**Novel approaches for quantifying the thermodynamics and kinetics of atmospheric gas-to-particle conversion**

**DO Topping, C Percival, AM Booth, I Riipinen, and J Reid**

**Summary:** Aerosol particles remain one of the largest uncertainties in climate change and air quality. Comprised of a large number of compounds with largely unknown physical and chemical properties, it is becoming increasingly apparent that these particles exist as complex viscous media that, coupled with large uncertainties in pure component vapour pressures, has huge implications for many environmental impacts. **Uncertainties in these fundamental parameters and lack of appropriate modeling tools ultimately restrict our ability to truly resolve aerosol impacts on the climate and environment, key challenges addressed by NERC and wider communities.** In this proposal we aim to reduce those uncertainties by i) providing novel bulk measurements of condensed phase viscosity, diffusivity and pure component vapour pressures, ii) provide new evaluations and improvements to existing predictive techniques to estimate these parameters, ii) develop a coupled gas/condensed phase transport model, using the developments listed in points ‘i’ and ‘ii’ to assess wider sensitivities and impacts and develop reduced complexity parameterizations for use in large scale models, iv) use single particle trapping experiments to evaluate model predictions. Results will feed into existing NERC funded programmes and modelling studies will be used to assess the atmospheric importance of results as they appear.

**Case for support part 1: Background of the Applicants**

The project team has all the relevant skills for the proposed project and has an established track record of successful recent collaborative research. At the host institution, David Topping is an internationally established researcher in determining and quantifying processes that dictate aerosol transformation and assessing methods of simplifying such behaviour for inclusion in predictive models. Carl Percival is an acknowledged world leader in the application of **c**hemical **i**onization **m**ass **s**pectrometry (CIMS) to both laboratory and field studies. Murray Booth is an expert in measurement of physical-chemical properties of pure compounds and multi-component mixtures. The research team has experience in atmospheric chemical kinetics, spectroscopy, mass spectrometry, theoretical chemistry and aerosol modelling, from process level to reduced complexity schemes. Regarding our sub-contractor. Ilona Riipinen is a world-renowned leader of a rapidly growing research group, which focuses on gas-aerosol interactions. Their theoretical kinetic representations at the single particle level are highly regarded as benchmark tools. Our project partner Jonathan Reid is a world renowned expert in developing new optical techniques to characterize and manipulate aerosol particles and understand their properties

The **Centre for Atmospheric Sciences** (CAS) in the School of Earth, Atmospheric and Environmental Sciences at the University of Manchester (UM) comprises 11 members of academic staff, 3 Fellows, 3 Instrument Scientists, 36 PDRAs and 25 PG students. The group currently holds over £14M in NERC grants (2004-present) and has recently moved into new laboratories funded (at a cost of >£3.5M) through the North West Development Agency. The group hosts 6 members of staff funded by the National Centre for Atmospheric Sciences (NCAS), three are Fellows supported by NCAS Composition Directorate and provide strategic scientific input in the area of aerosol science. CAS has many years experience in the field of atmospheric physics and chemistry. It maintains strong capabilities in areas of aerosol composition measurements and modelling and contributes significantly to the understanding of gas-aerosol and aerosol-cloud interaction and aerosol transformation processes using laboratory, field and modelling studies.

**Dr David Topping** is currently the NCAS research scientist in the area of aerosol modelling. His primary interests entail determining and quantifying processes that dictate aerosol transformation at the single particle level and their subsequent representation within large-scale models. His PhD (University of Manchester, 2005) involved constructing a state of the art diameter dependent thermodynamic equilibrium model for mixed inorganic/organic aerosols (ADDEM – Topping et al., 2005), which has enabled hygroscopic closure between field and laboratory studies on a level of complexity not previously available. Alongside this he works on improved representation of composition dependent processes within large scale prognostic models and an analysis of associated sensitivities. Current work includes implementation of such reduced thermodynamic frameworks within the aerosol module of the UKCA (UK coupled chemistry-climate model), providing reduced complexity organic models within the EUCAARI and QUEST framework and assisting implementation of the same schemes within the regional model WRF-CHEM. He holds 2 NERC grants for 1) improving datasets for fundamental predictive models of key aerosol processes using laboratory measurements, 2) developing novel environmental informatics software to predict gas/particle partitioning and is Co-I on a further 7 NERC grants. He has 32 peer-reviewed publications, written a book chapter on aerosol thermodynamics aimed at postgraduates in environmental science and is on the NERC technology review panel.

**Dr A. Murray Booth** is a PDRA in CAS; his present interests include measurement of physical-chemical properties of pure compounds and multi-component mixtures (including vapour pressures; specific heats; water activity, surface tension). He has developed the Knudsen Effusion Mass spectrometric method for deriving vapour pressures of multifunctional atmospheric organic compounds and is currently developing a Li+ ion attachment filament for atmospheric measurement. His PhD (University of Manchester, 2008) entailed assessing the impact of previously unused surface science and synchrotron techniques for evaluating pharmaceutical products. This required the design and construction of specialised UHV equipment and familiarity with a wide range of experimental methods. He has ~ 7 years of experience with vacuum system design and mass spectrometry. He has published 6 peer-reviewed papers, 5 completed over the last two years regarding fundamental properties and importance for gas/aerosol partitioning and CCN activation.

