crystalline Polymers" (to be published).


17. B. Jo, S. Joslin, and R. Farris, "The Transesterification for Blends of Poly(Butylene Terephthalate)/Liquid Crystalline Polyester" (to be published).

APPENDIX A

DERIVATION OF EXCLUDED VOLUME TERM FOR A GAS OF RODS

The following is a brief derivation of the orientational entropy and excluded volume terms for a system of rods as outlined in Chapter 10 of Doi and Edwards. Following the reasoning of Onsager, the probability distribution function for a system of N rods is given by

\[ P([R_i,u_i]) = A \exp(-\sum_{i>j} \frac{U(i,j)}{kT}) \]  

(A.1)

where \( R_i \) and \( u_i \) denote the position vector for the center of mass and the orientation direction for the ith rod, respectively. The quantity \( U(i,j) \) represents the interaction energy between the ith and jth rods and is a function of \( R_i, R_j, u_i, \) and \( u_j \).

The partition function for the system is separable into two parts

\[ Z[f(u)] = Z_0[f(u)] Z_1[f(u)] \]  

(A.2)

where \( Z_0[f(u)] \) corresponds to the orientational entropy of the rods and \( Z_1[f(u)] \) corresponds to the interactions. Both of these quantities are a function of \( f(u) \), the orientation distribution function for the rods. The orientational entropy term is easily evaluated

\[ Z_0[f(u)] = \frac{1}{N} \int \prod_{i} du_i \prod_{i} dR_i \ f(u) \]  

(A.3)
giving,

\[ A_0[f(u)] = -\frac{kT \ln Z_0}{V} = v kT[\ln v - 1 + \int d\mathbf{u} f(u) \ln f(u)]. \]  

(A.4)

The quantity \( Z_1[f(u)] \) is evaluated by considering only the two-body interactions, whereby,

\[ Z_1[f(u)] = \left< \exp\left( -\sum_{i>j} \frac{U(i,j)}{kT} \right) \right> = \prod_{i>j} \left< \exp\left( -\frac{U(i,j)}{kT} \right) \right>. \]

(A.5)

Considering a single term of the product in Equation A.5 and integrating out the \((\mathbf{R}_i-\mathbf{R}_j)\) variable we have

\[ \left< \exp\left( -\frac{U(i,j)}{kT} \right) \right> = 1 - \frac{1}{V} \int d\mathbf{u}_i \int d\mathbf{u}_j \beta(u_i,u_j) f(u_i) f(u_j) \]

(A.6)

where

\[ \beta(u_i,u_j) = \int d\mathbf{R} \left[ 1 - \exp\left( -U(u_i,\mathbf{R},u_j,0)/kT \right) \right] \]

(A.7)

and it represents the excluded volume arising from the steric interactions of the rods. This excluded volume can be easily expressed as a function of the orientations of a pair of rods from geometrical considerations. For rods of diameter, \( b \), and length, \( L \), the excluded volume term is given by

\[ \beta(u_i,u_j) = 2bL^2 [u_i \times u_j]. \]

(A.8)
Multiplying together all terms similar to Equation A.6 in the limit of \( V \) approaching infinity and keeping \( (N/V) \) constant we have,

\[
Z_1[f(u)] = \exp[- \frac{Vv^2}{2} \int du_i \int du_j \beta(u_i,u_j) f(u_i) f(u_j)]
\]

and

\[
A_1 = bL^2vkT \int du_i \int du_j [u_i x u_j] f(u_i) f(u_j).
\]
APPENDIX B
CODE FOR COMPUTING PHASE DIAGRAMS OF BLENDS

This program computes the phase diagram of a system composed of a blend of rigid and flexible molecules of molecular weight nr and np, respectively. The phase diagram is expressed in terms of the $\chi$ interaction parameter and volume fraction of rods. These two variables correspond to the two outermost do-loops. For each loop in $\chi$ and composition, a free energy value is computed and stored in a file called "blend.fc." This file is then printed and graphically inspected. After a visual inspection and with the help of the file "blend.tr" (which gives the location of the transitions), the program "comtang.f" is used to compute the common tangent values needed to map out the phase diagram. Any errors detected are written to the file "blend.err." The orientational two-body interaction term is precalculated by a program called "exvol.f" and stored in a file called "exvol.dat" given in Appendix D. This program also requires the use of a data file containing the zeros and coefficients for a Gauss quadrature integration routine, which is called "zeros24" in this case.

The subroutine "fluct" computes the various fluctuation free energy terms for given alpha, composition, and molecular weight values. The parameter n is the number of integration points on the intervals according to a Gauss quadrature integration procedure. The structure factor corresponds to Gaussian tapered rods that are assumed to be composed of discrete scattering centers. This program is designed to handle both large and small values of alpha (approximations must be made in the large alpha case).
implicit none

double precision feng, alpha, comp, free, ons, chiarr, ffluct, cutoff, 
& chpotl, w, e, mdfng, datarr, alchk, 
& pi, cr, nr, np, chi, minval, isoal, al, flnf, ffh, alph, aldiff

integer icr, iai, iaiimax, icrmax, i, j, alcnt, nmt, ici, ichimx, n, 
& isot, ii, k, i1, nemt

logical test, gap

icrmax = Number of composition variables.

ialmax = Number of alpha variables.

ichimx = Number of chi variables.

