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Non-Fickian diffusion in viscous aerosol particles

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Abstract

Slow condensed phase diffusion in organic aerosol particles can impede many chemical and physical processes associated with atmospheric aerosol (e.g. gas-particle equilibrium partitioning). The characteristic times associated with these high viscosity particles are typically modelled using a concentration-dependent diffusivity within a purely Fickian framework. In that model, the medium in which diffusion is taking place is treated as being inviscid as far as mass transport is concerned. In this report, we investigate the validity of assuming that the viscosity is equal to zero by using a transport model that includes viscous pressure gradients. It is found that the effect of viscosity is negligible for particles with radii that are larger than 100 nm but, below that radius, it can delay water uptake and loss by orders of magnitude for physically realistic viscosities. However, if the Stokes-Einstein relation is obeyed then, even for nanosized particles, viscosity can be ignored. In addition to numerical calculations, a dimensionless Deborah number is defined that indicates the significance of Fickian diffusion compared to the rheological response during water transport.

Keywords: Diffusion, Viscosity, Aerosol

1 Introduction

Volatile organic compounds (VOCs) in our atmosphere originate from both anthropogenic and biogenic emissions. Gas-phase reactions of VOCs with the OH radical and other oxidants result in an enormous number of oxidized organic compounds with much lower vapour pressures.^{1,2} These products are often classified using volatility ranges (e.g. as semi-volatile or low-volatility organic compounds) and can condense to form secondary organic aerosol (SOA) particles.³ SOA is the dominant component of organic particulate matter in the atmosphere⁴ and impacts both climate and air quality. Further, fine SOA particles can decrease visibility during photochemical smog episodes,⁵ result in a blue haze that is the namesake of several mountain ranges,⁶ exacerbate existing medical conditions, and increase mortality risk.⁷

While the broad strokes of SOA formation have been understood for many decades,⁵ elucidating the underlying dynamics and physical properties of SOA particles remains an ongoing challenge due to several complicating factors, one of which is that the number of unique organic constituents in the atmosphere is enormous.^{8,9} Various methods have been pursued in order to avoid directly dealing with the complex chemical nature of the SOA condensed phase. For instance, two-dimensional frameworks based around the volatility of SOA components can make understanding aerosol composition and chemical evolution a tractable problem.¹⁰⁻¹²

The SOA condensed phase is known to exist in a wide a range of viscosities associated with phase states such as liquids (less than 10^2 Pa·s), semisolids (between 10^2 and 10^{12} Pa·s) and solids (e.g. glasses with viscosities greater than 10^{12} Pa·s).¹³ These states and viscosities are very sensitive to water activity and can impede mass transport and result in much longer equilibration times with the surrounding gas phase.¹⁴ There are currently an array of laboratory-

based methods being used to investigate the viscosity atmospheric organic aerosol particles.^{15,16} These laboratory studies will often utilize binary mixtures of water and a single organic as proxies for SOA. Sucrose is one of the most popular organics in these studies for several reasons: (1) the physical properties of the water-sucrose system have been well-studied by food science researchers, (2) sucrose has an O:C ratio similar to oxidized material found in SOA, (3) it can form a glass under relative humidity (RH) and temperature conditions that are easily achievable in the laboratory, (4) it is known to possess viscosity and diffusivity similar to SOA for a range of atmospheric conditions, and (5) sucrose is cheap and easy to work with.^{17–25} Fig. 1 presents several diffusivity and viscosity datasets for aqueous sucrose.

The focus of this work is on condensed phase mass transport in SOA particles, specifically on water uptake and loss in the model system of water-sucrose. We seek to address the following question: does viscosity affect mass transport during uptake and loss or can the process be entirely explained using only Fickian diffusion? We explore this question using a model where the particle's equilibration with its surrounding environment is governed by both concentration-dependent diffusivity and viscous flow. The model developed here is similar to the viscous/Thomas-Windle model for case II diffusion²⁶ which has previously been used to model non-Fickian diffusion in glassy polymers.^{27,28}

2 Theory

2.1 Model and boundary value problem formulation

We present the governing and constitutive equations that are used in a model of mass flux that is driven by both by gradients in chemical potential and viscous pressure. Following

this, we focus on the moving boundary problem of a spherical aqueous particle containing a non-volatile solute that responds to a stepwise change in the surrounding RH.

The equation of continuity for species α in a non-reacting solution is

$$\frac{\partial \rho_\alpha}{\partial t} + \nabla \cdot \rho_\alpha \mathbf{v} = -\nabla \cdot \mathbf{j}_\alpha, \quad (1)$$

the continuity equation is

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \mathbf{v} = 0, \quad (2)$$

and the equation of motion is

$$\rho \left(\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} \right) = -\nabla p + \nabla \cdot \sigma + \rho \mathbf{g}, \quad (3)$$

where ρ_α is the mass concentration of species α , $\mathbf{v}$ is the mass average velocity, $\mathbf{j}_\alpha$ is the mass flux of species α , ρ is the mass density of the solution, p is the pressure, σ is the stress tensor, and $\mathbf{g}$ is the external force per unit mass.

