Diffusion through aerosol particles: a new framework and the implications for atmospheric processes

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

[1]School of Earth, Atmospheric 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

Aerosols are liquid or solid particles, submicron in diameter, suspended in a gas. Originating from natural sources and human activities they are essential for cloud formation, affecting both the hydrological cycle and the Earth's radiation balance.

Until now, diffusion through aerosol particles has been modelled using Fickian laws. However, recent evidence suggests that steep gradients in concentration can exist within individual particles, which indicates that mixing is inhibited [1].

In this study, we compare a new framework based on Maxwell-Stefan's laws of diffusion to the widely used Fickian framework [2] and discuss what implications this could have for atmospheric processes.

Frameworks of diffusion

Fickian diffusion is driven by a gradient in concentration; therefore only ideal interactions between the n components are considered in the diffusion coefficient.

$$\mathbf{J}_i = -c \sum_{i \neq j}^{n} \mathrm{D}_{ij} \nabla x_j$$

$\mathbf{J}_i$ diffusion flux of component i
∇x_j mole fraction gradient of component j
c a constant related to concentration
D_{ij} Fickian diffusion coefficient of component i through j

Maxwell-Stefan diffusion is driven by a gradient in chemical potential; therefore non-ideal effects of diffusion are included. The non-ideal effects are found by adjusting two parameters in the UNIFAC model based on the chemical functional groups.

$$\frac{x_i}{RT} \nabla \mu_i = -\sum_{i \neq j}^{n} \frac{c_i \mathbf{J}_j - c_j \mathbf{J}_i}{c^2 Đ_{ij}}$$

$\mathbf{J}_i$ diffusion flux of component i
x_i mole fraction of component i
$\nabla \mu_i$ chemical potential gradient of component i
c_i concentration of component i
c constant related to concentration
R gas constant
T temperature
$Đ_{ij}$ Maxwell-Stefan coefficient of diffusion of component i through j

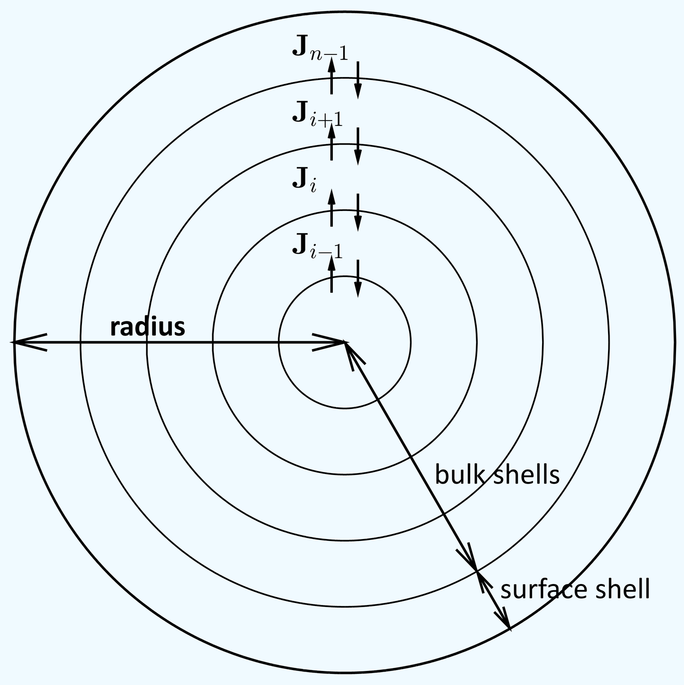

Figure 1: A schematic of the aerosol shell model, where J_i is the diffusion flux at the boundary of shell i. The diffusion fluxes at the shell boundaries are calculated and changing aerosol composition is investigated over time.

