Flory-Huggins theory

applied in atmospheric aerosol modelling

Fig. 1. Schematic representation of mixing two small molecules of equal size on a lattice.

○ Solvent

● Polymer segments

Fig. 2. Schematic representation of a polymer on a lattice.

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Preface

This project is aimed to give an introduction to the use of the Flory-Huggins theory for modelling of atmospheric aerosol. Most information on the theory and limitations was taken from a textbook on Polymer science and technology by Fried (2003). I have used some of the references I found when conducting a literature search. However, I have chosen to include references that may be of interest to someone that will "dig deeper" in a list at the end of the report in the section "further reading". These are beside the references in the main text, which are included in the reference list.

The project was based on the proposal for the work as suggested by David Simpson in June, 2008, but with some modifications to what was technically feasible in the weeks devoted to the project.

Hopefully the project will be of use to Robert Bergström, the PhD student of David Simpson who will (to my knowledge) continue working on the subject.

The Flory-Huggins theory

In the 1940s it was recognized that thermodynamics of polymeric systems needs to be treated in a special way (Fried, 2003). It was found that experimental data and Raoult law predictions for an ideal solution were not compatible.

To understand non-ideal polymer solutions Flory (1941) and Huggins (1941) independently developed a simple lattice model theory. Their model is based on a thought experiment, since it is based on occupations of a lattice (and molecules can not be given an exact position). Their theory is now commonly known as the Flory-Huggins theory.

The simplest thought experiment is that of mixing
- Low-molecular weight solvent
- Low-molecular weight solute
- Solvent and solute molecules are of the same size

Using the Boltzmann relation for increase in entropy due to mixing, using the probability function and Sterling approximation will lead to the expression for the (molar) entropy change of mixing for an *ideal* solution:

$$\Delta S_m{}^{id} = -R\sum_{i=1}^{N} x_i \ln x_i .$$

X_i is the mole fraction of the solvent and R is the gas constant. The expression can also be obtained through classical thermodynamics of an ideal solution.

The next thought experiment is to regard mixing of
- Low-molecular weight solvent
- High-molecular weight polymer

Each segment of the polymer is described by a position in a lattice which is as large as the solvent molecules. The entropy of mixing these will be smaller since it is restricted by the segments of the polymer being connected. Flory and Huggins gave an expression for the enthalpy of mixing, which would be zero for an ideal solution but is

$$\Delta H_m = z n_1 r_1 \phi_2 \Delta \omega_{12} ,$$

where ω_{12} is the mean field expression of the change in internal energy from mixing

$$\Delta \omega_{12} = \omega_{12} - 0.5(\omega_{11} - \omega_{22}) .$$

It is useful to define a single, dimensionless, energy parameter called the Flory interaction parameter, χ_{12}, which is inversely related to temperature but independent on concentration;

$$\chi_{12} = \frac{z r_1 \Delta \omega_{12}}{kT} .$$

From this the Gibbs free energy of mixing and the activity of the solvent can be deduced (e.g. Fried, 2003; Prausnitz et al. 1999; Petters et al., 2006). The activity for a binary solution will become

$$\ln a_w = \ln(1-\phi) + (1-\frac{1}{r})\phi + \chi\phi^2 , \qquad\qquad (1)$$

where a_w is the activity of water, ϕ is the volume fraction of polymer, r is the chain segment number (polymer volume to water volume ratio). For long-chain polymer the 1/r-term can be neglected.

Limitations to the Flory-Huggins theory

The Flory-Huggins theory is widely used still and has been successful, largely, in describing thermodynamics of polymer solutions. There are a number of limitations to the original formulation. The main ones are (Fried, 2003)

- Applicability only to solutions that are sufficiently concentrated that they have uniform segment density
- There is no volume change of mixing (whereas favourable interactions between polymer and solvent molecules should result in a negative volume change)
- There are no energetically preferred arrangements of polymer segments and solvent molecules in the solution
- The interaction parameter, χ_{12}, is independent of composition

It is also important to note that the Flory-Huggins is a mean-field theory (for the use of the formulation of the change in internal energy due to mixing).