**Dr Carl J. Percival:** Reader at SEAES, Manchester (2003-); CJP’s work over the last 15 years has involved the development of analytical techniques, in particular mass spectrometry, for the selective quantification of atmospheric species both in the laboratory and the field. PDRA with Dr. R. Anthony Cox at the University of Cambridge (1997-1999) investigating the heterogeneous reactions of nitric acid and halogen halides; PDRA (1995) with Professor Mario J. Molina (1995 Nobel Prize Laureate) at the Massachusetts Institute of Technology to study the reactions of halogen oxide radicals using turbulent chemical ionisation mass spectrometry; D. Phil. from the University of Oxford in the area of peroxy radical kinetics. He holds 1 EPSRC and 5 NERC grants for the construction of a turbulent flow chemical ionisation mass spectrometer and the study of the peroxy radical kinetics; 4 NERC grants for the development of a field CIMS system, 2 NERC grants for the development of mass spectrometric techniques to evaluate vapour pressures of binary and multi-component organic solutions in combination with inorganic compounds in atmospheric aerosols. 2 EPSRC and 1 Royal Society grant for acoustic wave applications to the detection of NO*x*, VOCs, atmospheric particulates and monitoring peptide-antigen binding. He has over 60 peer-reviewed publications and has supervised 10 PhD students. Member of the EPSRC Peer Review College (2002-2010) and the NERC college (2010-). Fellow of Royal Society of Chemistry (RSC) and secretary of RSC gas kinetics committee.

**Dr. Ilona Riipinen** is a senior lecturer / associate professor at the Department of Applied

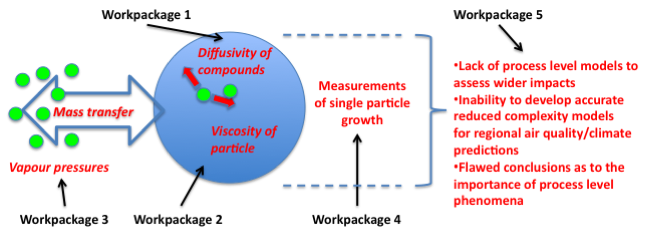
Environmental Science in Stockholm University, Sweden, where she is leading a rapidly growing research group. Dr. Riipinen’s work focuses on gas-aerosol interactions, their theoretical representation in nano- to global scale models, and the climate and health impacts of atmospheric fine particles. She did her MSc (2005) and PhD (2008) in physics in University of Helsinki, and spent two years (2009-2011) as Henry and Camille post-doctoral research fellow in the Center of Atmospheric Particle Studies in Carnegie Mellon University, PA, USA. In 2010 she received the Sheldon K. Friedlander Award of the American Association for Aerosol Research for her PhD work, along with the PhD award of the University of Helsinki, and the young researcher award of the Finnish Association for Aerosol Research (FAAR). She has published over 50 peer-reviewed articles in international scientific journals, 4 book chapters, and several articles aimed at the general public. Her work is currently supported by the European Research Council starting grant, along with 3 smaller national grants from Finnish and Swedish funding agencies.

**Dr Jonathan Reid** was promoted to Professor in Physical Chemistry in 2009. He has almost 90 publications in peer-reviewed journals in aerosols, optical spectroscopy, reaction dynamics and energy transfer. He moved to Bristol as a lecturer in 2004 and was promoted to Reader in 2006. He held an EPSRC Advanced Research Fellowship from 2004 and is now a Leadership Fellow. JPR was Chair of Faraday Discussion 137 on the *Spectroscopy and Dynamics of Microparticles*, was awarded by the RSC the 2004 Marlow Medal and the 2001 Harrison Memorial Medal. His research focuses on developing new optical techniques to characterise and manipulate aerosol particles and understand their properties. He is co-editor of a book entitled *Fundamentals and Applications in Aerosol Spectroscopy* with Prof. R. Signorell (University of British Columbia), published by Taylor and Francis in 2010. Recent research highlights relevant to this project have included: the first direct measurements of heat and mass transfer during condensation or evaporation on an optically trapped droplet, resolving the kinetics of sub-nanometre changes in particle size, published in Phys. Rev. Lett.; validation data for the ADDEM model with measurements of equilibrium droplet size and for vapour pressure determinations; and measurements of the timescales for mass transfer of water in glassy aerosol. He has numerous national and international collaborations, most pertinent to this project being those with Dr. I. Riipinen (kinetic modelling, Carnegie Mellon, USA, and U. of Helsinki, Finland) and Dr. U. Krieger (glassy aerosol, ETH, Switzerland).

**Case for support part 2: Description of the proposed research**

**1. Introduction**. Atmospheric aerosol particles, from anthropogenic and biogenic sources, remain a major uncertainty in the Earth system: they impact the climate by directly scattering and absorbing solar radiation (the direct effect), as well as regulating the properties of clouds (Hallquist et al., 2009) (the indirect effect). On regional scales, aerosols are among the main pollutants deteriorating air quality (Zhang et al., 2007), their impacts on both poorly quantified. Reducing these uncertainties requires accurate knowledge on the composition, concentrations and size distributions of these particles as they reside in the atmosphere. **Unfortunately, there are currently huge uncertainties in many fundamental parameters that are required to predict their environmental impacts.** This is largely down to the fact that a significant fraction of atmospheric aerosol particles are comprised of organic material (20-90% of particle mass) (Jimenez et al., 2009), containing potentially thousands of compounds with largely uncertain properties. In this proposal we will reduce these uncertainties through a combination of novel bulk and single particle measurements on fundamental parameters for which data isn’t even available, combined with newly developed modelling tools to assess wider impacts (figure 1).

