

232e Efficient Modelling of Phase Equilibria of Polydisperse Polymer Systems Using the Saft Equation of State

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Accurate prediction of the phase equilibria of polymers and polymer mixtures requires thermodynamic models which are able to deal with large size differences between molecules and strong deviations from ideal behaviour over wide ranges of operating conditions. One such advanced model is the SAFT (Statistical Associating Fluid Theory) equation of state which has proven particularly successful in predicting the thermodynamic behaviour of non-spherical molecules like polymers.

Most practical polymers are polydisperse, with their molecular weight (and possibly other quantities) being distributed over a wide range of values. The corresponding thermodynamic behaviour and properties depend continuously on their molecular weight distribution. A standard approach is to assume a mathematical form for the distribution and then to discretise it into a certain number of pseudo-components. This often leads to problems relating to the efficient handling of large number of pseudo-components, especially in view of the fact that advanced equations of state such as SAFT are already highly nonlinear.

We present a methodology for phase equilibrium calculations of polydisperse polymers. Given a polymer characterized by a set of measurable quantities, an optimization-based algorithm is first used to determine an accurate and computationally efficient discrete representation of the molecular weight distribution. The phase equilibrium problem for the polydisperse system is then solved via a homotopy/continuation algorithm making use of a physical continuation parameter. Starting from the corresponding monodisperse system, the homotopy continuously deforms the system to the desired polydisperse representation, while satisfying certain constraints throughout its path.

The algorithm is applied to several vapour-liquid and liquid-liquid equilibria problems, and is shown to be accurate and reliable, avoiding turning points, bifurcations or stiffness irrespective of the number of pseudo-components introduced by the discretisation.