

Measurements of Mass and Heat Transfer at a Liquid Water Surface during Condensation or Evaporation of a Subnanometer Thickness Layer of Water

Rachael E. H. Miles, Kerry J. Knox, Jonathan P. Reid, Adèle M. C. Laurain, and Laura Mitchem

School of Chemistry, University of Bristol, Bristol, BS8 1TS, United Kingdom

(Received 3 June 2010; revised manuscript received 13 August 2010; published 7 September 2010)

A novel approach for exploring the molecular dynamics during condensation or evaporation at a liquid water surface is reported at pressures between 2 and 100 kPa. By introducing or removing a heating laser illuminating an optically tweezed aqueous aerosol droplet, the temperature of the droplet can be controlled with sub-mK accuracy and the change in size to reequilibrate with the surroundings monitored with subnanometer accuracy. The time constant for equilibration is shown to provide important insight into the coupling of heat and mass transfer during condensation or evaporation.

DOI: 10.1103/PhysRevLett.105.116101

PACS numbers: 68.03.Fg, 64.70.F-, 82.70.Rr

Liquid-gas surfaces, although appearing quiescent, are extremely dynamic. Although the adsorbing (J_{ads}) and desorbing (J_{des}) molecular fluxes from the gas phase to the surface are in balance at equilibrium, an imbalance leads to a net flux (J_{net}) and condensation or evaporation. It is convenient to define the uptake coefficient γ as the ratio

$$\gamma = \frac{J_{\text{net}}}{J_{\text{coll,fm}}} = \frac{J_{\text{ads}} - J_{\text{des}}}{J_{\text{coll,fm}}}, \quad (1)$$

where $J_{\text{coll,fm}}$ is the gas kinetic (free molecule) flux of molecules colliding with the surface [1]. Although there are many techniques for characterizing the time-averaged equilibrium state of molecules at a liquid-gas surface (e.g., surface tension measurements and sum frequency generation spectroscopy), techniques for monitoring dynamic processes are much less common. However, the depletion of a trace gas species can provide an indirect measure of mass accommodation on a train of liquid droplets, a flat surface, or an ensemble of accumulation mode aerosol, while molecular beam studies can provide insights into the nature of molecular encounters with a liquid surface [2].

Investigating the mass transfer of water across a gas-water surface is particularly challenging [2,3], yet quantifying droplet growth rates is of critical importance for understanding the activation and growth of aerosol in the atmosphere [4]. The high vapor pressure of water precludes the use of molecular beam techniques and places an upper limit on the Knudsen number Kn that can be accessed for particles of a chosen size. Thus, a correction must be incorporated in Eq. (1) to account for the limitation on mass transfer imposed by transport in the gas phase [1,3,5]. Measurements of particle growth in an expansion chamber or of an evaporating liquid jet introduced into high vacuum can ameliorate this to some extent [6–8]. However, the aerosol starts far from equilibrium, and the coupling of heat and mass transfer must be explicitly included [4,6,7]. These measurements cannot currently be reconciled with measurements of mass transfer made on droplets close to

equilibrium in an electrodynamic balance or a droplet train [9,10].

Aerosol optical tweezers can be used to capture and manipulate single or multiple particles 1–15 μm in diameter [11]. By combining optical trapping with Raman spectroscopy, the size of an aqueous droplet can be determined with nanometer accuracy from the unique fingerprint of enhanced Raman scattering observed at wavelengths commensurate with whispering gallery modes. This has led to studies of aerosol hygroscopicity and the equilibrium state [11]. Optical absorption at the laser wavelength (532 nm) has been shown to lead to an elevation in the temperature of a trapped aqueous sodium chloride droplet of ~ 10 mK above the ambient temperature [12]. An equilibrium state is attained at which the droplet vapor pressure, governed by both the solute concentration and temperature elevation, is in balance with the surrounding relative humidity (RH). At this steady size, the heat flux to the droplet from optical absorption is balanced by heat conduction away from the droplet into the gas phase. Increasing the trapping laser power by 20% (~ 4 mW) was shown to lead to an increase in droplet temperature by ~ 4 mK and a decrease in radius by ~ 20 nm ($\sim 2 \times 10^{11}$ water molecules) for a 4.5 μm radius droplet at 99% RH. Here, we show that resolving the time evolution of this change in size provides a novel approach for investigating the mass and heat transfer accompanying condensation or evaporation at the gas-water surface.

The measurements presented involve several important developments from previous work [11,13]. First, it is essential to minimize the limitation on particle growth imposed by the rate of gas-phase diffusion if the impact of surface processes on a condensation or evaporation event is to be resolved [2,3]. This is achieved by lowering the gas pressure in the vicinity of a trapped droplet to ~ 2 kPa, a procedure possible only because of the strong optical restoring forces afforded by optical tweezers [11]. Kn is ~ 0.04 at atmospheric pressure for the lower limit of particle radius accessible to this technique (~ 3 μm), rising to

1.2 when the gas phase is pure water vapor alone at a pressure of ~ 2 kPa. The custom-fabricated trapping cell is sealed during a measurement and the RH maintained by incorporating a liquid reservoir within the cell.

