

Thermodynamic Models for Predicting Condensed Phase Equilibria in Polymer Systems

by

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The condensed phase properties of polymer systems are of significant engineering and scientific interest. These properties determine the synthesizability of polymers, their processability, and their performance in a myriad of applications ranging from drug encapsulation to energy storage devices to high performance composites. In addition, polymer systems occur throughout nature and their self-assembly via phase separation contribute to a variety of biological functions, including those of transcription and translation of DNA which are central to life. The importance of mixture phase properties has motivated nearly a century of thermodynamic model development aimed at providing a quantitative description of the phase equilibria of polymer systems. However, the complex thermodynamics of polymer systems have hindered the development of models which are accurate yet generalizable across many polymer systems. Modern advancements in computation and data-driven modeling prompt revisiting polymer mixture models. This thesis investigates new thermodynamic models for phase property predictions.

The first two sections of this thesis describe the development of a joint theory and data-driven thermodynamic model able to predict the phase properties of small molecule mixtures solely from unimolecular parameters. The developed universal fundamental relations (UFR) model not only achieves better correlation of the activity coefficient (a mixture thermodynamic property) but demonstrates an ability to extrapolate to vapor-liquid and liquid-liquid phase equilibria predictions well outside the training dataset. This motivates a similar modelling approach for polymer solutions; however, the lack of a comprehensive dataset of model-independent thermodynamic mixture properties is a strong roadblock. This thesis assembles such a dataset, compiling mixture properties for a range of polymer-solvent systems.

The last three sections of this thesis address the prediction of microstructures arising in melts of copolymers due to microphase separation. Copolymer melts are a model polymer system, with a robust thermodynamic model available in the form of self-consistent field theory (SCFT). However, SCFT has previously been constrained to block copolymer melts, precluding investigation of the larger design space of sequence-defined copolymers. In this thesis, an extension of SCFT is derived which allows prediction of microphase separation in sequence-defined copolymers. In addition, an inverse design algorithm is presented which predicts the sequence necessary for generating a desired microstructure. Unlike prior works, this algorithm learns the structure-to-sequence translation directly via the SCFT thermodynamic model. To complete the thesis, an investigation of sequence features responsible for microphase separation via a spectral approach is performed.

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