For a solution with N components (including the solvent), the generalized Maxwell-Stefan (MS) equations can be combined with the expression for the diffusional driving forces to yield²⁹

$$\begin{aligned} x_\alpha \nabla \ln a_\alpha + \frac{1}{cRT} \left((\phi_\alpha - w_\alpha) \nabla p - \rho_\alpha \mathbf{g}_\alpha + w_\alpha \sum_{\beta=1}^N \rho_\beta \mathbf{g}_\beta \right) \\ = - \sum_{\beta \neq \alpha}^N \frac{x_\alpha x_\beta}{\mathcal{D}_{\alpha\beta}} \left(\frac{D_\alpha^T}{\rho_\alpha} - \frac{D_\beta^T}{\rho_\beta} \right) (\nabla \ln T) - \sum_{\beta \neq \alpha}^N \frac{x_\alpha x_\beta}{\mathcal{D}_{\alpha\beta}} (\mathbf{v}_\alpha - \mathbf{v}_\beta). \end{aligned} \quad (4)$$

For species α , x_α is the mole fraction, a_α is the activity, $\phi_\alpha = \rho_\alpha \bar{v}_\alpha$ is the volume fraction, $\bar{v}_\alpha$ is the partial specific volume, w_α is the mass fraction, $\mathbf{g}_\alpha$ is the force per unit mass (acting on species α), D_α^T is the multicomponent thermal diffusion coefficient, and $\mathbf{v}_\alpha$ is the velocity. Additionally, c is the total molar concentration, R is the gas constant, T is the temperature, and $\mathcal{D}_{\alpha\beta}$ are the multicomponent MS diffusivities. The relationship $\mathbf{v}_\alpha = \mathbf{j}_\alpha / \rho_\alpha - \mathbf{v}$ connects

82 velocity to flux. The derivative in the expression $\nabla \ln a_\alpha$ is taken at constant T and p . Under
 83 isothermal conditions and in the absence of forced diffusion ($\mathbf{g}_\alpha = 0$), Eq. 4 reduces to

$$x_\alpha \nabla \ln a_\alpha = - \sum_{\beta \neq \alpha}^N \frac{x_\alpha x_\beta}{\mathcal{D}_{\alpha\beta}} \left(\frac{\mathbf{j}_\alpha}{\rho_\alpha} - \frac{\mathbf{j}_\beta}{\rho_\beta} \right) - \frac{\phi_\alpha - w_\alpha}{cRT} \nabla p. \quad (5)$$

84 The pressure in Eq. 5 is determined using Eq. 3. For the case when $\mathbf{g} = 0$ and inertia is
 85 neglected (i.e. the left-hand side of Eq. 3 is zero), this yields

$$\nabla p = \nabla \cdot \sigma. \quad (6)$$

86 The stress tensor is then found using a stress-strain constitutive equation. Here, we begin with
 87 the Maxwell model³⁰

$$\frac{1}{E} \frac{\partial \sigma}{\partial t} = - \frac{\sigma}{\eta} + \frac{\partial \varepsilon}{\partial t}, \quad (7)$$

88 where ε is the infinitesimal strain tensor, E is the Young's modulus, and η is the concentration-
 89 dependent viscosity of the dashpot in the Maxwell model.

90 Eq. 7 can be reduced to the viscous model

$$\sigma = \eta \frac{\partial \varepsilon}{\partial t}, \quad (8)$$

91 when E is assumed to be infinite. The rate-of-strain tensor is

$$\frac{\partial \varepsilon}{\partial t} = \frac{1}{2} [\nabla \mathbf{v} + (\nabla \mathbf{v})^T]. \quad (9)$$

92 With the auxiliary relations

$$\sum_{\alpha=1}^N \mathbf{j}_\alpha = 0 \quad \text{and} \quad \mathcal{D}_{\alpha\beta} = \mathcal{D}_{\beta\alpha}, \quad (10)$$

93 and Eq. 5, the mass fluxes for a binary system ($N = 2$) are found to be

$$\mathbf{j}_\alpha = -\rho_\alpha \mathcal{D}_{12} \left(\frac{1-w_\alpha}{1-x_\alpha} \right) \left(\nabla \ln a_\alpha + \frac{\phi_\alpha - w_\alpha}{c_\alpha RT} \nabla p \right), \quad (11)$$

where α is either 1 or 2 and c_α is the molar concentration of species α .

Multiplying both sides of Eq. 1 by $\bar{v}_\alpha$, summing the result over all N components, and then applying the relation

$$\sum_{\alpha=1}^N \bar{v}_\alpha \rho_\alpha = 1, \quad (12)$$

will result in

$$\mathbf{v} = - \sum_{\alpha=1}^N \bar{v}_\alpha \mathbf{j}_\alpha. \quad (13)$$

This equation is useful as it allows the mass average velocity to be replaced by a sum of the products of mass fluxes with their respective partial specific volumes. For a binary system, when Eq. 13 is used along with the first auxiliary relation from Eq. 10, then Eq. 1 can be written as

$$\frac{\partial \rho_\alpha}{\partial t} = -\bar{v}_\beta \nabla \cdot \rho \mathbf{j}_\alpha, \quad (14)$$

where $\beta = 2$ when $\alpha = 1$ and $\beta = 1$ when $\alpha = 2$. Once $\mathbf{j}_\alpha$ is known from Eq. 11, then the rate of change of the mass concentration can be calculated.

