Modelling component diffusion in aerosol particles using Maxwell-Stefan's laws and the implications for cloud particle formation

A53D-0330

Follow the link for more information and PDF of poster.

Kathryn Fowler[1], Paul Connolly[1] and David Topping[1,2]

[1]School of Earth and Environmental Sciences, The University of Manchester, Manchester, M13 9PL
[2]National Centre for Atmospheric Sciences (NCAS), The University of Manchester, Manchester, M13 9PL

Kathryn.Fowler@manchester.ac.uk

Key Findings

- **The Maxwell-Stefan model implicitly includes solubility or the non-ideal effects of diffusion.**
- **Sustained component separations within aerosol particles can only be modelled with the inclusion of non-ideal effects.**
- **We confirm that understanding the composition of aerosol particles is essential to better model their interactions with cloud systems.**

Model Description

In this study we use a numerical model to solve the Maxwell-Stefan law of diffusion,

$$x_i \nabla \ln a_i = -\sum_{j \neq i}^{n} \frac{c_i \mathbf{J}_j - c_j \mathbf{J}_i}{c^2 \text{Đ}_{ij}}, \qquad (1)$$

where x_i is mole fraction, a_i is activity, c_i is concentration and $\mathbf{J}_i$ is the concentration flux of component i. Comparing our results with the Fickian description of diffusion,

$$\frac{\partial c}{\partial t} = \nabla \cdot D \nabla c. \qquad (2)$$

The diffusion flux is solved on the shell boundaries of an aerosol particle as seen in Figure 1. A moving boundary has been included to account for the addition or loss of water.

The two descriptions of diffusion are related through the so called thermodynamic factor Γ (Xin, 2013),

$$D = \text{Đ}\Gamma, \qquad (3)$$

which is derived using activity coefficients from the UNFAC model.

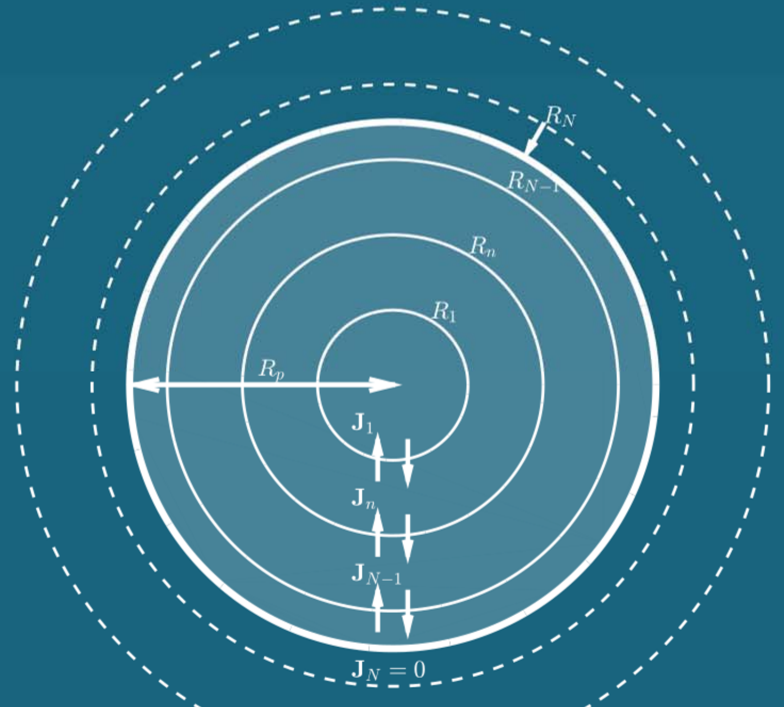

Figure 1 A schematic of the aerosol shell model.

Introduction

Aerosol particles are an uncertain component of the Earth's atmosphere, interacting directly and indirectly with radiation. Properties of aerosol particles depend upon their size and composition. Predicting changes in the composition of individual aerosol particles is difficult theoretically and computationally.