********************************************************
NOTE: IF ICHIMX CHANGED, THE FORMAT 144 STATEMENT MUST AGREE
********************************************************

parameter(icrmax=51, iaiimax=22, ichimx=21)
dimension feng(icrmax), chiarr(ialmax), w(160), e(160),
& alpha(icrmax), comp(icrmax), free(ialmax), datarr(ichimx, icrmax),
& ons(ialmax), alchk(ialmax), alph(2), aldiff(icrmax), mdfng(icrmax)

common /stuff/ np, nr, pi

data (alpha(ial), iai=1, iialmax)/0.01d0, 2.0d0, 5.0d0, 10.0d0, 20.0d0,
& 50.0d0, 100.0d0, 200.0d0, 350.0d0, 500.0d0, 750.0d0, 1000.0d0, 1500.0d0
& , 2000.0d0, 3000.0d0, 4000.0d0, 5000.0d0, 6000.0d0, 7000.0d0, 8000.0d0, 
& 9000.0d0, 10000.0d0/

np = Number of segments in polymer coil.
nr = Number of segments in rod-like polymer.
cutoff = Upper limit for the k-space integral of the fluctuation
free energy term.
n = Number of Gauss quadrature points.

pi = datan(1.0d0) * 4.0d0
np = 50.0d0
nr=50.0d0
cutoff=1.257d0
n=24
c
Read zero and coefficient files for Gauss quadrature routine.
c e= Tabulated zeros of nth degree Legendre polynomial.
c z= Tabulated weighting coefficients.
c
c************************************************************************************************************************************************
c NOTE: if n is changed above, the corresponding filename must also be changed here!!!
c************************************************************************************************************************************************
c
c open(unit=50, file='zeros24')
do 22 i=1,n
read(50,111)e(i),w(i)
111 format(1x,f12.9,1x,f12.9)
22 continue
close(unit=50)
c
c Open the output files.
c
c open(unit=57, file='blend.fc')
open(unit=56, file='blend.tr')
open(unit=55, file='blend.err')
c
Read data file for two-body orientational interaction term.
c
c open(unit=50, file='exvol.dat')
do 23 ial=1,ialmax
read(50,157)alchk(ial),ons(ial)
157 format(1x,f10.3,1x,e16.8)
c
A check is performed to ensure that the alpha values in the
data file correspond to the values initialized in the data
statement at the beginning of this program.
if (alchk(ial).ne.alpha(ial))then  
   write(55,*)'wrong 'exvol.dat' file -- alpha mismatch'  
   close(unit=50)  
   go to 999  
endif  
23  continue  
   close(unit=50)  
  c  
  c Load composition array.  
  c cr= Volume fraction of rods.  
  c comp= Array storing composition values.  
  c  
   comp(1)=0.001d0  
   comp(icrmax)=0.999d0  
   do 91 i=2,icrmax-1  
      comp(i)=(i-1)*0.02d0  
91  continue  
  c  
  c Load chi array.  
  c chiarr= Array storing chi values.  
  c chi= Chi interaction parameter.  
  c  
   do 101 ichi=1,ichimx  
      chiarr(ichi)=(ichi*0.02d0)-0.22d0  
101  continue  
  c  
  c Chi loop begins here.  
  c  
   do 1 ichi=1,ichimx  
      chi=chiarr(ichi)  
  c  
  c Initialize variables used to identify location of chimney  
  c region on the phase diagram. Variables will be defined later  
  c in the program.  
  c
isot=0
gap=.false.

Composition loop begins here.

do 2 icr=1,icrmax
   cr=comp(icr)

Alpha loop begins here.

do 3 ial=1,ialmax
   al=alpha(ial)

Calculation of free energy for as a function of nr, np, chi, cr, and alpha.
If alpha is greater than 200.0d0, a suitable approximation is made for the orientational entropy term in order to avoid an overflow error in the computer.

flnf= Orientational entropy free energy term.
ffh= Flory-Huggins free energy terms.
ffluct= Free energy term from fluctuations.
free= Array storing total free energy terms for all values of alpha for given composition and chi values.

if(al.le.200.0d0)then
   flnf=(cr/nr)*(dlog(al/(dtanh(al)*4.0d0*pi))+(datan(dsinh(al))/&dsinh(al))-1.0d0)
else
   flnf=(cr/nr)*(dlog(al/(dtanh(al)*4.0d0*pi))-1.0d0)
endif

ffh=((cr/nr)*dlog(cr)+(((1.0d0-cr)/np)*dlog(1.0d0-cr)) &+(chi*cr*(1.0d0-cr))

ffluct=0.0d0
test=.true.
Call the subroutine that computes the fluctuation free energy term
Subroutine inputs: al, cr, chi, w, e, n, cutoff
Subroutine outputs: ffluct, test
test = Logical test variable that indicates spinodal instability
when it's value is .false. Computationally, this occurs
when the argument of the log term in the 'fluct' subroutine
is negative.

call fluct(al, cr, chi, w, e, n, cutoff, ffluct, test)

c If test = .false., then the free energy term can not be computed for
this set of parameters because it is within the spinodal region.
Continue by incrementing the composition variable.

if(test.eq..false.)then
    gap = .true.
    feng(icr)=9.99d0
    aldiff(icr)=0.0d0
    goto 2
endif

c Summation of all of the free energy terms.
on= Term obtained from the 'exvol.dat' data file. When multiplied by
    (cr**2) this gives the free energy arising from the excluded
    volume interaction between rods.

c free(ial)=((cr**2)*ons(ial))+flnf+ffh+ffluct

c Next alpha

3 continue

c Minimize free energy with respect to alpha in order to determine
the type of phase(s) present for a given value of chi and composition.
minval=free(1)
isoval=minval
alcnt=0

c
minval= Minimum value of free energy with respect to alpha.
alcnt= Incremented once for each local nematic minima.
alph= Array where the values of the local nematic minima are stored.
c
do 244 j=2,ialmax-1
   if(free(j).lt.minval)minval=free(j)
   if((free(j).lt.free(j-1)).and.(free(j).lt.free(j+1)))then
      alcnt=alcnt+1
      alph(alcnt)=free(j)
   endif
244 continue
   if(alcnt.gt.2)write(55,*)'alcnt greater than 2'
c
If 'aldiff' is positive, indicates second nematic phase.
If 'aldiff' is negative, indicates first nematic phase.
If 'aldiff' is zero, indicates first nematic or isotropic phase.
c
   if(alcnt.eq.2)aldiff(icr)=alph(1)-alph(2)
   if(alcnt.lt.2)aldiff(icr)=0.0d0

c
Test to see if the last value is the global minimum. If this is the
case then the set of alpha values does not go high enough and higher
cvalues of alpha should be included in the array.
c
   if(free(ialmax).lt.minval)then
      minval=free(ialmax)
      write(55,*)'alpha-message 1','chi=',chi,'comp='
   elseif(free(ialmax).lt.free(ialmax-1))then
      write(55,*)'have not scanned high enough alpha--message 2'
   endif

c
This part of the program identifies the nematic and isotropic
chimney regions of the phase diagram.