We will examine the problem of water uptake and loss in a spherical particle with a time-dependent radius $s(t)$ and where $\alpha = 1$ is water and $\alpha = 2$ is a non-volatile solute. In spherical coordinates, if the mass concentration is always radially symmetric, we can use the fact that the velocity field only has a radial component to set $\sigma_{\phi\phi} = \sigma_{\theta\theta}$. Therefore, Eq. 6 will be

$$\frac{\partial p}{\partial r} = \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \sigma_{rr}) - \frac{2\sigma_{\theta\theta}}{r}. \quad (15)$$

The stresses for the viscous model can be determined using Eqs. 8 and 9. The components of the stress tensor relevant to Eq. 15 will be

$$\sigma_{rr} = \eta \frac{\partial v_r}{\partial r} \quad \text{and} \quad \sigma_{\theta\theta} = \eta \frac{v_r}{r}, \quad (16)$$

where v_r is the radial component of the mass average velocity.

As only the radial component of the mass flux of each species, $j_{r,\alpha}$, will be non-zero, v_r in Eqs. 16 can be replaced with the mass flux using Eq. 13. Combining these results allows Eq. 11 to be written as

$$j_{r,\alpha} = -\rho_\alpha \mathcal{D}_{12} \left(\frac{1-w_\alpha}{1-x_\alpha} \right) \left[\frac{\partial \ln a_\alpha}{\partial r} + \Delta \bar{v} \frac{\phi_\alpha - w_\alpha}{c_\alpha RT} \left(\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \eta \frac{\partial j_{r,\alpha}}{\partial r} \right) - \frac{2\eta j_{r,\alpha}}{r^2} \right) \right], \quad (17)$$

where $\Delta \bar{v} = \bar{v}_2 - \bar{v}_1$ for $\alpha = 1$ and $\Delta \bar{v} = \bar{v}_1 - \bar{v}_2$ for $\alpha = 2$. Applying Eq. 14 allows the partial derivatives of $j_{r,\alpha}$ with respect to r in Eq. 17 to be eliminated. However, if the resulting equation is then solved for $j_{r,\alpha}$, it will yield a fairly cumbersome expression. To avoid this, we assume that Eq. 14 can be approximated as

$$\frac{\partial \rho_\alpha}{\partial t} = -\frac{\bar{v}_\beta \rho}{r^2} \frac{\partial}{\partial r} (r^2 j_{r,\alpha}). \quad (18)$$

Applying this equation to Eq. 17 yields the approximate mass flux in the viscous model:

$$j_{r,\alpha} = -\frac{\rho_\alpha \mathcal{D}_{12}}{\varphi} \left(\frac{1-w_\alpha}{1-x_\alpha} \right) \left[\frac{\partial \ln a_\alpha}{\partial r} - \frac{\Delta \bar{v}}{\rho \bar{v}_\beta} \frac{\phi_\alpha - w_\alpha}{c_\alpha RT} \frac{\partial}{\partial r} \left(\eta \frac{\partial \rho_\alpha}{\partial t} \right) \right], \quad (19)$$

where

$$\varphi = 1 - 2\rho_\alpha \mathcal{D}_{12} \frac{\Delta \bar{v}}{r} \left(\frac{1-w_\alpha}{1-x_\alpha} \right) \left(\frac{\phi_\alpha - w_\alpha}{c_\alpha RT} \right) \frac{\partial \eta}{\partial r}. \quad (20)$$

When Eq. 19 is inserted into Eq. 14, the resulting partial differential equation will be in a form that has been previously studied in one dimensional cartesian coordinates when modelling case II diffusion in polymers.^{31,32} However, the partial differential equations in those studies were derived using a coordinate transformation that cannot be directly applied to spherical coordinates (even with radial symmetry) and hence our differing approach.

Due to symmetry, the boundary conditions at the centre of the spherical particle are

$$v_r = 0, \quad \frac{\partial \rho_\alpha}{\partial r} = 0, \quad \text{and} \quad j_{r,\alpha} = 0 \quad \text{at} \quad r = 0. \quad (21)$$

At the surface, we choose the boundary condition that

$$a_1 = \frac{\text{RH}}{100\%} \quad \text{at} \quad r = s(t), \quad (22)$$

where a_1 is the activity of water at the surface and RH is the percent relative humidity of the environment surrounding the particle for $t > 0$. The boundary condition in Eq. 22 is typically used when condensed phase diffusion is much slower than gas phase diffusion and is often suitable for water uptake and loss in high viscosity atmospheric particles.^{33,34} Prior to the stepwise change in RH at $t = 0$, the activity of the entire particle will be uniform at its initial value.

Finally, the rate of change of the radius can be found by applying the law of conservation of mass to a non-volatile species at the surface of the particle³⁵

$$\frac{ds}{dt} = \frac{j_{r,\alpha}}{\rho_\alpha} + v_r \quad \text{at} \quad r = s(t). \quad (23)$$

Here, Eq. 23 will be applied to $\alpha = 2$ which is a non-volatile solute.