Until now, non-reactive mixing through secondary organic aerosols has been modelled using the Fickian laws of diffusion (Shiraiwa, 2013; O'Meara, 2016). Atmospheric aerosols are comprised of components with varying physical and chemical properties, including solubility. This is confirmed by virtue of the fact that liquid-liquid phase separations can exist within individual aerosol particles (Bertram, 2011). This spectrum of solubility means that modelling diffusion according to the Fickian definition is subject to unknown errors.

In this study, we introduce a new framework of diffusion through aerosol particles based on Maxwell-Stefan's law. This framework uses a gradient in chemical potential to drive mixing through individual particles, for which we use the UNIFAC model. Including non-ideal effects of diffusion allows changes in solubility to be treated alongside any changes in viscosity.

General Model Behaviour

The Fickian model has been initiated with the ideal diffusion coefficient given in Figure 2(b). Including the non-ideal effects of diffusion with the thermodynamic factor in Figure 2(a) allows the model to be component specific, resulting in the Maxwell-Stefan diffusion coefficients in Figure 2(c).

The solubility of a specific component affects the rate of diffusion in three possible ways:

1. ***Fast diffusion***, in the case of a soluble material such as sucrose. The thermodynamic factor is greater than one, hence the Maxwell-Stefan diffusion coefficient is greater than the corresponding ideal diffusion coefficient.

2. ***Inhibited diffusion***, in the case of butyric acid, a monocarboxylic acid with four carbon atoms. The thermodynamic factor has a value between zero and one, hence the diffusion coefficient is less than in the ideal case.

3. ***Reverse diffusion***, in the case of caproic acid, a monocarboxylic acid with six carbon atoms. The thermodynamic factor becomes negative hence diffusion occurs against the concentration gradient and a separation forms.

The corresponding model runs are shown in Figure 3.

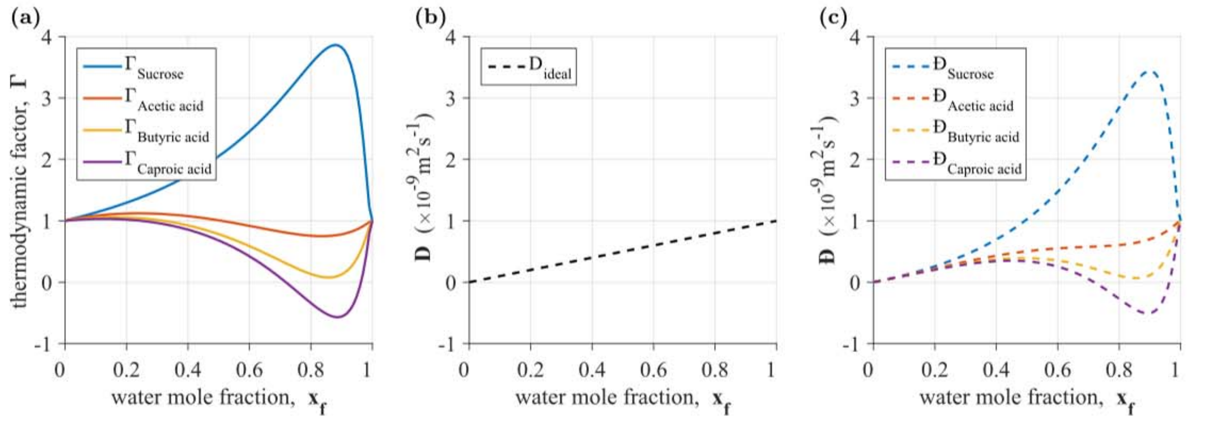

Figure 2 Shows the relationship between (a) the thermodynamic factor, (b) the ideal diffusion coefficient and (c) the resulting Maxwell-Stefan diffusion coefficients from Equation 3. The ideal coefficient of diffusion has been found using the Darken equation, predicting a linear relationship between water mole fraction and diffusion coefficient.