isot = Number of compositions in isotropic region.
nemt = Number of compositions in nematic region.
feng = Array containing the minimum free energy values for all values of the composition.

if(minval.eq.isoval)then
  isot=isot+1
elseif(gap.eq..false.)then
  nemt=nemt+1
endif
feng(icr)=minval

Next composition.

continue

Computation of chimney region compositions.

cp1 = Low composition.
cp2 = High composition.

Modify feng array by subtracting out linear chemical potential term.

chpotl = Chemical potential term. This term is multiplied by the composition and subtracted from the corresponding feng value. This defines the highest and lowest compositions as having zero free energy. Note that this does not affect the location of the transitions on the phase diagram.

if((feng(1).eq.9.99d0).or.(feng(icrmax).eq.9.99d0))then
  write(55,*)'feng(1)=',feng(1),'feng(icrmax)=',feng(icrmax)
  write(55,*)'cant print chi=',chi
go to 1
endif
chpotl=(feng(icrmax)-feng(1))/(comp(icrmax)-comp(1))
do 27 i=1,icrmax
if(feng(i).ne.9.99d0) then
  mdfng(i)=feng(i)-(chpot*(comp(i)-comp(1)))-feng(1)
else
  mdfng(i)=0.00d0
endif
27  continue

c
nmt=0
do 212 k=1,icrmax
   if(aldiff(k).eq.0.0d0) go to 212
   c
   Only interested in the case where there are two nematic phases.
   c
   if((aldiff(k)*aldiff(k+1)).lt.0.0d0) then
      nmt=k
      goto 190
   endif
212  continue
190  continue

*** Output ***********************************************************

do 143 ii=1,icrmax
   datarr(ichi,ii)=mdfng(ii)
143  continue
   if(nemt.ne.0) then
      write(56,145)chi,comp(isot),comp(nmt)
      145  format(1x,f8.5,2( ,f6.4))
   else
      write(56,146)chi,comp(nmt)
      146  format(1x,f8.5,' ','9.99999',' ,f6.4)
   endif

c
   Next chi value.

c
1  continue

112
do 147 i1=1,icrmax
   write(57,144)comp(i1),(datarr(j,i1), j=1,ichimx)
144   format(1x,f6.4,21(' ',f9.6))
147   continue
   close(unit=57)
   close(unit=56)
   close(unit=55)
999   stop
end

subroutine fluct(al,cr,chi,w,e,n,cutoff,ff1,test)
   implicit none
   double precision w,e,x,pi,pi2,point,xmax,xmin,xmn2,xpn2,
      &a,b,c,d,ee,f,g,ii,j,k,l,m,nn,o,q,arg1,arg2,a1,a2,ea1,ea2,
      &t2,iocssr,t1,x1,xintfl,zintfl,sr,nrq2f,alpha,sp,q2rg2,
      &r,z,cr,rmin,rmax,zmin,zmax,rg,cp,np,chi,al,ff1,
      &cutoff,rmn2,rpn2,zmn2,zpn2,lnckfl,pointt,xinflt,zinflt,
      &twpijg2
   integer ix,n,ir,iz,i,i1,i2,i3
   logical test

c   parameter (a=3.5156229d0,b=3.0899424d0,
      &c=1.2067492d0,d=0.2659732d0,ee=0.0360768d0,f=0.0045813d0,
      &g=0.39894228d0,h=0.01328592d0,ii=0.00225319d0,j=-0.00157565d0,
      &k=0.00916281d0,l=-0.02057706d0,m=0.02635537d0,nn=-0.01647633d0,
      &o=0.00392377d0)
   dimension w(n),x(n),r(n),e(n),iocssr(n),point(n)
      &,xintfl(n),zintfl(n),z(n)
common /stuff/np,nr,pi

\[ cp = (1.0d0 - cr) \]
\[ pi2 = pi \times pi \]
\[ twpi = 2.0d0 \times pi \]
\[ rg2 = np / 6.0d0 \]

c
Set integration limits and compute transformation factors.
The \( r \) and \( z \) intervals are from 0 to cutoff.

c
\[ ff1 = 0.0d0 \]
\[ test = .true. \]
\[ rmax = cutoff \]
\[ rmin = 0.0d0 \]
\[ rmn2 = (rmax - rmin) / 2.0d0 \]
\[ rpn2 = (rmax + rmin) / 2.0d0 \]
\[ zmax = cutoff \]
\[ zmin = 0.0d0 \]
\[ zmn2 = (zmax - zmin) / 2.0d0 \]
\[ zpn2 = (zmax + zmin) / 2.0d0 \]

do 12 i = 1, n
\[ r(i) = rpn2 + (rmn2 \times e(i)) \]
\[ z(i) = zpn2 + (zmn2 \times e(i)) \]
12 continue

c
*** MAIN LOOPS

***********************************************
c
r(ir) loop.
c
do 20 ir = 1, n
c
c
z(iz) loop.
c
do 30 iz = 1, n
c
The x interval is from 0 to 1.