Numerical solution

The moving-boundary problem defined by Eqs. 14 and 17 and the boundary conditions in Eqs. 21 and 22 is solved using an adaptive grid finite-volume scheme.^{36–38} For the adaptive grid part of the scheme, the spherical particle is divided into K shells where each shell has a thickness of $\Delta r = s(t)/K$. Therefore, the time-dependent thickness of each shell is

$$\frac{\partial \Delta r}{\partial t} = \frac{1}{K} \frac{ds}{dt} = \frac{\Delta r}{s} \frac{ds}{dt}, \quad (24)$$

where ds/dt is calculated using Eq. 23. The radial coordinates of the k th shell are $r_k = (k-1/2)\Delta r$ for the centre, $r_{k+1/2} = k\Delta r$ for the outer edge, and $r_{k-1/2} = (k-1)\Delta r$ for the

inner edge. The time-dependent position of the shell centre is

$$\frac{\partial r_k}{\partial t} = (k-1/2) \frac{d\Delta r}{dt} = \frac{r_k}{s} \frac{ds}{dt}. \quad (25)$$

Eq. 14 is discretized using the finite volume method by integrating over the k th spherical shell. After some manipulation, this yields

$$\frac{4}{3}\pi(r_{k+1/2}^3 - r_{k-1/2}^3) \left(\frac{\partial \rho_{\alpha,k}}{\partial t} + \frac{3\rho_{\alpha,k}}{s} \frac{ds}{dt} \right) - 4\pi \left[\frac{r^3 \rho_{\alpha}}{s} \frac{ds}{dt} - r^2 \bar{v}_{\beta} \rho j_{r,\alpha} \right] \Big|_{r_{k-1/2}}^{r_{k+1/2}} = 0, \quad (26)$$

where

$$\rho_{\alpha,k} = \frac{1}{\Delta r} \int_{r_{k-1/2}}^{r_{k+1/2}} \rho_{\alpha} dr. \quad (27)$$

The boundary condition at the surface of the sphere is given in Eq. 22 and is implemented by adding an additional shell at $K+1$ that always satisfies the condition. At the centre of the sphere, the symmetry condition stated in Eq. 21 is implemented in Eq. 26 by setting $j_{r,\alpha}(r_{1/2}) = 0$. At each time step, the mass fluxes at all of the shell edges not located at either of the two boundaries are found by solving Eq. 17 numerically using the finite difference method. Then, explicit time integration is used to solve Eq. 26 and the size of each time step, Δt , is calculated using $\Delta t = \mu(\Delta r)^2 / \max\{\mathcal{D}_{12}\}$, where $\max\{\mathcal{D}_{12}\}$ is the largest value of $\mathcal{D}_{12}$ in any one of the shells at the current time. The value of μ is set to 0.05 in all calculations. The radius at $t+\Delta t$ is calculated using Eq. 23.

3 Results and discussion

Aqueous sucrose particles were used here as the model system for SOA (species 1: water, species 2: sucrose). Temperature and concentration-dependent parameterizations were used for both the water activity, a_1 , and the binary (Fickian) diffusion coefficient, D_{12} .¹⁷ The density of

aqueous sucrose was calculated using $\rho = 1/(\bar{v}_1 w_1 + \bar{v}_2 w_2)$, where $\bar{v}_1 = 1.000 \times 10^{-3} \text{ m}^3/\text{kg}$ and $\bar{v}_2 = 6.320 \times 10^{-4} \text{ m}^3/\text{kg}$. These parameters were found by fitting tabulated measurements.³⁹ The MS diffusivity was calculated using the relation⁴⁰

$$\mathcal{D}_{12} = \Gamma_{12}^{-1} D_{12}, \quad (28)$$

where

$$\Gamma_{12} = 1 + x_1 \left. \frac{\partial \ln \gamma_1}{\partial x_1} \right|_{T,p}. \quad (29)$$

In Eq. 29, γ_1 is the activity coefficient for water in aqueous sucrose and connects the activity and mole fraction through the relationship $a_1 = \gamma_1 x_1$.

The Stokes-Einstein equation was used to calculate the viscosity

$$\eta_{\text{SE}} = \frac{k_B T}{6\pi r_0 D_{12}}, \quad (30)$$

where k_B is the Boltzmann constant and r_0 is the molecular radius. For the aqueous solutions studied here, r_0 was set to 0.2 nm.¹⁸ From Eq. 30 it is immediately apparent that if D_{12} has a strong dependence on water activity and temperature then η_{SE} will as well.

Fig. 2 shows the reduced characteristic equilibration time, τ/s_0^2 , for either water uptake or loss for a step-wise increase in RH (1 to 50%) or decrease in RH (50 to 1%). The characteristic equilibration time, τ , is itself defined using

$$s(\tau) = (s_0 - s_\infty)/e + s_\infty \quad (31)$$

where s_0 is the particle radius at $t = 0$, s_∞ is the particle radius as $t \rightarrow \infty$, and $s(\tau)$ is the radius at which $t = \tau$. The quantity τ/s_0^2 was plotted in Fig. 2 rather than simply τ because it is independent of the initial radius when water uptake or loss is governed only by Fickian diffusion (even for a concentration-dependent diffusivity). Thus, deviations from the constant

τ/s_0^2 make it straightforward to distinguish between cases when viscosity impacts uptake and loss and when it does not.