Figure 1 – Basic schematic highlighting the uncertainties in fundamental properties and process level understanding (red text) and where the work packages defined in this proposal aim to reduce those uncertainties (black text)



As aerosols reside in the atmosphere, condensation of low volatility organic compounds changes their concentration and composition, thus climatic and health impacts. This condensation is highly dynamic and driven by the difference between the actual vapour pressure of the condensing molecules and their equilibrium vapour pressure over the aerosol surface. There are 3 fundamental restrictions in reconciling this behaviour from a single particle to wider scales.

**1)** It is becoming increasingly evident that aerosols exist as metastable amorphous states, rather than simple liquid/solid mixtures (Virtanen et al., 2010). Indeed, empirical evidence suggests that particles can form glass like substances (Zobrist et al., 2008). As the glass transition temperature is approached, an increase in viscosity leads to a reduced rate of molecular diffusion and an arrested non-equilibrium structure (Tong et al., 2011). Partitioning between the gas and condensed phase is kinetically limited in such amorphous states. Traditional organic aerosol models do not account for this, they assume that 1) the aerosol phase is a well-mixed non-viscous liquid; 2) the aerosol phase instantaneously equilibrates with the gas phase constituents. This adds significant uncertainty to predictions of gas/particle mass transfer as mixing timescales are ultimately governed by the diffusion coefficients of the aerosol constituents in the aerosol, which, on the other hand, are connected to the viscosity of the particulate matter (figure 2). For typical aerosol sizes, the characteristic time for mixing could increase from a few milliseconds to hours or even days (Shiraiwa et al., 2011). This has several important implications for climatic and health effects of organic aerosol: The low diffusivity of water within an aerosol particle might influence its ability to grow in a humid environment and thus effect the direct climatic effect (Tong et al., 2011); the low diffusivity of individual organic molecules in solid/amorphous organic mixtures could directly affect their mass transfer, and thus the loading and composition whilst ice nucleation has been observed to be suppressed (Murray et al., 2008).

**2)** The equilibrium vapour pressure of each aerosol constituent is determined by its pure component saturation vapour pressure, which depends on the molecular properties. Saturation vapour pressures of organic components are currently poorly known, particularly for the least volatile compounds (Barley and McFiggans, 2010). Uncertainty in this parameter is already known to introduce 4 orders of magnitude uncertainty in predicted mass (McFiggans et al., 2010)!

**3)** Finally, to assess the atmospheric importance of these phenomena, modelling approaches that treat the organic condensation/evaporation as a dynamic process and couple the gas phase transport to the condensed phase diffusion are urgently needed. Whilst these remain almost non-existent, some progress has been made (Shiraiwa et al., 2011). To develop these tools, quantitative information on the molecular properties governing the transport in both the gas and condensed phases are required.

**Presently, there is a fundamental lack of data and modelling tools that underpin our ability to resolve these topical issues.** Viscosity as a function of temperature is widely known for common liquids (~ 200 in CRC, ~5000 in YAWS (2003)), most references for glassy material are pharmaceutical polymers (Cui, 2007). For condensed-phase diffusion there is very little quantitative information available for non-aqueous systems, except for a handful in non-viscous common organic solvents (benzene/acetone/hexane) (Grossmann and Winkelmann, 2007). As aerosol particles exist as complex mixtures, the lack of data for even binary systems is critical. For vapour pressures, most of the data models are based on are collected for structurally simple compounds (particularly hydrocarbons) and most of the compounds found in the atmosphere will not have vapour pressure data available in the standard databases (Barley and McFiggans, 2010). Predictive models for all three properties exist, but as they were originally developed for industrial engineering purposes, they are not typically applicable to atmospherically representative systems (Barley and McFiggans, 2010) and, for diffusivity and viscosity, remain unevaluated.

The main science question we aim to address in this proposal is: **To what extent does the kinetics of mass transfer effect the environmental impacts of atmospheric aerosol and can we reliably predict this dynamic behaviour?** To address this the proposal workflow is split into five distinct strands, each populating targeted work-packages (WP):

1) Compilation of new data for diffusion (WP1), viscosity (WP2), glass transition (WP2) (at various temperatures and number of compounds within aqueous and non-aqueous systems) and pure component vapour pressures (WP3).  
2) Testing/improving current predictive techniques for all studied parameters (WP1,2,3).

3) Single particle trapping experiments to verify model predictions described in point ‘4’ (WP4) conducted at the University of Bristol (see letter of support).  
4) New single particle model studies on the coupled gas- and condensed phase transport, using the measured properties and our project partner in Stockholm (see letter of support – Stockholm) (WP5). This allows quantification of the mixing time scales of atmospheric organic aerosol and the importance of condensed phase transport in atmospheric gas-aerosol partitioning.