The assumptions/limitations as stated by Flory (1942) himself are

- Quasi-solid lattice in the liquid
- Inter-changeability of segments (not necessarily the same as the polymer structure units) of polymer and solvent molecules in the lattice
- Independence of lattice constants on composition (artificial)
- Polymer molecules are of same size
- Average concentration of polymer segments in cells adjacent to cells unoccupied by the polymeric solute is taken to be equal to the overall average concentration
- The expected number of available positions for each successive segment is overestimated in the formulation as the formula includes double counting of segments, separated by 2 or more segments in the same chain, that will fall on the same position twice

The applicability of Flory-Huggins, mainly for biochemical applications, is discussed in Chan and Dill (1997). They find that Flory-Huggins is more applicable for articulate molecules like crosses and Ls, and it is a reasonable approximation for flexible chains, while globular molecules are better treated in "classical models". The issues and benefits are further discussed in the paper.

Further developments to the Flory-Huggins theory

Here I will only give a short introduction to a few developments of the Flory-Huggins theory. The interested reader is referred to Fried (2003).

Numerous developments to the original theory have been made. One of these is the Flory-Kriegbaum which is a thermodynamic theory for dilute polymer solutions. In this theory individual chains are isolated and surrounded by regions of solvent molecules (the segment density can not be considered as uniform).

The agreement of the original Flory-Huggins theory has also been improved by Koningsveld et al. (1974) using experimental data to empirically modify χ_{12}. Then χ_{12} can become composition dependent and polymer dispersity can be taken into account.

In the case of a thermodynamically good solution the volume change of mixing can be significant; however, this is not accounted for by Flory-Huggins neither for any of the two modifications above. This can lead to weakness in prediction of phase equilibrium. Adopting a statistical-thermodynamics approach based upon the equation of state has substantially improved the theoretical treatment. Different such treatments exist, for example one first suggested by Flory (1965), Sanchez (1978) and Simha (1980). The treatment proposed by Flory (1965) is described in Fried (2003).

The applicability on atmospheric aerosol modelling

In most SOA models the Pankow (1994) formulation of partitioning has been used so far

$$\frac{A_i}{G_i} = C_{OA} \frac{RT}{<MW> \gamma_i p^0},$$

where A_i is aerosol phase, G_i is gas phase and $<MW>$ is average molar weight. His idea was based on the Raoult equation. The Raoult law is really only meant for ideal solutions and therefore only really applicable to dilute conditions such as cloud droplets. However it has been used with the assumption that the solution water activity scales with the mole fraction of water (Petters et al., 2006), or stated differently: the partial pressure of the organic material scales with the mixing ratio of the organic material (personal communication with David Simpson). However, even taking into account the possibility of highly non-ideal solution behaviour it is difficult to explain the unexpectedly large and surprisingly similar equilibrium water contents below 100% RH observed for different polymer and oligomers (Petters et al., 2006).

Suggested by Neil Donahue mixing ratio is probably a poor indicator of what happens in the mixtures, since volume probably is more relevant. Such a theory could be the Flory-Huggins theory (or one further development thereof). This is also suggested by Prausnitz et al. (1999). Even for a zero interaction parameter in the activity equation (1) we can expect large negative deviations from the Raoult law simply due to differences in molecular sizes of solvent and solute (Prausnitz et al., 1999). This is consistent with observations (Petters et al., 2006). Further, (1) is consistent with the observed behaviour of activity being strongly dependent on polymer length for smaller molecules, but less important for longer molecules, especially minimal dependence of SOA water content on degree of polymerisation after a certain amount of time (Baltensperger et al., 2005).

Petters et al. (2006) applied a Flory-Huggins based theory for polymer-water interactions to describe the water activity in aqueous solutions of atmospherically relevant oligomers and polymers (PEG and PAA). They showed by comparison to experiment on particle composed of commercial polymers that it is consistent with observed particle hygroscopic growth and cloud formation behaviour. They call the model a semi-empirical Flory-Huggins/Köhler (FHK) theory.

Prenni et al (2007, same group as Petters et al, 2006) presented that measured droplet activation were inconsistent with hygroscopicity measured below water saturation and Köhler theory expressions based on Raoult law for several parameterizations for water activity. The droplet activation were conducted on SOA in a smog chamber under atmospheric conditions. When using the Flory-Huggins/Köhler theory they note that all solute molecules have to be assumed to be oligomers (which may not be true). FHK can capture the features of the data. However, the good comparison could come from the good flexibility of the equation.