The calculations in Fig. 2 were performed across a large range of particle radii, temperatures, and multiples of the Stokes-Einstein viscosity. Concerning this last choice, direct measurements of the viscosity of aqueous sucrose have shown that measured viscosity can exceed Stokes-Einstein predictions by several orders of magnitude below 60% RH. For instance, at a RH of 28%, viscosity that is a factor of 10^6 larger than the Stokes-Einstein prediction has been observed.⁴¹ This breakdown is also clearly seen with the measurements presented in Fig. 1. Therefore, all of the cases studied here are at least physically plausible.

When viscosity obeys the Stokes-Einstein relation, its effect on the reduced equilibration time is negligible. This can be seen in all panels of Fig. 2 where the curves $\eta = \eta_{SE}$ and $\eta = 0$ are indistinguishable from each other even at the smallest radii. However, if the viscosity is much larger than that predicted by the Stokes-Einstein equation, then the reduced equilibration time can increase significantly for particles with smaller radii. For instance, in the case of $\eta = 10^6 \eta_{SE}$, as s_0 falls below 100 nm the reduced equilibration time shows a rapid increase and, at $s_0 = 1$ nm, can be over two orders of magnitude larger than the Fickian equilibration time ($\eta = 0$). This may have implications for atmospheric SOA where sizes below 100 nm are common.^{42–44} For laboratory-based measurements of water uptake and loss on SOA surrogates, micron-sized particles are often used so it should be satisfactory to neglect viscous effects and use a Fickian framework. Although only two RH steps are shown here, qualitatively similar results were observed for other RH changes (e.g. stepwise RH changes of 20 and 30%, 10 and 30%, 10 and 40% were also calculated).

Another striking feature in Fig. 2 is that, while the equilibration times differ between

the six panels, the family of curves in each panel are all qualitatively similar. This similarity suggests that a dimensionless group can be used to predict the onset of viscous effects during water transport. The ratio of the characteristic relaxation time of the material, τ_η , to the characteristic diffusion time, τ_D , can be used to define a diffusional Deborah number as $De = \tau_\eta/\tau_D$.^{27,30,45–47} If we assume for the moment that the time-dependence of the radius and concentration-dependence of D_{12} and η can be ignored, then, for the viscous model used here, an estimate for the dimensionless group can be written as

$$De = \frac{D_{12}\eta\bar{v}_1M_1}{s^2RT}. \quad (32)$$

Of course, this is not directly useful due to the previously mentioned dependencies. However, if $\eta = \eta_{SE}$, then Eq. 32 can be written as

$$De = \frac{\lambda\bar{v}_1M_1}{6\pi N_A s_0^2 r_0}, \quad (33)$$

where $N_A = R/k_B$ and is the Avogadro number. We have assumed that s in Eq. 32 is the initial radius of the particle. We have also introduced a multiplicative factor, λ , so that cases where deviations from the Stokes-Einstein equation occur can be readily be calculated (e.g. if $\lambda = 0$ then the viscosity is zero, if $\lambda = 1$ then the standard Stokes-Einstein viscosity is used, if $\lambda = 10$ then ten times Stokes-Einstein viscosity is used, etc.).

For the current work, when $De \ll 1$ viscosity will not be significant and the uptake or loss processes will be controlled by Fickian diffusion. As De approaches unity, then viscous effects can no longer be neglected. In Fig. 2, radii corresponding to $De = 0.1$, 1, and 10 are indicated on all of the curves. These values were chosen as they cover the transition from the Fickian to the viscous model. It is clear that as De increases in this regime, large discrepancies between the $\eta \neq 0$ curves and the $\eta = 0$ (Fickian) curve begin to emerge. Therefore, the Deborah

number calculated using Eq. 33 adequately predicts the radii at which the uptake and loss of water transitions from the Fickian to full viscous model.

A more detailed examination of the role of viscosity in two specific cases in Figs. 3 and 4. In one case, the effect of viscosity is negligible ($\eta = \eta_{SE}$), while in the other, the effect of viscosity is significant ($\eta = 10^6 \eta_{SE}$). In Fig. 3a and b, it can be seen that the uptake curves are qualitatively similar, although the $\eta = 10^6 \eta_{SE}$ case more slowly approaches equilibrium after closely matching the $\eta = \eta_{SE}$ curve for $t/\tau < 1.5$. The main difference between the two calculations is that the characteristic equilibration time for the $\eta = 10^6 \eta_{SE}$ case ($\tau = 0.241$ s) is much longer than the $\eta = \eta_{SE}$ case ($\tau = 0.0380$ s).