\[ sr=0.0 \times 10^{-6} \]
\[ xmax=1.0 \times 10^{-6} \]
\[ xmin=0.0 \times 10^{-6} \]
\[ xmn2=((xmax-xmin)/2.0) \]
\[ xpn2=((xmax+xmin)/2.0) \]

\[ do \ 11 \ i=1,n \]
\[ x(i)=xpn2+(xmn2*e(i)) \]
\[ 11 \ continue \]

\[ q=dsqrt((r(i)^2)+(z(i)^2)) \]
\[ q2rg2=rg2*(q^2) \]
\[ sp=1.0+((-2.0*np)/(q2rg2^2))*(1.0-q2rg2-dexp(-q2rg2)) \]
\[ sp=1.0 \]

\[ nrq2f=((nr*q)^2)/4.0 \]
\[ arg1=(al*z(i))/q \]
\[ arg2=(al*r(i))/q \]

\[ do \ 17 \ i=1,n \]
\[ a1=(arg1*x(i))-(nrq2f*(x(i)^2)) \]
\[ a2=(-arg1*x(i))-(nrq2f*(x(i)^2)) \]
\[ x1=arg2*dsqrt(1.0d0-(x(i)^2)) \]

This branch is used if alpha is less then 200.0d0.

\[ if(al.lt.200.0d0)then \]
\[ if(abs(x1).le.3.75d0)then \]
\[ t2=(x1/3.75d0)**2 \]
\[ if(a1.lt.-200.0d0)then \]
\[ ea1=0.0 \]
\[ else \]
\[ ea1=dexp(a1) \]
\[ endif \]
\[ if(a2.lt.-200.0d0)then \]
\[ ea2=0.0 \]
else
ea2=dexp(a2)
endif

$iocssr(i)=(1.0d0+t2*(a+t2*(b+t2*(c+t2*(d+t2*(e+t2*(ee+(t2*f)))))))*$
&\((ea1+ea2)/(2.0d0*dsinh(al)))$

else
t1=3.75d0/x1
if((a1+x1).lt.-200.0d0)then
ea1=0.0d0
else
ea1=dexp(a1+x1)
endif
if((a2+x1).lt.-200.0d0)then
 ea2=0.0d0
else
ea2=dexp(a2+x1)
endif

$iocssr(i)=(1.0d0/dsqrt(x1))*(g+t1*(h+t1*(i+t1*(j+t1*(k+
 &t1*(l+t1*(m+t1*(nn+(t1*o)))))))))*(ea1+ea2)/(2.0d0*dsinh(al)))$
endif

This branch is used if alpha is greater than 200.0d0.

else
if(abs(x1).le.3.75d0)then
t2=(x1/3.75d0)**2
if((a1-al).lt.-200.0d0)then
 ea1=0.0d0
else
ea1=dexp(a1-al)
endif
if((a2-al).lt.-200.0d0)then
 ea2=0.0d0
else
ea2=dexp(a2-al)
endif

\[ \text{iocssr}(i) = (1.0d0 + t2^2(a + t2^2(b + t2^2(c + t2^2(d + t2^2(ee + t2^2(f)))))))^* \]
& (ea1 + ea2)

else
\[ t1 = 3.75d0/x1 \]
if((a1 + x1 - al).lt.-200.0d0) then
\[ ea1 = 0.0d0 \]
else
\[ ea1 = \text{dexp}(a1 + x1 - al) \]
endif
if((a2 + x1 - al).lt.-200.0d0) then
\[ ea2 = 0.0d0 \]
else
\[ ea2 = \text{dexp}(a2 + x1 - al) \]
endif
\[ \text{iocssr}(i) = (1.0d0/\text{dsqrt}(x1))^*(g + t1^2(h + t1^2(i1 + t1^2(j + t1^2(k + t1^2(l + t1^2(m + t1^2(nn + t1^2(o))))))))^*(ea1 + ea2) \]
endif
endif

17 continue

\[ \text{Do } x(ix) \text{ loop.} \]

\[ \text{do } 40 \text{ ix}=1,n \]
\[ \text{point}(ix)=w(ix)*\text{iocssr}(ix) \]
40 continue

\[ \text{pointt}=0.0d0 \]
\[ \text{do } 41 \text{ i1}=1,n \]
\[ \text{pointt}=\text{pointt}+\text{point}(i1) \]
41 continue
\[ \text{sr}=(al*nr*xmn2*\text{pointt})+1.0d0 \]

\[ \text{lnckfl}=((1.0d0/(cp*sp))+(1.0d0/(cr*sr))-(2.0d0*chi)) \]

Return control to main program if the argument of the log is negative.
A negative argument indicates the unstable spinodal region.
if(lnckfl.lt.0.0d0)then
  test=.false.
  return
endif

xintfl(iz)=w(iz)*(dlog(lnckfl)+dlog(cp*cr*sr*sp))

continue
xinflt=0.0d0
   do 31 i2=1,n
       xinflt=xinflt+xintfl(i2)
   31 continue
zinflt=0.0d0
   do 21 i3=1,n
       zinflt=zinflt+zintfl(i3)
   21 continue
.ff1=(1.0d0/(4.0d0*pi2))*rrmn2*zinflt

return
end
APPENDIX C

CODE FOR COMPUTING PHASE DIAGRAM OF DIBLOCKS

This program computes the stability of the ordered and disordered phases in the diblock composed of a rigid and flexible segment. The code is a modification of that used to compute the phase diagram of the blend of rigid and flexible molecules in Appendix B. This program roughly determines the location of the spinodal region and then scans more accurately to find the transitions to a higher degree of precision. The locations of the transitions are stored in a file called "diblock.dl." The orientational two-body interaction term is precalculated and stored and called from a file called "onsal.dat." This program also requires the use of a data file containing the zeros and coefficients for a Gauss quadrature integration routine, which is called "zeros20" in this case.
implicit none