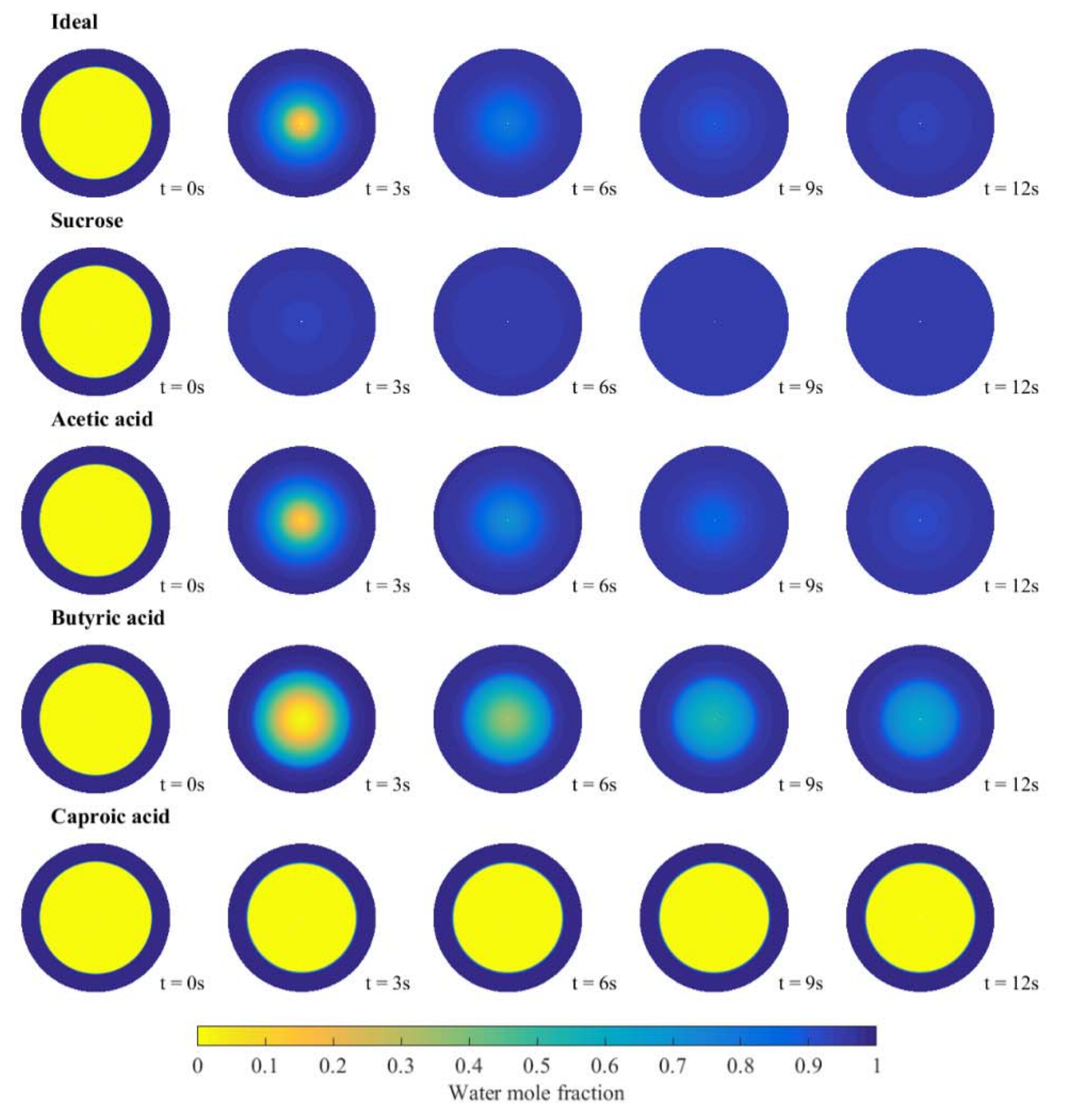

Figure 3 Shows the change in water mole fraction across a particle of radius R_p with liquid water outer shell. The model has been initiated with $R_p=10^{-7}$ m and the diffusion coefficients from Figure 2.