Fig. 4 shows the following profiles at several different times for the two cases: the concentration of water, the concentration of sucrose, the mass average velocity, and the components of the stress tensor. For the chosen RH step, the uptake of water in both Fig. 4a and b proceeds through a sharp diffusion front travelling from the particle surface towards its centre. Physically this behaviour is often discussed in terms of a glassy core that is nearly impervious to water penetration and a rubbery shell where diffusion is fast.⁴⁸ In Fig. 4g-h, the stress profiles at any time are sharp peaks located at the position of the diffusion front (the glass-rubber interface). For the $\eta = 10^6 \eta_{SE}$ case, the stresses are several orders of magnitude larger than the $\eta = \eta_{SE}$ case. Finally, in the case of $\eta = \eta_{SE}$, the sharp diffusion front has reached the particle centre in between $t = 4\tau$ and $t = 5\tau$ and the curves for $t = 5\tau$, 7τ , and 10τ are nearly identical. However, for the $\eta = 10^6 \eta_{SE}$ curves, the diffusion front is still travelling towards the centre at $t = 10\tau$. In fact, the front slows down as it approaches the centre of the particle.

In summary, for the model system of a spherical aqueous sucrose particle, a Fickian framework provides a suitable description for water uptake and loss if the Stokes-Einstein relation

holds. Results for the $\eta = 0$ case are indistinguishable from the $\eta = \eta_{\text{SE}}$ case for any atmospherically relevant particle size. However, if there is a breakdown in the Stokes-Einstein relation then it is possible that viscous pressure gradients can impede water transport. This effect becomes more pronounced with decreasing particle size and can lead to an orders of magnitude increase in equilibration time.

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Figure 1: Experimental measurements of Fickian diffusivity (closed points) and viscosity (open points) from various sources for aqueous sucrose.^{17,19,24,25,35,41,49–51} Data points shown here were measured at temperatures between 291 and 296 K. Conversions from viscosity to diffusivity or vice-versa were calculated using the Stokes-Einstein equation (Eq. 30). A temperature of 293 K was used in this conversion so that all of the data points could be shown on the same plot.

Figure 2: Reduced characteristic equilibration time, τ/s_0^2 , as a function of initial radius, s_0 , for water uptake (a, c, and e) and water loss (b, d, and f) in a viscous particle. Radii corresponding to Deborah numbers, De , of 0.1, 1, and 10 are indicated on all curves with a square, circle, and diamond, respectively.

Figure 3: (a) Time-dependent radius, $s(t)$, divide by the initial radius, s_0 and (b) total mass of water in a particle as a function of t/τ during during water uptake (1% to 50% stepwise change in RH at $t = 0$). Two cases are shown: $\eta = \eta_{SE}$ and $\eta = 10^6 \eta_{SE}$. The characteristic time, τ , for each case is listed in the inset. The initial radius of the particle is 10 nm and $T = 273$ K.

Figure 4: Various profiles at several times inside a particle during water uptake (1% to 50% stepwise change in RH). The panels on the left are for the case when $\eta = \eta_{SE}$ and the panels on the right are for the case when $\eta = 10^6 \eta_{SE}$. The profiles plotted are (a and b) mass concentration of water, (c and d) mass concentration of sucrose, (e and f) radial component of the mass average velocity, and (g, h, i and j) components of the stress tensor. The initial radius of the particle is 10 nm and $T = 273$ K.

References

1. Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H. *et al.* The formation, properties and impact of secondary organic aerosol: current and emerging issues. *Atmos. Chem. Phys.* **9**, 5155–5236 (2009).
2. Bilde, M., Barsanti, K., Booth, M., Cappa, C. D., Donahue, N. M., Emanuelsson, E. U., McFiggans, G., Krieger, U. K., Marcolli, C., Topping, D. *et al.* Saturation Vapor Pressures and Transition Enthalpies of Low-Volatility Organic Molecules of Atmospheric Relevance: From Dicarboxylic Acids to Complex Mixtures. *Chem. Rev.* **115**, 4115–4156 (2015).
3. Kroll, J. H. & Seinfeld, J. H. Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere. *Atmos. Environ.* **42**, 3593–3624 (2008).
4. Donahue, N. M., Robinson, A. L. & Pandis, S. N. Atmospheric organic particulate matter: From smoke to secondary organic aerosol. *Atmos. Environ.* **43**, 94–106 (2009).
5. Haagen-Smit, A. J. Chemistry and physiology of Los Angeles smog. *J. Ind. Eng. Chem.* **44**, 1342–1346 (1952).
6. Went, F. W. Blue Hazes in the Atmosphere. *Nature* **187**, 641–643 (1960).
7. Lelieveld, J., Evans, J. S., Fnais, M., Giannadaki, D. & Pozzer, A. The contribution of outdoor air pollution sources to premature mortality on a global scale. *Nature* **525**, 367–371 (2015).