double precision w,e,alpha,al,np,nr,f,alchk,ons,chi,flnf,
         &pi,ffluct,onsag,cutoff,free,nt
integer ialmax,ial,n,i,icp,icpmax,ichi,ichimx,icp2,ial2
logical test,oldtst,oldtst2,test2
parameter(ialmax=8,ichimx=18,icpmax=9)

c
dimension w(120),e(120),alpha(ialmax),alchk(ialmax),ons(ialmax)
         &,free(ialmax)

 data (alpha(ial),ial=1,ialmax)/0.01d0,1.0d0,5.0d0,10.0d0,20.0d0,
         &50.0d0,100.0d0,200.0d0/

c
         pi=datan(1.0d0)*4.0d0
         n=20
         cutoff=2.50d0
         nt=60.0d0

 c***********************************************************************

 c read zero and coefficient files
 c
 c NOTE: if n is changed above the corresponding filename must also
 c
 c be changed here!!!

c
         open(unit=50, file='zeros20')
         do 22 i=1,n
               read(50,111)e(i),w(i)
         111 format(1x,f12.9,1x,f12.9)
         22 continue
         close(unit=50)

 c

 c *** output files ***
   open(unit=55, file='diblock.dr')
   write (55,*) 'nt=',nt
   write (55,*) 'n=',n
   write (55,*) 'cutoff=',cutoff

c
 c *** read data file for 2-body orientational interaction term.
open(unit=50, file='exvol.dat')
do 23 ial=1,ialmax
   read(50,157)alchk(ial),ons(ial)
format(1x,f10.3,1x,e16.8)
if (alchk(ial).ne.alpha(ial))then
   write(55,*)'wrong onsager file -- alpha mismatch'
close(unit=50)
go to 999
endif
23  continue
   close(unit=50)
c
*** loops start here **************************************
c
do 1 ichi=1,ichimx
   chi=(ichi*0.0005d0)+0.001d0
oldtst=.true.
test=.true.
c
do 2 icp=1,icpmax
   f=icp*0.10d0
   nr=f*nt
   np=nt-nr
c
do 3 ial=1,ialmax
   al=alpha(ial)
c
call fluct(al,np,nr,chi,w,e,n,cutoff,ffluct,test)
if(test.ne.oldtst)then
   oldts2=oldtst
   oldtst=test
do 4 icp2=0,20
   f=((icp-1)*0.10d0)+(icp2*0.005d0)
   nr=f*nt
   np=nt-nr
c
do 5 ial2=1,ialmax
   al=alpha(ial2)
   call fluct(al,np,nr,chi,w,e,n,cutoff,ffluct,test2)
   if(test2.ne.oldts2)then
      write(55,100)chi,f
      goto 2
   endif
   c
   *** next alpha ***
   5 continue
   4 continue
   endif
   c
   *** next alpha ***
   3 continue
   2 continue
   1 continue
   close(unit=55)
   c
999 stop
   end
   c
   c
   c
   c
   c
   c
   subroutine fluct(al,np,nr,chi,w,e,n,cutoff,ffluct,test)
   implicit none
   double precision w,e,x,pi,hrrpt,xmax,xmin,xmn2,xpn2,
                     &a,b,c,d,ee,f,g,h,ii,j,k,l,m,nn,o,arg1,arg2,a1,a2,ea1,ea2,
                     &t2,t1,x1,xintfl,zintfl,hpp,hrr,hrp,hrpott,hrrpt,
                     &r,z,rmin,rmax,zmin,zmax,np,chi,nr,al,iocs,ffluct,
                     &cutoff,rnn2,rpn2,zmn2,zpn2,lnckfl,hrrptt,xinflt,zinflt
   c
integer ix,n,ir,iz,i,i1,i2,i3
logical test
parameter (a=3.5156229d0,b=3.0899424d0,
&c=1.2067492d0,d=0.2659732d0,ee=0.0360768d0,f=0.0045813d0,
&g=0.39894228d0,h=0.01328592d0,ii=0.00225319d0,j=-0.00157565d0,
&k=0.00916281d0,l=-0.02057706d0,m=0.02635537d0,nn=-0.01647633d0,
&o=0.00392377d0)

dimension w(n),x(n),r(n),e(n),iocs(n),hrppt(n),hrppt(n)
&,xintfl(n),zintfl(n),z(n)

c
pi=datan(1.0d0)*4.0d0

c
*** set integration limits and compute transformation factors ***
c
*** the r and z intervals are from 0 to cutoff ***
c
ffluct=0.0d0
test=.true.
rmax=cutoff
rmin=0.0d0
rmn2=((rmax-rmin)/2.0d0)
rpn2=((rmax+rmin)/2.0d0)
zmax=cutoff
zmin=0.0d0
zmn2=((zmax-zmin)/2.0d0)
zpn2=((zmax+zmin)/2.0d0)