General model behaviour

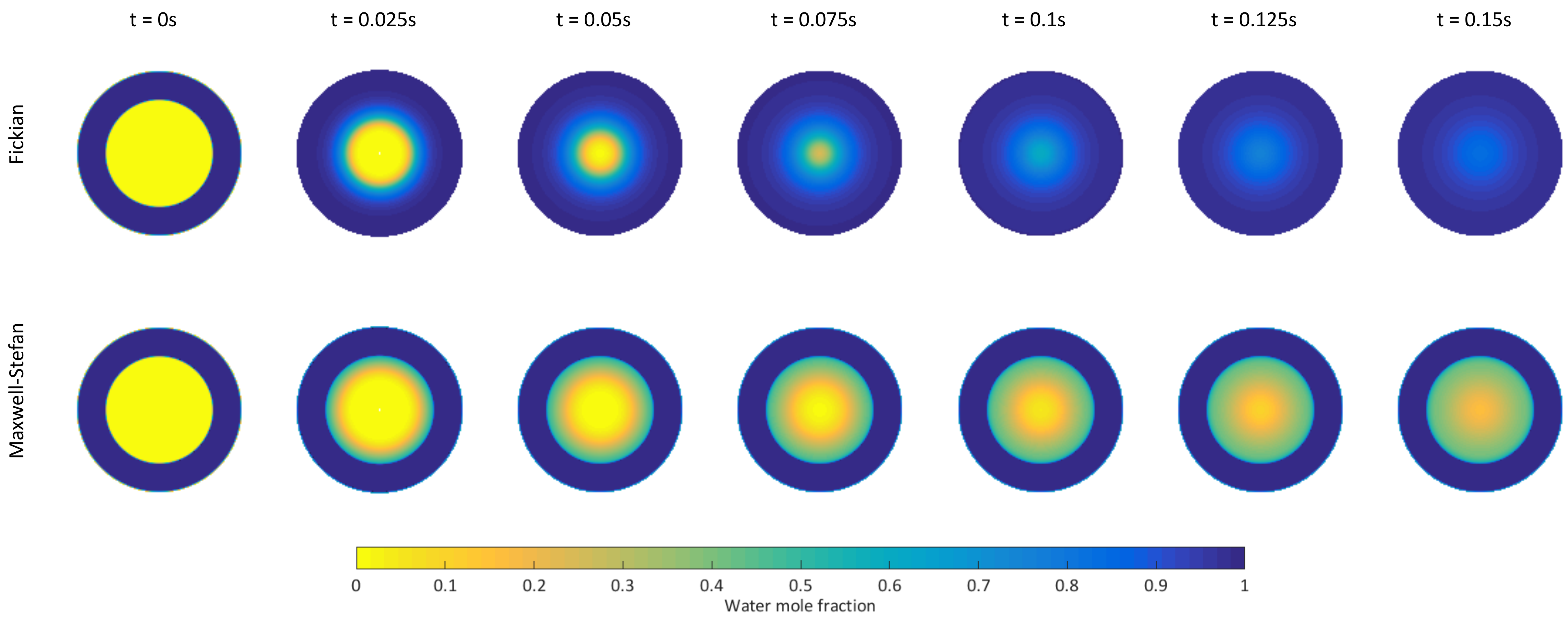

Figure 3: Shows the change in water mole fraction with time through an aerosol particle. The initial radius of a hexanoic acid particle is 10^{-7} m, with a liquid water shell around the outside. Hexanoic acid has been chosen as organic compounds, such as carboxylic acids account for up to 70% of matter in the atmosphere. Using the Fickian model and ignoring the non-ideal effects of diffusion causes the aerosol particle to equilibrate very quickly compared to the Maxwell-Stefan model, where a separation between the two compounds is sustained. The key factors that affected the rate of mixing in this modelling study were; aerosol solubility, particle size, initial composition and aerosol viscosity.

The study has compared the rate of diffusion for other organic compounds. These results can be found by following the QR code below.