5) New parameterisations for process level investigations in large-scale models (WP5).

**2. Work packages.** Systems have been chosen to represent a range of atmospherically important compounds and systems known to exhibit the amorphous behaviour indirectly. We will systematically analyse binary mixtures in both aqueous and organic media, and more complex mixtures at a range of temperatures. Wherever possible, measurements of viscosity and diffusivity of the same systems will be carried out across the same concentrations. Predictive techniques will be used to test the ability to replicate/extrapolate measurements. Glass transition temperature of the same systems will be studied and compared with predictive techniques. Similarly, the vapour pressure of each compound will be directly measured in the KEMS where data is not available.

**WP1 New diffusion coefficient measurements and predictive technique evaluation.**

**Aims:** i) New diffusion measurements of aqueous solutions and non-aqueous solutions covering a range of viscosity and temperatures. ii) Using existing model frameworks to test reliability in extrapolating to multiple concentrations and temperatures.

**Work description**: Taylor dispersion is a popular choice for the measurement of both binary and multi-component mutual diffusion coefficients (Riberio et al., 2010; Ray and Leaist 2010). Amongst other benefits, it allows measurements of diffusion coefficients at infinite dilution (thus enabling predictive model evaluation, described shortly) and can be carried out with standard HPLC-equipment (Ven-Lucassen et al., 1995). A Taylor dispersion apparatus consists of a peristaltic pump to create a laminar carrier stream through a Teflon dispersion tube that is immersed in a temperature bath. An injection valve introduces the sample as a short pulse (δ-function). As a result of a combination of diffusion and shear force caused by friction from the walls of the tube, the concentration profile downstream is smeared out and becomes Gaussian in shape. The diffusion coefficients can then be calculated from the measured response curve. A conductivity meter is used to detect the concentration of electrolyte species and a differential refractometer to detect the concentration of the organic species. The detectors output a signal voltage, V(t), which is fitted to a dispersion equation to obtain the diffusion coefficient, in the simple case of a binary solution the equation is given by (Riberio et al., 2010);



where r is the internal radius of the dispersion tube. The fitting parameters are; tr the mean sample retention time, Vmax the peak height, V0 the baseline voltage and V1 the baseline slope. The fitting procedure can be extended to multi-component systems with different approaches being used for mixtures with similar and dissimilar diffusivities (Ray and Leaist, 2010). Immersing the dispersion tube within a temperature bath controls the temperature across the range T=250-300K. The range of diffusivities is limited by the necessity of flow through a narrow tube, preventing measurements of solids (figure 2). The measureable range of diffusivities is from 10‑5 cm2s‑1 for a small molecule in a low viscosity fluid (e.g. 1-propanol in water, Ray and Leaist 2010) to 10-9 cm2s-1 for a large molecule in a very viscous fluid (e.g. 2,2′-bis(4,4-dimethylthiolan-3-one) dye in glycerol, Heuberger and Sillescu, 1996). Data is lacking for 3 important classes; (i) ternary systems, (ii) organic compounds known to be present in atmospheric aerosols, e.g. α-pinene oxidation products (iii) systems where the carrier stream isn’t water, including systems where water is the diffusant. Initially we will validate our Taylor dispersion kit by measuring mixtures of electrolytes and organics with known diffusion coefficients; phenol, benzoic acid, (Yang and Matthews 2000; Castillo et al., 1992; Sharma and Kalia 1977) and sodium chloride (Guggenheim, 1954; Harned and Hildreth, 1951). Once this is complete we will measure (at different temperatures) four systems categories of atmospheric importance:

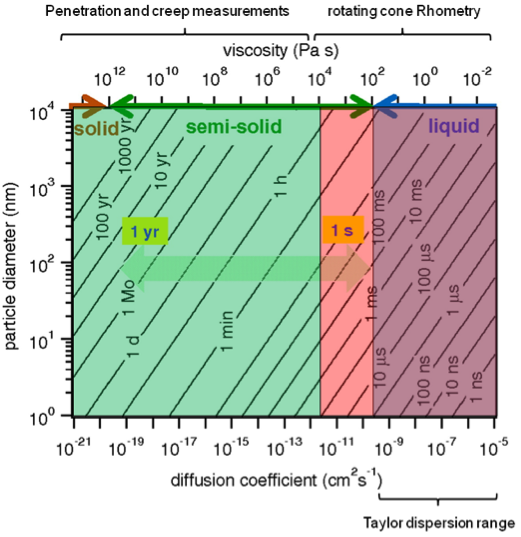


Figure 2. Characteristic timescales for mixing as a function of diffusivity (bottom axis), viscosity (top axis) and particle size (left axis). (Shiraiwa et al 2001) The range attainable using our chosen instruments are highlighted in each axis, the extrapolation to much lower diffusivity available through multiple predictive techniques defined in the text

**1.C2-C10 dicarboxylic acids with NaCl/NH4SO4**. Straight chain aliphatic Dicarboxylic acids are ubiquitous organic constituents of aerosol particles (Kawamura et al., 2005). They are also frequently used as model compounds and, together with ammonium sulphate and sodium chloride, used as test systems for a several aerosol based measurement techniques including HTDMA (Riipinen et al., 2007) EDB (Soonsin et al., 2010) and laser tweezers (Pope et al., 2010). While there are binary aqueous measurements for some of the diacids (e.g. Leaist, 2007;Manea et al., 2007) there are no data for these acids as ternary systems with atmospherically relevant electrolyte species, which would be useful in interpreting evaporation measurements where these compound are used as model systems. (e.g. Zardini et al., 2010).