do 12 i=1,n
r(i)=rpn2+(rmn2*e(i))
z(i)=zpn2+(zmn2*e(i))
12 continue

c
*** MAIN LOOPS

******************************************************************************

c
*** r(ir) loop ***
c
do 20 ir=1,n
c
*** z(iz) loop ***
c
do 30 iz=1,n
c
*** the x interval is from 0 to 1 ***
c
hrr=0.0d0
hrp=0.0d0
hpp=0.0d0
xmax=1.0d0
xmin=0.0d0
xmn2=((xmax-xmin)/2.0d0)
xpn2=((xmax+xmin)/2.0d0)
c
do 11 i=1,n
  x(i)=xpn2+(xmn2*e(i))
11 continue
c
q=dsqrt((r(ir)**2)+(z(iz)**2))
hpp=(8.0d0/(q**4))*((np*q*q*0.5d0)-1.0d0+dexp(-q*q*np*0.5d0))
arg1=(al*z(iz))/q
arg2=(al*r(ir))/q
do 17 i=1,n
  a1=(arg1*x(i))
  a2=(-arg1*x(i))
  x1=arg2*dsqrt(1.0d0-(x(i)**2))
c
if(al.lt.200.0d0)then
  if(abs(x1).le.3.75d0)then
t2=(x1/3.75d0)**2
  if(al.lt.-200.0d0)then
    eal=0.0d0
  else
else
eal = exp(a1)
endif
if(a2.lt.-200.0d0)then
ea2 = 0.0d0
else
ea2 = exp(a2)
endif
iocs(i) = (1.0d0 + t2*(a + t2*(b + t2*(c + t2*(d + t2*(e + t2*(f)))))))
&(eal + ea2)/(2.0d0 * dsinh(al))
else
t1 = 3.75d0/x1
if((al + x1).lt.-200.0d0)then
ea1 = 0.0d0
else
ea1 = exp(a1 + x1)
endif
if((a2 + x1).lt.-200.0d0)then
ea2 = 0.0d0
else
ea2 = exp(a2 + x1)
endif
iocs(i) = (1.0d0/dsqrt(x1)) *(g + t1*(h + t1*(i + t1*(j + t1*(k + &t1*(m + t1*(n + (t1*o))))))))*(eal + ea2)/(2.0d0 * dsinh(al))
endif
c
c *** branch if alpha > 200.0 ***
c
derf
if(abs(x1).le.3.75d0)then
t2 = (x1/3.75d0)**2
if((a1-al).lt.-200.0d0)then
ea1 = 0.0d0
else
ea1 = exp(a1-al)
endif
if((a2-al).lt.-200.0d0)then

e2=0.0d0
else
e2=dexp(a2-al)
endif
iocs(i)=(1.0d0+t2*(a+t2*(b+t2*(c+t2*(d+t2*(ee+(t2*f)))))))
&(ea1+ea2)
else
tl=3.75d0/xl
if((al+xl-al).lt.-200.0d0)then
ea1=0.0d0
else
ea1=dexp(al+xl-al)
endif
if((a2+xl-al).lt.-200.0d0)then
ea2=0.0d0
else
ea2=dexp(a2+xl-al)
endif
iocs(i)=(1.0d0/dsqrt(xl))*(g+tl*(h+tl*(i+i1*(j+tl*
&(k+tl*(l+tl*(m+tl*(nn+(tl*o))))))))))*(ea1+ea2)
endif
endif

17 continue

*** do x(ix) loop ***

do 40 ix=1,n
hrrpt(ix)=w(ix)*iocs(ix)*((dsin(0.5d0*nr*q*x(ix))/x(ix))*2)
hrrppt(ix)=w(ix)*iocs(ix)*((dsin(nr*q*x(ix))/x(ix)))

40 continue
hrrptt=0.0d0
hrrpptt=0.0d0
do 41 i1=1,n
hrrptt=hrrptt+hrrpt(i1)
hrrpptt=hrrpptt+hrrppt(i1)


```fortran
41  continue
    hrr = (4.0d0 * al * xmn2 * hrptt) / (q ** 2)
    hrp = (6.0d0 * (1.0d0 - dexp((-q * q * np) / 6.0d0)) * al * xmn2 * hrptt) / (q ** 3)
c
    lnckfl = ((hrr + hpp + (2.0d0 * hrp)) / ((hrr * hpp) - (hrp * hrp))) - (2.0d0 * chi)
c *** return control to main program if neg. log error *****
    if (lnckfl .lt. 0.0d0) then
        test = .false.
        return
    endif
c
    xintfl(iz) = w(iz) * dlog(lnckfl)
c
30  continue
    xinflt = 0.0d0
    do 31 i2 = 1, n
        xinflt = xinflt + xintfl(i2)
    31  continue
    zintfl(ir) = r(ir) * zmn2 * xinflt * w(ir)
20  continue
    zinflt = 0.0d0
    do 21 i3 = 1, n
        zinflt = zinflt + zintfl(i3)
    21  continue
    fluct = (1.0d0 / (4.0d0 * pi * pi)) * rmn2 * zinflt
c
    return
end
```
APPENDIX D
CODE USED TO PRECALCULATE THE EXCLUDED VOLUME TERM

This program performs a three-dimensional Gauss quadrature integration where \( n \) is the number of quadrature points on the intervals. This solves for the free energy of a solution of rods arising out of the excluded volume effect as defined by Onsager. Note that this program generates the 'exvol.dat' files used in the programs "blend.f" and "diblock.f."

The values stored in the file have to be multiplied by concentration squared to give the free energy associated with the excluded volume for a system of rods.
implicit none

double precision w,e,x,pi,exvlar,xmax,xmin,xmn2,xpn2,
&y,ymax,ymin,ymn2,ypn2,p,pmax,pmin,pmn2,ppn2,ptot,ytot,xtot,
&al,sx,sy,yttl,xttl,alpha

integer ix,iy,ip,i,n,ial,ialmax

NOTE: if you change the n value here be sure to change the
corresponding zero-coefficient filename to be read below!!!!

cparameter (n=20,ialmax=27)
parameter (pi=3.141592653589793d0)
dimension w(n),x(n),e(n),y(n),p(n),xtot(n),ytot(n),ptot(n)
&,alpha(ialmax),exvlar(ialmax)

data (alpha(ial),ial=1,ialmax)/0.01d0,2.0d0,5.0d0,10.0d0,20.0d0,
&50.0d0,100.0d0,200.0d0,350.0d0,500.0d0,750.0d0,1000.0d0,
&1500.0d0,2000.0d0,3000.0d0,4000.0d0,5000.0d0,6000.0d0,7000.0d0,
&8000.0d0,9000.0d0,
&10000.0d0,15000.0d0,20000.0d0,25000.0d0,30000.0d0,35000.0d0/

c Alpha loop

c open(unit=55, file='exvol.dat')
do 40 ial=1,ialmax
   al=alpha(ial)

c Set integration limits and compute transformation factors

c xmax=1.0d0
xmin=-1.0d0
xmn2=((xmax-xmin)/2.0d0)
xpn2=((xmax+xmin)/2.0d0)
ymax=1.0d0
ymin=-1.0d0
ymn2=((ymax-ymin)/2.0d0)
ypn2=((ymax+ymin)/2.0d0)
pmax=2.0d0*π
pmin=0.0d0
pmn2=((pmax-pmin)/2.0d0)
ppn2=((pmax+pmin)/2.0d0)

Read zero and coefficient files and rescale the integration interval.