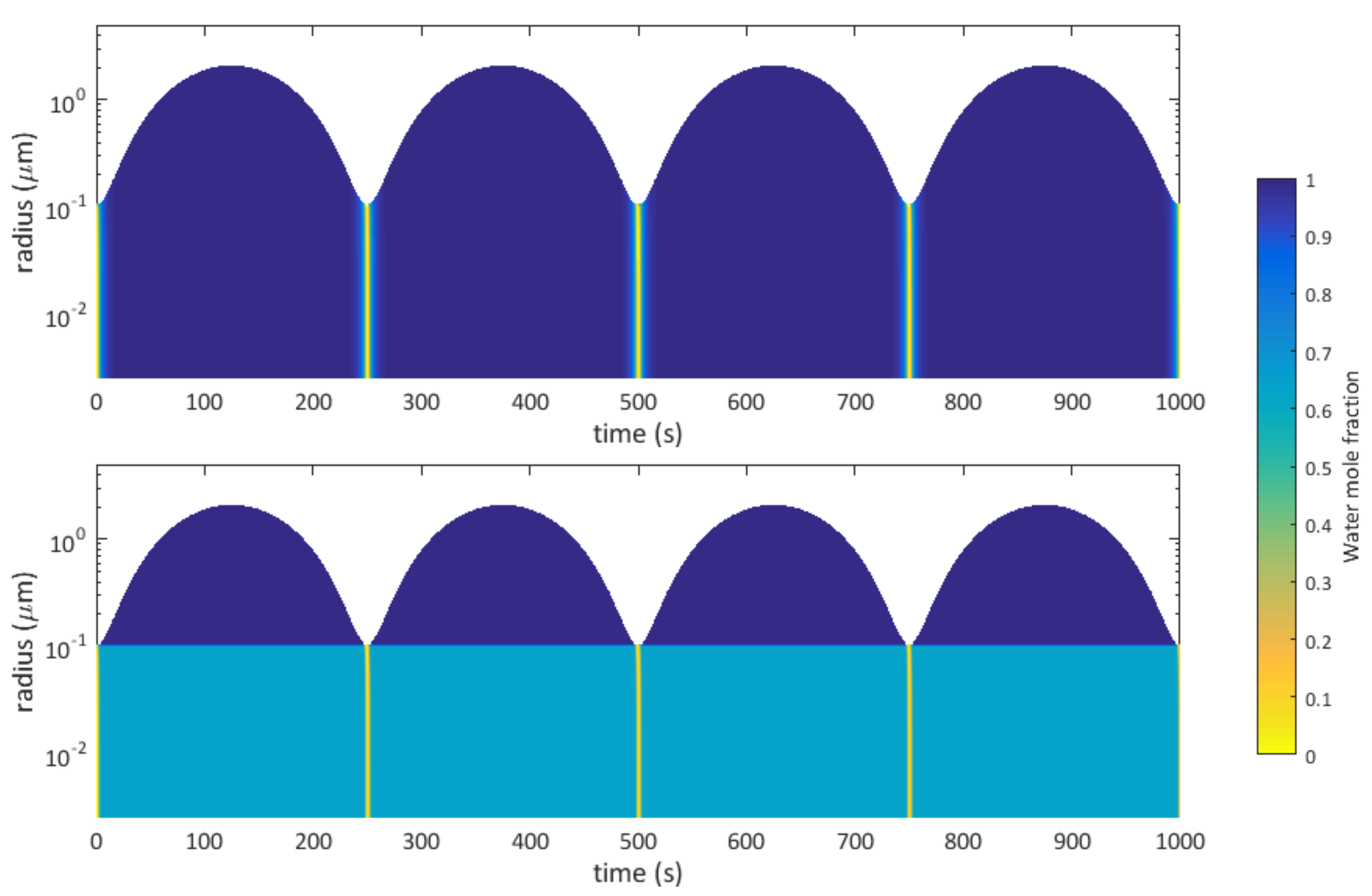

Figure 4: A hexanoic acid aerosol with an initial radius of 10^{-7}m undergoes a series of cycles where water is deposited on the surface of the particle. The figure shows how the radial composition of the aerosol changes through time, the upper pannel uses the Fickian framework and lower panel the Maxwell-Stefan framework. If aerosol particles do not equilibriate to a constant composition on the scale of atmospheric processes, this could have a significant impact on cloud lifetimes, precipitation rates and the radiative properties of modelled cloud systems.

Conclusions

- The Maxwell-Stefan diffusion model allows the existence of liquid-liquid phase separations, however the Fickian model will always diffuse a substance from area of greatest concentration to lowest concentration.
- The Maxwell-Stefan model is suited to describing complex multicomponent diffusive systems through tested mixing rules; these systems are commonly found in atmospheric aerosol particles.
- The composition of an atmospheric aerosol particle can have significant implications for water uptake, which is key to the formation and growth of liquid cloud droplets, the formation of ice, the way aerosols interact with radiation and chemical reactions occurring within cloud systems [3].
- This study questions whether the current Fickian frameworks used to describe diffusion through aerosol particles are the most physically appropriate [4], giving an alternative diffusion framework based on the Maxwell-Stefan laws.

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