Group Contribution Model for Predicting Critical Volume with the Flory-Huggins Theory Asymptotic Behavior

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An assumption that has been made by the BYU DIPPR 801 staff in estimating property values for large molecules is that all families eventually converge to the n-alkane family with increasing chain length. For this purpose, much effort has gone into examining the n-alkane family. Specifically, the properties of n-alkanes as the carbon number approaches infinity have been studied to establish asymptotic convergence to other families. Since the critical point is an essential value for many predictive methods of thermophysical and transport properties, it is particularly important to the DIPPR 801 database. Historically, group contribution (GC) models for predicting the critical volume (VC) have assumed a constant contribution from each functional group. This assumption mathematically renders a critical density curve as a function of carbon number that monotonically increases until reaching a limiting value. However, in 1990 Teja reported an experimental maximum in critical density followed by a decrease for the n-alkane, 1-alkene, and 1-alcohol families. Siepmann verified this observed phenomenon by performing Gibbs Ensemble Monte Carlo simulations on large n-alkanes. With the findings of Teja and Siepmann, new prediction models needed to be developed. However, currently there exist two accepted models for predicting VC that have fundamentally different limiting behaviors that cause the correlations to diverge considerably around C_{20}. This research focuses on simulating molecules large enough to determine the infinite carbon length behavior by performing rigorous nonlinear statistical analysis on a generic VC model. Having concluded which asymptotic trend is correct, a novel GC model was developed to agree with experimental data and the accepted trend. This new model reconciles traditional GC theory with Flory-Huggins polymer theory and provides flexibility when predicting small and large molecules of various families. Model validation is obtained by demonstrating how the new VC model improves liquid density prediction for large compounds.