NOTE: if n is changed above the corresponding filename must also be changed here!!!

open(unit=50, file='zeros20')
do 20 i=1,n
   read(50,111)e(i),w(i)
111    format(1x,f12.9,1x,f12.9)
x(i)=xpn2+(xmn2*e(i))
y(i)=ypn2+(ymn2*e(i))
p(i)=ppn2+(pmn2*e(i))
20    continue
close(unit=50)

Main loop

do 100 ix=1,n
   sx=dsqrt(1.0d0-(x(ix)**2))
do 110 iy=1,n
   sy=dsqrt(1.0d0-(y(iy)**2))
do 120 ip=1,n
   ptot(ip)=w(ip)*dsqrt(1.0d0-((x(ix)*y(iy))+(sx*sy*dcos(p(ip))))**2)
120    continue
   yttl=0.0d0
   do 1 i=1,n
      yttl=yttl+ptot(i)
1    continue
if(al.le.200.0d0)then
   ytot(iy)=((yttl*pmn2*dcosh(al*y(iy)))/dsinh(al))
else
    c    ytot(iy)=yttl*pmn2*((dexp(al*y(iy))+dexp(-al*y(iy)
    c    &))/(dexp(al)-dexp(-al)))
    ytot(iy)=yttl*pmn2*(dexp(al*(y(iy)-1.0d0))+dexp(al*(-y(iy)
    &-1.0d0)))
    endif
110 continue
    xttl=dotproduct(ytot,w)
    if(al.le.200.0d0)then
        xtot(ix)=((xttl*ymn2*dchosh(al*x(ix)))/dsinh(al))
    else
        c    xtot(ix)=xttl*ymn2*((dexp(al*x(ix))+dexp(-al*x(ix)
        c    &))/(dexp(al)-dexp(-al)))
        xtot(ix)=xttl*ymn2*(dexp(al*(x(ix)-1.0d0))+dexp(al*(-x(ix)
        &-1.0d0)))
    endif
100 continue
    exvlar(ial)=((al**2)/(8.0d0*pi))*xmn2*dotproduct(xtot,w)
    write(55,157) al,exvlar(ial)
157 format(1x,f10.3,1x,e16.8)
40 continue
    close(unit=55)

c
end
APPENDIX E
CODE USED TO FIND THE COMMON TANGENT POINTS

This program interactively fits a common tangent to two quadratic curves. It is to be used in conjunction with the program "blend.f" to map out the phase diagram. The program "blend.f" creates a file called "blend.fc" which contains the free energy composition curves for several chi values. This file is to be opened and read by this program. This program was written to find the common tangent for three cases: a curve with a curve, a point with a curve, and a curve with a point.
implicit none
double precision a1,b1,c1,a2,b2,c2,arg,comp,datarr,x1,x2,y1,y2,
&cx,cy,pharr
integer pts,i,n2,n1,j,ichi,type,ans,col,dum
character*10 name,name1
dimension comp(51),datarr(50,51),cx(30),cy(30),pharr(4,35)
c
print*, 'Name of output file?'
read(*,'(a10)')name1
print*, 'l=old file, 2=new file'
read*, ans
c *** initialize the array, pharr.
  if(ans.eq.2)then
    do 17 i=l,35
      do 16 j=l,4
         pharr(j,i)=0.0d0
16     continue
17     continue
  elseif(ans.eq.1)then
    open(unit=57,file=name1)
    do 38 i=l,35
       read(57,l12) dum,(pharr(j,i),j-1,4)
38     continue
    close(unit=57)
  endif
c
c
print*, 'What free energy vs. comp. file do you want to open?'
read(*,'(a10)') name
print*, 'NOTE: The number of chi values is set at 21'
print*, 'Change if necessary!!!'
print*, 'Output file is set at 4 columns max!!!'
open(unit=57,file=name)
do 20 i=l,51
c *** NOTE: the j variable corresponds to the number of chi values
c *** Remember to change the value in both the read and the format
c *** statements -- as well as the print statement above!!!(1)
    read(57,30)comp(i),(datarr(j),j=1,21)
30    format(1x,f6.4,21('   ',f9.6))
20    continue
    close(unit=57)

c
5    print*, 'Do you want to print the table? (1=yes, 2=no)'
    read*, ans
    if(ans.eq.1)then
        do 48 i=1,35
            write(*,112) i,(pharr(j,i),j=1,4)
48    continue
        goto 5
    endif

c
    print*, 'Which chi number do you want (type 0 to quit)'
    write(*,*)'The most recent chi value was: ', ichi
    read *, ichi
    if(ichi.eq.0)goto 999
    print*, 'CHOOSE CALCULATION TYPE (type a 1, 2, or 3):
    print*, '1 -- curve: curve'
    print*, '2 -- curve: point'
    print*, '3 -- point: curve'
    read *, type

c
    c *** curve/curve

********************************************************************

    if(type.eq.1)then
        print*, 'input comp. # for STARTING POINT on curve 2'
        read *, n2
        x2=comp(n2)
        y2= datarr(ichi,n2)
        print *, 'input lowest composition NUMBER of curve 1:'
        read *, n1
        print *, 'input number of data points:'
        read *, pts