**2. α-pinene oxidation products:** α-pinene oxidation is a particularly well studied biogenic SOA formation pathway (Capouet et al., 2004:Linuma et al., 2004) which produces many semi- and low-volatility compounds, many of which have been found in aerosols (Bilde and Pandis, 2001). While α-pinene itself already has diffusion coefficient data in the literature (Yaws, 2003) its low-volatility oxidation products; pinane, nopinone, pinolic acid, cis pinonic acid, pinic acid and pinanediol do not, even as binary solutions, have any diffusion coefficient data. Measurements of these compounds will be important in constraining modelling work (see WP5).

**3. Diffusion of water in organic media**: In relatively dry atmospheric particles, partitioning will be limited by the diffusion of the volatile organic compounds through a matrix consisting primarily of other organic material. The water content of aerosols is of critical importance to direct and indirect climate effects, so our understanding of the diffusion of water through organic aerosols needs to be refined. We will measure the diffusion of water and malonic acid in a series of organic solvents of increasing viscosity (acetone (3×10-4 Pa s), oleic acid (2×10-2 Pa s) and glycerol (1.4 Pa s)) as a proxy for the bulk organic of the aerosol.

**4. Diffusion of compounds in sucrose solutions**: Recent interest in the possibility of glassy aerosols (Zobrist et al., 2008) has focused on sugars as model compounds; glucose (Zobrist et al., 2008) sucrose (Zobrist et al., 2011; Tong et al., 2011), raffinose (Zobrist et al., 2011; Tong et al., 2011) and levoglucosan (Zobrist et al., 2008). While there is diffusion data for pure sugars (Riberio et al., 2006; van de Ven-Lucassen and Kerkhof, 1999) and sucrose with some salts (Leaist 1990) there is still a need for data for both mixed sugars and inorganics in water, and measurements with viscous sugar solutions as the carrier and water/inorganics as the diffusing phases.

**Evaluating predictive techniques:** As experimental data is scarcely available for atmospheric systems, it is important to evaluate currently available predictive techniques. In addition, we would preferably like to measure at diffusivities lower than 10-9 cm2s-1. These methods offer routes for extrapolating diffusivity of components in solutions at higher concentrations. In the first instance, we will quantify empirical relationships between diffusivity and viscosity. To assess more detailed methods, diffusion problems are assessed theoretically using Ficks law or the Maxwell-Stefan (MS) equation, the latter separating diffusion effects from thermodynamic non-idealities (Taylor and Krishna 1993). For predicting Fick diffusion coefficients directly, a group contribution method GC-UNIMOD relies on temperature independent interactions parameters fit to experimental data (Hsu et al., 2000). For MS approaches, simple interpolation schemes from infinite dilution include those of Vignes (1966) and Darken (1948). More complex models, that require predictions of viscosity, self -diffusion coefficients and pure component properties, include that of Li et al., (2001). In WP2, we will measure viscosity directly, removing the need to utilize another predictive technique. In each case, the quality of the diffusivity models are judged from comparisons with experimental Fick diffusion coefficients as measured directly in this work package. To convert MS predictions requires diffusion coefficients at infinite dilution. Estimation of this value can introduce large uncertainties (Bosse 2005), which we avoid through direct measurement using chosen apparatus. Another requirement is calculation of activity coefficients, which we can perform using the benchmark model AIOMFAC (Zuend et al., 2011).

**WP2 New measurements of viscosity and glass transition for atmospherically important systems. Aims:** 1) Viscosity measurement of atmospherically relevant liquid binary solutions in aqueous and organic media; 2) Viscosity/Glass transition measurement of atmospherically relevant complex mixtures

**Work description:** Viscosity is a measure of the resistance (typically of a fluid) to deformation by stress. Materials are generally considered liquids when they have a viscosity in the range of 10-3 −102 Pa s. Rubbers, gels and ultra viscous liquids (such as pitch) are in the range 102−1012 Pa s and glassy solids >1012 Pa s. Koop et al., (2011) show that for markedly slowed down equilibration times of 1 min - 1h in 100 nm particles viscosities of 105 - 107 Pa s are needed. To this end, in order to measure a full range of viscosity measurements from diffuse aqueous solutions to glassy and rubbery organic mixtures we require a Malvern Kinexus rhelogical measurement system that can perform both standard rotational shear viscometery measurements, as well as creep/strain measurements for measuring rubbery and glassy samples (up to 1012 Pa). For liquid viscosity measurements a shallow cone is lowered into the sample and rotated. The torque required to rotate the cone gives the viscosity, this can be done at different shear rates to determine if the fluid is Newtonian (exhibiting a linear stress versus strain relationship). For semi solid and solid materials the viscosity is determined by measuring the deformation of the material under a known force (shear) in a given time (shear rate) as a function of temperature. Additionally, viscosity will change dramatically at the glass transition temperature (which will also be measured separately using difference scanning calorimetry DSC). This necessitates excellent temperature control. The system can measure from -30°C to 200°C with a resolution of 0.01°C. This will allow us to accurately measure over a large range of tropospheric temperatures that might be encountered by atmospheric aerosol particles. For each system studied to measure viscosity, we will use DSC to identify the glass transition. With the proposed rheological system here we can measure a greater range in viscosity than we can with our diffusion system, indeed we can measure across the full range of predicted viscosities. We will therefore relate our diffusion and liquid viscosities where both sets of measurements overlap using the available predictive techniques discussed in WP1. We will look at the following systems:

**1. Mixtures of C3-C10 dicarboxylic acids with salts.** Measurements of these diacids will tie in with the diffusion data in WP1. Additionally Cappa et al., (2008) has found evidence that dry mixtures of these diacids display highly non-ideal, liquid like behaviour due to mutual melting point depression. We need to characterise this system as an example of the organic matrix in which diffusion of water will occur, covering dry highly viscous mixtures to aqueous mixtures where we can relate our dispersion measurements. It has been suggested (Cappa et al., 2008) that semi-liquid behaviour and glass formation persists in mixed systems at high inorganic mole fractions. We will therefore include inorganics with these diacids. Experiments with this model system will aid in verifying the relationship between viscosity and diffusivity using WP1.

**2. α-pinene oxidation products**: As with diacids, mixtures of pinane, nopinone, pinolic acid, cis pinonic acid, pinic acid and pinanediol to exhibit mutual melting point depression and semi-liquid behaviour. Cis-pinonic and pinic acid have glass transition temperatures around -10°C (Koop et al., 2011) which allow us to observe viscosity changes between semi-solid and glassy states.  
**3. Sugars with salts**: Measurements of viscosity as a function of temperatures is important for model sugar systems due to the likelihood of glass transitions at or near room temperature. This will tie into the diffusion measurements in WP1 as well as those of (Zobrist et al., 2011; Tong et al., 2011). Glass transition temperatureis known to increase in polysaccharides as a function of monomer number (Slade and Levine, 1994; Orford et al., 1989), even in mixed systems with high inorganic fractions (~50%). Studying viscosities of both mixed systems, and sugar solutions of increasing monomer length (e.g maltose, maltriose & Raffinose) will allow us to understand the impact of glass formation in aerosols, It will also illustrate the importance of any oligimerisation reactions (Kroll and Seinfeld, 2005) in aerosols with regards to changes aerosol properties.

**Evaluating predictive techniques**: Poling et al., (2001) review predictive techniques available for multi-component solutions. Available methods include group contribution schemes based on the UNIFAC model (Gaston-Bonhomme et al., 1994, Wu et al., 1986, Cao et al., 1993). Testing these schemes against data derived here will provide useful insight for the rest of the community. To replicate the measured glass transition of mixtures there are mixing rules available such as the Gordon–Taylor approach and the Couchman–Karasz equation (Koop et al., 2011) that is based on thermodynamic concepts. However, as Koop et al., (2011) states, at present, none of these different approaches seems superior in accurately predicting the glass transition of multi-component mixtures, which is in part due to the fact that only limited data sets exist to which the models can be compared and improved. In this project we aim to address this data gap whilst providing valuable model evaluations on the systems studied above.

**WP3 Vapour pressure measurements using Knudsen Effusion Mass Spectrometry**

**Aims:** Direct vapour pressure measurements of compounds relevant to WP1 and WP2.

**Work description:** In order to quantitatively separate gas and particulate phase phenomena in the gas-aerosol transport processes, accurate information of the saturation vapour pressures of the condensing/evaporating species is needed in addition to the diffusion coefficients and viscosities (figure 1). Here we will use the well-established Knudsen Effusion Mass Spectrometry (KEMS) constructed at Manchester (Booth et al., 2009), allowing us to probe only the volatility without raising issues of aerosol kinetics. KEMS consists of a temperature controlled cell with an effusing orifice i.e. the size of the orifices is << mean free path of the effusing molecules. The sample effuses creating a molecular beam proportional to the vapour pressure inside the cell, without disturbing the thermodynamic equilibrium in the cell. Vapour pressures are then derived by calibrating the mass spectrometer signal to a sample of known volatility. It is frequently necessary to have (sub-cooled) liquid vapour pressures (e.g. Cappa 2008), rather than the solid state measured by KEMS. They can be inter-converted using Differential Scanning Calorimeter (DSC) data (Booth et al., 2010) and the Prausnitz equation (Prausnitz et al., 1986). There are relatively few measurements of highly oxygenated multifunctional low-volatility compounds (Barley and McFiggans, 2010) and many of those that are present are extrapolated down from much higher temperatures than those relevant for atmospheric science. This lack of data causes estimation methods to remain inaccurate for many atmospherically relevant multifunctional organics (Booth et al., 2010; 2011). In this work we will measure groups of compounds to compliment the diffusivity and viscosity measurements in WP1 and WP2. This will feed into the modelling WP4, removing our need to rely on inaccurate estimation methods. Straight chain dicarboxylic acids (Booth et al., 2009, Riipinen et al., 2007) and products of α-pinene; trans-norpinic, pinic, (Bilde and Pandis, 2001) and cis-pinonic (Booth et al., 2011) have already been measured at room temperature. This will let us concentrate on saccarides and polyols in providing complementary data to WP1 and WP2. See Appendix for all specific compounds. Specifically, we will look at:

**Di and Trisaccarides**: As model compounds for glassy materials in both EDB and optical tweezers it is important to have accurate vapour pressures if we wish to model mass transfer in any of these systems. Some of the simple sugars have been measured previously, Oja and Suuberg (1999) have measured glucose, xylose and together with Booth et al., (2011) measured levoglucosan, an important tracer for biomass burning. Longer chain sugars such as raffinose, maltose and maltriose have not been measured and due to their multi-functional nature, estimation methods are likely to be inaccurate (Barley and McFiggans, 2010). Additionally, due to the increase of glass transition temperature with monomer number, we will be able to measure vapour pressures across the glass transition for Maltose and other disaccharides.

**Polyols;** Glycerol has a fairly low vapour pressure (~0.2 Pa at 298K) and other polyols are likely to be in a similar range. Together with acids (Booth et al., 2010; 2011), aliphatic alcohol groups are known to be problematic for vapour pressure estimation methods (Moller et al., 2008). The dataset for polyols is rather limited owing to the difficult nature of measuring low volatility vapour pressures. More data is needed if models are to improve and it will be important for the sort of multifunctional compounds that may form atmospheric glasses.

**WP4 Single particle measurements of growth using optical tweezers**

**Aims:** (i)Direct investigations of the influence of slow water diffusion within glassy and viscous aerosol particles on equilibration timescales.(ii) Resolving the influence of surface accommodation on vapour uptake by organic aerosols. (iii) Comparison of measured particle mass transfer with a novel model developed in WP5.

**Work description:** Dynamic modelling of gas-aerosol partitioning requires quantitative estimates on the accommodation coefficients of the evaporating or condensing compounds. Unfortunately direct measurements are scarce for atmospherically relevant compounds – although significant progress has been made recently in designing experiments to constrain these values (e.g. Miles et al., 2010). By measuring actual growth rates of a single droplet with model predictions (see WP5), accurate information on the saturation vapour pressures and diffusion coefficients in WP1-3 will help constraining accommodation coefficientsfor the studied compounds. Specifically, the data derived in WP1-3 will be complemented by observations from experiments utilizing trapped droplets of aqueous solutions of organic compounds and electrolytes at the University of Bristol (see letter of support, Miles et al., 2010; Pfrang et al., 2011) and existing data on the dynamic evaporation and condensation of these systems (Bilde et al., *in preparation*). These complementary experiments provide insights into the experimental uncertainties in the measured saturation vapour pressures and diffusivities, mass accommodation coefficients and aqueous phase activities of the studied compounds.

[Optical tweezers](javascript:popupOBO('CMO:0000946','b609713h')) allow the control of a single droplet and have been used extensively at the University of Bristol (Reid 2009). Typical particle sizes span the 1–10 µm diameter range. When coupled with spectroscopic techniques for probing evolving particle size (with nanometre accuracy), composition, phase and [mixing](javascript:popupOBO('CMO:0001685','b609713h')) state, detailed investigations of the thermodynamic properties of aerosol, the kinetics of particle transformation, and the nature of interparticle forces and [coagulation](javascript:popupOBO('GO:0050817','b609713h')) can be undertaken (Wills et al., 2009, Reid 2009). While previous measurements of kinetic diffusion using the optical tweezers were limited by the availability of viscosity and diffusivity data, we can utilise the data derived in WPs 1-3 directly to study the same systems in the optical trap: aqueous binary to multicomponent mixed aqueous inorganic/organic systems at multiple relative humidity’s. As the project proceeds, we will use the bulk measurements in WP1-2 to define systems of a range of viscosities to test and also some systems with same viscosity but different organic functionality and molecular mass to compare.

**WP5 Modelling of gas and particulate phase transport in atmospheric gas-aerosol conversion, development of parameterisations for large-scale models**

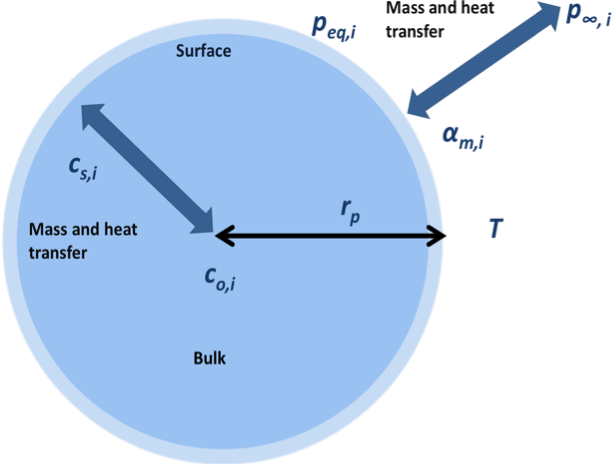
**Aims:** (i) Development of microphysical mass and heat transport models that quantitatively couple condensed and gas phase transport in the gas-aerosol conversion. (ii) Model evaluation using the diffusivities, viscosities and saturation vapour pressure developed in WPs 1-3, single particle trapping experiments (WP4). (ii) Sensitivity studies on 1) the mixing timescales of atmospherically relevant organic aerosol; 2) impacts on coupled gas and particle phase transport on gas-aerosol conversion at atmospherically relevant conditions. (iii) Simplifications of dynamic gas-aerosol conversion and parameterisations of organic aerosol mass, size distribution and chemical composition in typical atmospheric conditions.

