THERMODYNAMIC DESCRIPTION OF BRANCHED MOLECULES

K. Langenbach*, D. Browarzik°, C. Browarzik*, S. Enders*

*Technische Universität Berlin, Chari of Thermodynamics BH 7-1, Ernst-Reuter-Platz 1, 10587 Berlin, Germany.
°Martin-Luther University Halle-Wittenberg, Chemistry / Physical Chemistry, Mühlpforte 1, 06108 Halle (Saale), Germany.

EXTENDED ABSTRACT

In equilibrium thermodynamics physically based equations of state, like the perturbed-chain statistical associating fluid theory [1] of state, have undergone great advancement during the past two decades. These theories based on Wertheim's perturbation theory [2–5] focus on the different functional groups present in the molecule, but assume the molecules to be linear chains. It is often possible to describe branched molecule despite that assumption, but this description demands the adjustment of new pure component parameters. Moreover, for strongly branched molecules like hyper-branched polymers, these kinds of models are not able to describe vapour-liquid equilibria and liquid-liquid equilibria simultaneously [6], even though using a second order perturbation theory. The introduction of molecular architecture, however, does involve higher order perturbation theories. Local correlations between different segments have to be introduced and in this process unknown radial distribution functions occur that have to be approximated somehow [7].

This difficulty can be overcome by assuming the molecules to live on a lattice, where local correlations can be introduced through a Mayer like [8] series expansion in the inverse coordination number z^{-1} and the reduced segmental nearest neighbour interaction energy ε/k_BT. Freed and co-workers [e.g. 9] derived the Lattice Cluster Theory (LCT) in such a manner, with local correlations of up to four consecutive segments. This lattice free energy was made compressible by Dudowicz and Freed [10] by introducing holes into the lattice. However, the LCT in the multi-component formulation is quite unwieldy due to its large equations. Also it is prone to numerical error due to heavy summations. This issue is usually addressed by breaking down the multi-component approach to a lower and specified number of compounds [e.g. 11–14]. However, in this contribution a way is shown to lower the complexity of the multi-component version without loosing any algebraic information, effectively reducing the number of contributions to the free energy from 102 in the original papers [10] to 26 in the new version. Moreover the theory is shown to depend only on the numbers of singly connected self avoiding walks of specific lengths on the graph representation of the respective molecule and no longer on some unconnected or crossing paths, which are usually employed in the equations.

Using the new equations for the free energy of multi-component lattice trees, the mixing behaviour of some hypothetical compounds is calculated in order to assess the influence of architecture on the phase equilibrium of upper critical solution liquid-liquid behaviour. Moreover the vapour-liquid equilibrium of branched alkanes is predicted from the knowledge of the phase behaviour, their linear counterparts show. Mixtures of linear and linear alkanes are investigated and the prediction on the basis of simple mixing rules is compared to experimental data. Furthermore the phase behaviour of Boltorn H3200 in propane correlated with LCT shows the ability of the theory to simultaneously describe vapour-liquid, liquid-liquid and vapour-liquid-liquid behaviour of this hyper-branched polyester with alkane end-groups in propane. Together the theoretical investigations show that LCT in this new version is a highly versatile tool for the description and prediction of the thermodynamics involving branched and highly branched molecules.

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