********************************************************************
do 140 i=1,pts
   cx(i)=comp(n1+i-1)
   cy(i)=datarr(ichi,n1+i-1)
140  continue

   call fit(a1,b1,c1,cx,cy,pts)
   if(a1.lt.0.0d0)then
      print *, 'curve 1 has negative curvature'
      go to 5
   endif

   arg=(x2**2)+(((b1*x2)-y2+c1)/a1)
   if(arg.lt.0.0d0)then
      print*,'Imaginary result'
      goto 5
   endif

   x1=x2-dsqrt(arg)
   y1=(a1*(x1**2))+(b1*x1)+c1
   write (*,111)x1,y1
111    format(1x,'x= ',f8.4,5x,'y= ',f8.4)

   print*,'ENTER COLUMN TO SAVE IN (0 to not enter).'
   read *,col
   if(col.ne.0)then
      pharr(col,ichi)=x1
   endif

   print *, 'input lowest composition NUMBER of curve 2:'
   read *,n2
   print *, 'input number of data points:'
   read *,pts
   do 141 i=1,pts
      cx(i)=comp(n2+i-1)
      cy(i)=datarr(ichi,n2+i-1)
141  continue

   call fit(a2,b2,c2,cx,cy,pts)
   if(a2.lt.0.0d0)then
      print *, 'curve 2 has negative curvature'
go to 5
endif
c

arg=(x1**2)+(((b2*x1)-y1+c2)/a2)
if(arg.lt.0.0d0)then
    print*,'Imaginary result'
goto 5
endif

x2=x1+dsqrt(arg)
y2=(a2*(x2**2))+(b2*x2)+c2
write(*,111)x2,y2
print*,'ENTER COLUMN TO SAVE IN (0 to not enter).'
read*,col
if(col.ne.0)then
    pharr(col,ichi)=x2
endif
c  !*** curve/point *******************************************
elseif(type.eq.2)then
n2=51
x2=comp(n2)
y2=datarr(ichi,n2)
print*,'input lowest composition NUMBER of curve 1:'
read*,n1
print*,'input number of data points:'
read*,pts
do 40 i=1,pts
cx(i)=comp(n1+i-1)
cy(i)=datarr(ichi,n1+i-1)
40 continue
call fit(a1,b1,c1,cx,cy,pts)
if(a1.lt.0.0d0)then
    print*,'curve 1 has negative curvature'
go to 5
endif
c

arg=(x2**2)+(((b1*x2)-y2+c1)/a1)
if(arg.lt.0.0d0)then
  print*, 'Imaginary result'
goto 5
endif

x1=x2-dsqrt(arg)
y1=(a1*(x1**2))+(b1*x1)+c1
write (*,111)x1,y1
print*,'ENTER COLUMN TO SAVE IN (0 to not enter).'
read *,col
if(col.ne.0)then
  pharr(col,ichi)=x1
  pharr(4,ichi)=1.0d0
endif

elseif(type.eq.3)then
  n1=1
  x1=comp(n1)
y1=datarr(ichi,n1)
print*,'input lowest composition NUMBER of curve 2:'
read *,n2
print*,'input number of data points:'
read *,pts
do 41 i=1,pts
  cx(i)=comp(n2+i-1)
cy(i)=datarr(ichi,n2+i-1)
41 continue
call fit(a2,b2,c2,cx,cy,pts)
if(a2.lt.0.0d0)then
  print*,'curve 2 has negative curvature'
go to 5
endif

c
arg=(x1**2)+(((b2*x1)-y1+c2)/a2)
if(arg.lt.0.0d0)then
  print*, 'Imaginary result'
goto 5
endif
x2=x1+dsqrt(arg)
y2=(a2*(x2**2))+(b2*x2)+c2
write (*,111)x2,y2
print*,'ENTER COLUMN TO SAVE IN (0 to not enter).'
read *,col
if(col.ne.0)then
    pharr(col,ichi)=x2
    pharr(1,ichi)=0.0d0
endif
endif

** SAVE THE VALUES IN PERMANENT OUTPUT FILE **

open(unit=57,file=name1)
do 18 i=1,35
    write(57,112) i,(pharr(j,i), j=1,4)
112    format(1x,i2,4(' ',f8.4))
18 continue
close(unit=57)
goto 5

999 stop
end

This is a curve fitting subroutine.
This subroutine performs a least squares fit to the expression:
y=ax**2+bx+c

subroutine fit(a,b,c,x,y,pts)
implicit none
double precision x,u,y,a,b,c,x2,one,hold,hold1
integer i,j,k,l,pts
dimension u(3,4),y(pts),x(pts),one(pts),x2(pts)
c
do 12 i=1,pts
   x2(i)=x(i)*x(i)
one(i)=1.0d0
12    continue
c
   u(1,1)=dotproduct(x2,x2)
   u(1,2)=dotproduct(x2,x)
   u(1,3)=dotproduct(x,x)
   u(1,4)=dotproduct(x2,y)
   u(2,1)=dotproduct(x2,x)
   u(2,2)=dotproduct(x,x)
   u(2,3)=dotproduct(x,one)
   u(2,4)=dotproduct(x,y)
   u(3,1)=dotproduct(x,x)
   u(3,2)=dotproduct(one,x)
   u(3,3)=dotproduct(one,one)
   u(3,4)=dotproduct(y,one)
c
do 1 i=1,3
   hold1=u(i,i)
do 2 j=1,4
      u(i,j)=u(i,j)/hold1
2    continue
   do 3 k=1,3
      if(k.eq.i)go to 3
      hold=u(k,i)
do 4 l=1,4
      u(k,l)=u(k,l)-(u(i,l)*hold)
4    continue
3    continue
1    continue
a=u(1,4)
\[ b = u(2,4) \]
\[ c = u(3,4) \]

\begin{verbatim}
c
    return
end
\end{verbatim}
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