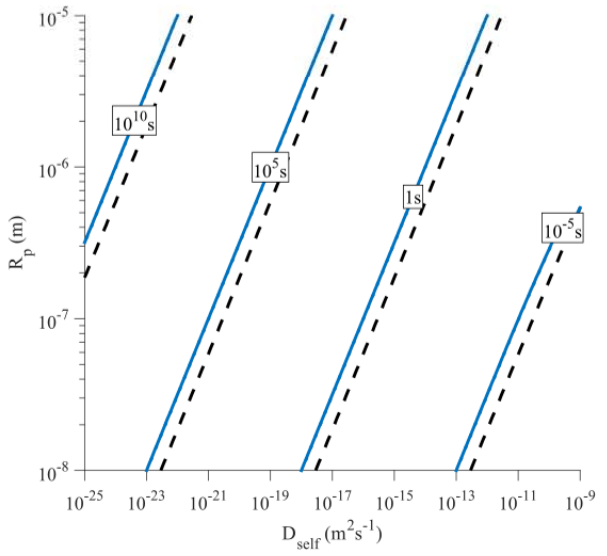

Figure 4 shows lines of constant e-folding time as defined by Zaveri (2014). The dashed line was calculated using the Fickian model and the blue line shows the shift in e-folding times for sucrose calculated using the Maxwell-Stefan model.

Atmospheric Implications

It is important to understand changes in atmospheric aerosol particle composition and how this could impact upon their hygroscopic response to changing conditions of temperature, pressure and relative humidity. The main micro-physical processes that could be affected by aerosol composition are

- Particle hygroscopicity, or the ability of a cloud particle to take up water is highly dependent on aerosol composition.
- The activation of cloud condensation nuclei, will be particularly dependent on non-ideal and solubility effects. This can be inferred from Figure 4, which shows that there is a shift in e-folding time under all conditions of radius and diffusivity.
- At low temperatures, where viscosity is high or the diffusion coefficient is small, the rate and mode of ice nucleation has been found to be affected (Wagner, 2012).
- Particle composition could also have a profound impact on the way aerosols interact directly with radiation.

Conclusion

Through simple binary systems of water and a secondary organic aerosol, we have shown that there is a complicated relationship between the ideal and non-ideal effects of mixing. Atmospheric aerosols are much more complicated systems, with a far greater number of components, all with differing properties. Therefore further study is required to test these frameworks of diffusion against laboratory data. We are also implementing the Fickian and Maxwell-Stefan frameworks into a cloud parcel model to investigate the sensitivity of particle activation on their composition.

References

Bertram, A. K., Martin, S. T., Hanna, S. J., Smith, M. L., Bodsworth, A., Chen, Q., … Zorn, S. R. (2011). Predicting the relative humidities of liquid-liquid phase separation, efflorescence, and deliquescence of mixed particles of ammonium sulfate, organic material, and water using the organic-to-sulfate mass ratio of the particle and the oxygen-to-carbon ele. Atmospheric Chemistry and Physics, 11(21), 10995–11006.

O'Meara, S., Topping, D. O., & McFiggans, G. (2016). The rate of equilibration of viscous aerosol particles. Atmospheric Chemistry and Physics, 16(8), 5299–5313.

Shiraiwa, M., Zuend, A., Bertram, A. K., & Seinfeld, J. H. (2013). Gas-particle partitioning of atmospheric aerosols: interplay of physical state, non-ideal mixing and morphology. Physical Chemistry Chemical Physics, 15(27), 11441.

Xin, L. (2013). Diffusion in Liquids: Equilibrium Molecular Simulations and Predictive Engineering Models. PhD Thesis, Delft U. of T.

Zaveri, R. A., Easter, R. C., Shilling, J. E., & Seinfeld, J. H. (2014). Modeling kinetic partitioning of secondary organic aerosol and size distribution dynamics: representing effects of volatility, phase state, and particle-phase reaction. Atmospheric Chemistry and Physics, 14(10), 5153–5181.

Acknowledgements

EAO NERC SCIENCE OF THE ENVIRONMENT MANCHESTER 1824 The University of Manchester National Centre for Atmospheric Science NATURAL ENVIRONMENT RESEARCH COUNCIL