**Work description:** In this work package we will develop models that couple the condensational transport of molecules from the ambient gas phase to/aerosol particles (see Fig. 3), using diffusion theory and kinetic theory of gases (see e.g. Riipinen et al., 2011 and references therein). The diffusion coefficients, viscosities, saturation vapour pressures, and surface accommodation coefficients measured in WPs 1-4 will be used as input to these models, as they are crucial in determining the rate of molecular transport between the gas and condensed phases. In addition to the mass transport equations, the heat transport resulting from the release/absorption of latent heat upon condensation/evaporation will be simulated (see e.g. Vesala et al., 1997). The models will be evaluated with observations of dynamic evaporation/condensation and diffusional transport of atmospherically relevant compounds, using the observations from WP 4.

Furthermore the models will be applied to quantify the mixing time scales of organic aerosol, and investigate the sensitivity of atmospheric gas-aerosol partitioning to condensed vs. gas phase transport processes. This will be achieved via an ensemble of simulations with varying 1) particle size; 2) temperature; 3) relative humidity or water content; 4) aerosol composition. The molecular properties determined in WPs 1-4 will be used as model inputs, and sensitivities of the predictions to fundamental molecular properties will be tested. In particular, sensitivity studies will be conducted for the systems studied in WPs 1-4:

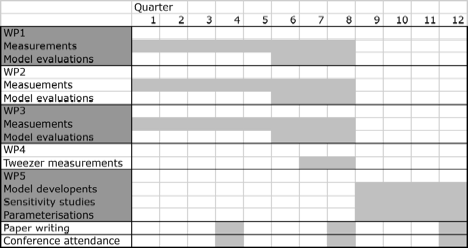
**1) C2-C10 dicarboxylic acids with NaCl/NH4SO4:** The timescales of mixing for regular aqueous solutions will be investigated to calibrate the model for a regular, well mixed, yet atmospherically relevant organic mixtures. The particle size at which mixing time scales start to be comparable to those of evaporation/condensation will be probed. These time scales are expected to negligible in atmospheric context, but will serve as a useful means of evaluating the model using well-defined compounds with known properties (see e.g. Zardini et al., 2010).

**2) α-pinene oxidation products:** Diffusion of water molecules as well as organics with a range of molecular properties will be studied in a condensed phase matrix consisting of organic material produced in atmospheric oxidation reactions. The diffusion coefficients, viscosities, saturation vapour pressures and accommodation coefficients determined in WPs 1-4 will be used to describe the molecular properties of the organic aerosol mixtures. The effects of particulate phase mixing and the sensitivity of organic aerosol formation, growth and evaporation to the transport properties of organic molecules will be tested.



**Figure 3.** A schematic illustrating the coupled aerosol and gas phase transport processes described in the microphysical models. *rp* refers to particle radius, *T* the temperature, *peq,i* the equilibrium vapour pressure of the condensing or evaporating species *i* at the particle surface (which is determined by the saturation vapour pressure, liquid phase activity and particle curvature), *p∞,i* is the partial vapour pressure (or concentration) of *i* far away from the particle, and *αm,i* the mass accommodation coefficient. *cs,i* is the condensed phase concentration of *i* at the particle surface, and *c0,i* at the center of the particle – the difference in which is the driving force for the condensed phase molecular transport.

In addition our modelling studies will provide input for designing experiments that address the most important unknown parameters in these processes. Finally, the model predictions will be utilized to parameterise and simplify the organic and water vapour uptake and evaporation of atmospheric aerosol particles – accounting for the coupled gas and condensed phase mass and heat transport. The impacts of condensed-phase transport on aerosol mass production, size distributions and (surface) composition will be parameterised as function of ambient conditions (temperature, RH, gas phase concentrations) and particle size using the systat TableCurve software. This enables us to combine a powerful surface fitter with the ability to find the ideal equation, from over 36000, to describe the kinetic impacts on the gas-aerosol partitioning of organic compounds. Reduced model parameters will then be subsequently fit as a function of composition, separating the commonly used broad metrics of O:C ratio and molecular weight and more detailed functionality. As the project proceeds, the parameterisations will be implemented and tested in a box-model developed in Manchester for α-pinene aerosol, comparing directly with pre-measured aerosol dynamics. In addition, the host institution currently develops schemes for use if the WRF-CHEM regional climate model over the UK. As the sensitivity studies from the single particle and box-model studies evolve, we will be able to drop reduced complexity formulisms into this framework to assess any wider sensitivity as detailed further in the impact summary.

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**Management:** As displayed in the GANTT chart and noted in the justification of resources, the bulk phase measurement and predictive technique evaluation will be performed in the first two years whilst the optical tweezer measurements and sensitivity/parameterised modelling will proceed toward the end of the second year as the data from previous work packages becomes finalised.

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