- 272 8. Hamilton, J. F., Webb, P. J., Lewis, A. C., Hopkins, J. R., Smith, S. & Davy, P. Partially
273 oxidised organic components in urban aerosol using GCXGC-TOF/MS. *Atmos. Chem.*
274 *Phys.* **4**, 1279–1290 (2004).
- 275 9. Goldstein, A. H. & Galbally, I. E. Known and unexplored organic constituents in the earth's
276 atmosphere. *Environ. Sci. Technol.* **41**, 1514–1521 (2007).
- 277 10. Donahue, N. M., Epstein, S. A., Pandis, S. N. & Robinson, A. L. A two-dimensional
278 volatility basis set: 1. organic-aerosol mixing thermodynamics. *Atmos. Chem. Phys.* **11**,
279 3303–3318 (2011).
- 280 11. Donahue, N. M., Kroll, J. H., Pandis, S. N. & Robinson, A. L. A two-dimensional volatility
281 basis set-Part 2: Diagnostics of organic-aerosol evolution. *Atmos. Chem. Phys.* **12**, 615–634
282 (2012).
- 283 12. Cappa, C. D. & Wilson, K. R. Multi-generation gas-phase oxidation, equilibrium partition-
284 ing, and the formation and evolution of secondary organic aerosol. *Atmos. Chem. Phys.*
285 **12**, 9505–9528 (2012).
- 286 13. Koop, T., Bookhold, J., Shiraiwa, M. & Pöschl, U. Glass transition and phase state of
287 organic compounds: dependency on molecular properties and implications for secondary
288 organic aerosols in the atmosphere. *Phys. Chem. Chem. Phys.* **13**, 19238 (2011).
- 289 14. Zobrist, B., Marcolli, C., Pedernera, D. A. & Koop, T. Do atmospheric aerosols form
290 glasses? *Atmos. Chem. Phys.* **8**, 9263–9321 (2008).
- 291 15. Reid, J. P., Bertram, A. K., Topping, D. O., Laskin, A., Martin, S. T., Petters, M. D.,

Pope, F. D. & Rovelli, G. The viscosity of atmospherically relevant organic particles. *Nat. Comm.* **9**, 1–14 (2018).

16. Richards, D. S., Trobaugh, K. L., Hajek-Herrera, J., Price, C. L., Sheldon, C. S., Davies, J. F. & Davis, R. D. Ion-molecule interactions enable unexpected phase transitions in organic-inorganic aerosol. *Sci. Adv.* **6** (2020).

17. Zobrist, B., Soonsin, V., Luo, B. P., Krieger, U. K., Marcolli, C., Peter, T. & Koop, T. Ultra-slow water diffusion in aqueous sucrose glasses. *Phys. Chem. Chem. Phys.* **13**, 3514–3526 (2011).

18. Bones, D. L., Reid, J. P., Lienhard, D. M. & Krieger, U. K. Comparing the mechanism of water condensation and evaporation in glassy aerosol. *Proc. Natl. Acad. Sci. U.S.A.* **109**, 11613–11618 (2012).

19. Davies, J. F. & Wilson, K. R. Raman spectroscopy of isotopic water diffusion in ultraviscous, glassy, and gel states in aerosol by use of optical tweezers. *Anal. Chem.* **88**, 2361–2366 (2016).

20. Price, H. C., Mattsson, J. & Murray, B. J. Sucrose diffusion in aqueous solution. *Phys. Chem. Chem. Phys.* **18**, 19207–19216 (2016).

21. Chenyakin, Y., Ullmann, A. D., Evoy, E., Renbaum-Wolff, L., Kamal, S. & Bertram, K. A. Diffusion coefficients of organic molecules in sucrose-water solutions and comparison with Stokes-Einstein predictions. *Atmos. Chem. Phys.* **17**, 2423–2435 (2017).

22. Bastelberger, S., Krieger, U. K., Luo, B. & Peter, T. Diffusivity measurements of volatile organics in levitated viscous aerosol particles. *Atmos. Chem. Phys.* **17**, 8453–8471 (2017).

23. Evoy, E., Maclean, A. M., Rovelli, G., Li, Y., Tsimpidi, A. P., Karydis, V. A., Kamal, S., Lelieveld, J., Shiraiwa, M., Reid, J. P. *et al.* Predictions of diffusion rates of large organic molecules in secondary organic aerosols using the Stokes–Einstein and fractional Stokes–Einstein relations. *Atmos. Chem. Phys.* **19**, 10073–10085 (2019).
24. Nadler, K. A., Kim, P., Huang, D.-L., Xiong, W. & Continetti, R. E. Water diffusion measurements of single charged aerosols using H₂O/D₂O isotope exchange and Raman spectroscopy in an electrodynamic balance. *Phys. Chem. Chem. Phys.* **21**, 15062–15071 (2019).
25. Richards, D. S., Trobaugh, K. L., Hajek-Herrera, J. & Davis, R. D. Dual-Balance Electrodynamic Trap as a Microanalytical Tool for Identifying Gel Transitions and Viscous Properties of Levitated Aerosol Particles. *Anal. Chem.* **92**, 3086–3094 (2020).
26. Thomas, N. L. & Windle, A. H. A theory of case II diffusion. *Polymer* **23**, 529–542 (1982).
27. Durning, C. J., Spencer, J. L. & Tabor, M. Differential sorption and permeation in viscous media. *J. Polym. Chem., Polym. Lett. Ed.* **23**, 171–181 (1985).
28. Jou, D., Camacho, J. & Grmela, M. On the nonequilibrium thermodynamics of non-Fickian diffusion. *Macromolecules* **24**, 3597–3602 (1991).
29. Bird, R. B., Stewart, W. E. & Lightfoot, E. N. *Transport Phenomena, Revised 2nd Edition* (John Wiley & Sons, 2006).
30. Wu, J. C. & Peppas, N. A. Modeling of penetrant diffusion in glassy polymers with an integral sorption Deborah number. *J. Polym. Sci., Part B: Polym. Phys.* **31**, 1503–1518 (1993).