Further reading

I choose not to include all references that I have found in my literature search since I believe them outside of the scope and time limit of this project. Still, I wish to give a list of them, in case they are of interest to others. The list of references (that I have not referred to previously, which can be found in the reference list) will follow below:

- *Solvation: Effects of molecular size and shape.* **Hue Sun Chan and Ken A. Dill. 1994. *J. Chem. Phys. 101, 8 7007-7026.*** Detailed study of the generalised Flory-Huggins theory. Related treatments of Hildebrand and Sharp et al are also studied. They found that when solutes and solvents have sufficient complexity they can interfere with each other in a solution, this means an "entropy of coupling". This is approximated by Flory-Huggins but not by the other theories.
- *Evaluation of the validity of the Flory-Huggins solution theory in terms of miscibility in dextran systems.* **Didem Z. Icoz and Jozef L. Kokini. 2006. *Carbohydrate polymers, 68, 59-67.***
- *Annual reviews of computational physics VI. Montecarlo simulations of interfaces in polymere blends.* **Stauffer, D. (ed). 1999. *Pp 59-128.*** http://books.google.se/
- *On the validity of Flory-Huggins approximation for semiflexible chains.* **Gujrati, P.D. and Goldstein, M. 1981. *J. Chem. Phys., 74, 2596-2603.*** They conclude that in the case of using the Flory-Huggins model for phase transition (for semiflexible chains without a solvent) one must take great care, since the Flory model can not have a first order transition from a disordered phase to a completely ordered crystal (which can be observed in reality).
- Lecture notes found on the internet: *Activity coefficient estimation method* by **Bharat Chandramouli, February 5, 2002.** There are 2 group contributions methods commonly used for the activity of OM. 1/calculation from solubility parameters and 2/ UNIFAC calculation. UNIFAC is the UNIversal functional group Activity Coefficient method. It can be divided between combinational part

and interaction part (which is a residual part) which is fit from experimental data. The Hansen solubility parameter method calculates activity from the solubility parameter and the theory is based on Hildebrand's theory of cohesive energy for disperse systems and extended by Hansen for polar and Hydrogen bonds. Part of this includes the size effect term which is from the Flory-Huggins (for infinitely dilute solutions…). Etc.

- *A note on the Flory-Huggins and self-consistent field theories for polymers.* **Masters, 2007.** *EPL, 78, 26004.*
- *Mixing plate-like and rod-like molecules with solvent: a test of Flory-Huggins lattice statistics.* **Di MArzio et al., 1995.** *J Res. Nat. Inst. Stand. Techn., 100, 2, 173-186.*
- *Assumption of separability of the excluded-volume interaction in polymer physics: Flory-Huggins theory reviewed.* **Bhuttacharjee, 1986.** *Physical review B, 34, 3, 1624-1630.*
- *Chain connectivityand conformal variability of polymers: clues to an adequate thermodynamic description of their solutions, 2a.* **Wolf, 2003.** *Macromolecular Chemistry and Physics, 204, 1381-1390.*
- *Molecular implications of hydrophobic organic partitioning theory.* **Christman and Pfaender, 2006.** *Acta hydrochim hydrobiol, 34, 367-374.*
- *Polymer-polymer interactions: consistent modeling in terms of chain connectivity and conformal response.* **Wolf, 2003.** *Macromolecular chemistry and physics, 207, 65-74.*
- *Free energy of mixing for polymer solutions.* **Yamamoto et al., 2004.** *Macromolecules, 37, 3475-3486.*
- *Extension of the Flory-Huggins theory to study incompatible polymer blends in solution from phase separation data.* **Campos et al., 1996.** *Polymer, 37, 15, 3361-3372.*

Disclaimer

Many formulations were taken directly from the references for 1/lack of time for reformulations 2/ formulations were found adequate and well formulated. Therefore this work should not be used in a formal publication as it is but needs some reformulation and condensation. Some references were not read but only referred to as they were referred to in the articles read (see reference list).

Acknowledgements

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