- 334 31. Wu, J. C. & Peppas, N. A. Numerical simulation of anomalous penetrant diffusion in
335 polymers. *J. Appl. Polym. Sci.* **49**, 1845–1856 (1993).
- 336 32. Witelski, T. P. Traveling wave solutions for case II diffusion in polymers. *J. Polym. Sci.,*
337 *Part B: Polym. Phys.* **34**, 141–150 (1996).
- 338 33. Moridnejad, A. & Preston, T. C. Models of isotopic water diffusion in spherical aerosol
339 particles. *J. Phys. Chem. A* **120**, 9759–9766 (2016).
- 340 34. Fowler, K., Connolly, P. J., Topping, D. O. & O'Meara, S. Maxwell–Stefan diffusion: a
341 framework for predicting condensed phase diffusion and phase separation in atmospheric
342 aerosol. *Atmos. Chem. Phys.* **18**, 1629–1642 (2018).
- 343 35. Preston, T. C., Davies, J. F. & Wilson, K. R. The frequency-dependent response of single
344 aerosol particles to vapour phase oscillations and its application in measuring diffusion
345 coefficients. *Phys. Chem. Chem. Phys.* **19**, 3922–3931 (2017).
- 346 36. Bertrand, T., Peixinho, J., Mukhopadhyay, S. & MacMinn, C. W. Dynamics of Swelling
347 and Drying in a Spherical Gel. *Phys. Rev. Appl.* **6**, 5–20 (2016).
- 348 37. MacMinn, C. W., Dufresne, E. R. & Wettlaufer, J. S. Large Deformations of a Soft Porous
349 Material. *Phys. Rev. Appl.* **5**, 044020–30 (2016).
- 350 38. Wallace, B. J., Price, C. L., Davies, J. F. & Preston, T. C. Multicomponent diffusion in
351 atmospheric aerosol particles. *Environ. Sci.: Atmos.* **1**, 45–55 (2021).
- 352 39. Rumble, J. R. *CRC handbook of chemistry and physics* (CRC Press, 2019), 100th edn.
- 353 40. Taylor, R. & Krishna, R. *Multicomponent mass transfer* (John Wiley & Sons, 1993).

- 354 41. Power, R. M., Simpson, S. H., Reid, J. P. & Hudson, A. J. The transition from liquid to
355 solid-like behaviour in ultrahigh viscosity aerosol particles. *Chem. Sci.* **4**, 2597 (2013).
- 356 42. Bonn, B. & Moortgat, G. K. New particle formation during α - and β -pinene oxidation
357 by O₃, OH and NO₃, and the influence of water vapour: Particle size distribution studies.
358 *Atmos. Chem. Phys.* **2**, 183–196 (2002).
- 359 43. Riipinen, I., Yli-Juuti, T., Pierce, J. R., Petäjä, T., Worsnop, D. R., Kulmala, M. &
360 Donahue, N. M. The contribution of organics to atmospheric nanoparticle growth. *Nat.*
361 *Geosci.* **5**, 1–6 (2012).
- 362 44. Zaveri, R. A., Shilling, J. E., Zelenyuk, A., Liu, J., Bell, D. M., D'Ambro, E. L., Gaston,
363 C. J., Thornton, J. A., Laskin, A., Lin, P. *et al.* Growth kinetics and size distribution
364 dynamics of viscous secondary organic aerosol. *Environ. Sci. Technol.* **52**, 1191–1199 (2018).
- 365 45. Vrentas, J. S., Jarzebski, C. M. & Duda, J. L. A Deborah number for diffusion in polymer-
366 solvent systems. *AIChE J.* **21**, 894–901 (1975).
- 367 46. Vrentas, J. S. & Duda, J. L. Diffusion in polymer–solvent systems. III. Construction of
368 Deborah number diagrams. *J. Polym. Sci., Polym. Phys. Ed.* **15**, 441–453 (1977).
- 369 47. Brazel, C. S. & Peppas, N. A. Modeling of drug release from swellable polymers. *Eur. J.*
370 *Pharm. Biopharm.* **49**, 47–58 (2000).
- 371 48. Thomas, N. L. & Windle, A. H. A deformation model for case II diffusion. *Polymer* **21**,
372 613–619 (1980).

- 373 49. Quintas, M., Brandão, T. R. S., Silva, C. L. M. & Cunha, R. L. Rheology of supersaturated
374 sucrose solutions. *J. Food Eng.* **77**, 844–852 (2006).
- 375 50. Price, H. C., Murray, B. J., Mattsson, J., O’Sullivan, D., Wilson, T. W., Baustian, K. J. &
376 Benning, L. G. Quantifying water diffusion in high-viscosity and glassy aqueous solutions
377 using a Raman isotope tracer method. *Atmos. Chem. Phys.* **14**, 3817–3830 (2014).
- 378 51. Song, Y.-C., Haddrell, A. E., Bzdek, B. R., Reid, J. P., Bannan, T., Topping, D. O.,
379 Percival, C. & Cai, C. Measurements and Predictions of Binary Component Aerosol Particle
380 Viscosity. *J. Phys. Chem. A* **120**, 8123–8137 (2016).

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