A further development is the addition of a second laser beam, designated as the *heating beam*, aligned to the position of the optical trap formed from the *trapping beam*. The two beams are produced from a single laser source using a 70:30 beam splitter. The heating beam is aligned through a mechanical shutter, allowing instantaneous (< 5 ms) introduction or removal. This beam is recombined with the trapping beam at a second beam splitter, with independent positional control of the two beams achieved through manipulation of two mirrors mounted at the conjugate plane of the back aperture of the microscope objective used to focus the beams. The time scale for the equilibration in droplet temperature can be estimated as < 1 ms by using the expressions of Chan [14], considerably shorter than the time scale of either the mechanical shutter or growth or evaporation event. The Biot number for the trapped droplet can be shown to be $\ll 1$, suggesting that a steady and uniform temperature profile arising from laser heating can be assumed. This is a consequence of the rapid conduction of heat within the condensed phase compared to the slow transport of heat away to the gas phase. By adjustment of neutral density filters, the power of the heating beam relative to the trapping beam can be varied; the heating beam has a power of between ~ 1 and 2 mW in this work, inducing a perturbation of ~ 1 –2 mK in the droplet temperature and radius changes of 2–10 nm, depending on RH. Although a time resolution of ~ 0.1 s can reduce the signal-to-noise ratio in the Raman spectrum, it remains possible to track the wavelength of at least one whispering gallery mode. This can allow the evolving size during a growth or evaporation event to be followed with high time resolution and subnanometer accuracy.

Examples of the reequilibration in particle size at low (~ 6.5 kPa) and high (100 kPa) pressures, reported as the fractional progress towards equilibrium, and the associated mass fluxes are shown in Fig. 1. In addition to showing one growth event at each pressure and a fit to a first-order kinetic rise, the envelopes of observed trends are shown. At $t = 0$ s, the mechanical shutter is closed, blocking the heating laser and leading to an instantaneous drop in the temperature of the droplet. The resulting drop in vapor pressure at the droplet surface leads to a gradient in the partial pressure of water and a net mass flux to the droplet, diluting the solute and raising the vapor pressure to once again match the surrounding partial pressure of water. The inset displays a single growth event at 100 kPa, illustrating that a change of < 0.5 nm in radius can be resolved. This growth is initiated by a drop in temperature of ~ 1 mK, estimated from the difference between the initial and final steady sizes and the associated change in vapor pressure

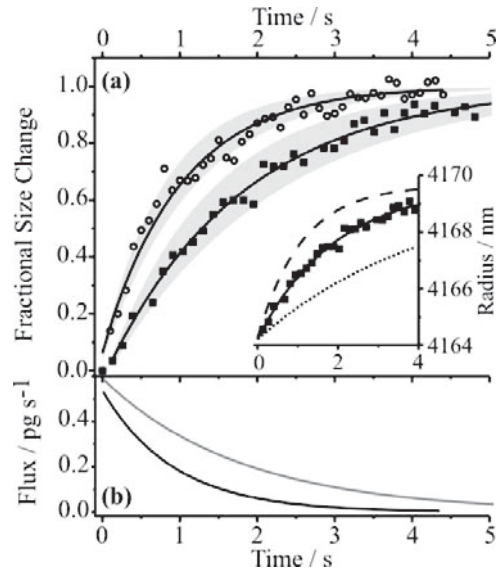


FIG. 1. (a) Comparison of the envelopes of equilibration events (gray shaded) observed at 6.5 kPa (circles and fit line, one event) and 100 kPa (squares and fit line, one event). The inset shows the absolute radius during an event compared with the model predictions (dashed line, neglecting latent heat; dotted line, latent heat dissipated into the gas phase at steady droplet temperature). (b) Mass fluxes estimated from the kinetic fits for the low (black line) and high (gray line) pressure events in (a).

due to the change in solute concentration. This must exactly oppose the change in vapor pressure due to the change in temperature.

The envelopes for many growth events suggest that there is considerable variability (as much as a factor of 7) in the time constants estimated for the first-order kinetic rise, and a systematic dependence of the time constant on the starting size is apparent when all of the data are examined (Fig. 2). All of the growth events shown were induced, over a period of 30 minutes, by removing the same heating laser power from the same droplet. A downward drift in starting size from ~ 4050 to 3970 nm results from a drift in RH from 98.75% to 98.68% over the course of the experiment.

Despite the constant value of the heating laser power, it is apparent that the size changes for all of the growth events are not the same, varying from as little as 1 nm up to 8 nm. When compared with the variation with droplet size of the absorption efficiency (Q_{abs}) at 532 nm, it is clear that the level of light absorption of the trapping laser can change appreciably as the droplet reequilibrates. In these cases, the reequilibration time scale is dependent not only on the rate of change in the solute concentration occurring through mass transfer, but also on the evolution of the level of light absorption and the concomitant change in temperature which occurs as the droplet changes in size [15]. These concurrent processes lead to time scales for equilibration that are significantly reduced. Indeed, for some growth events, the droplet need only grow very marginally

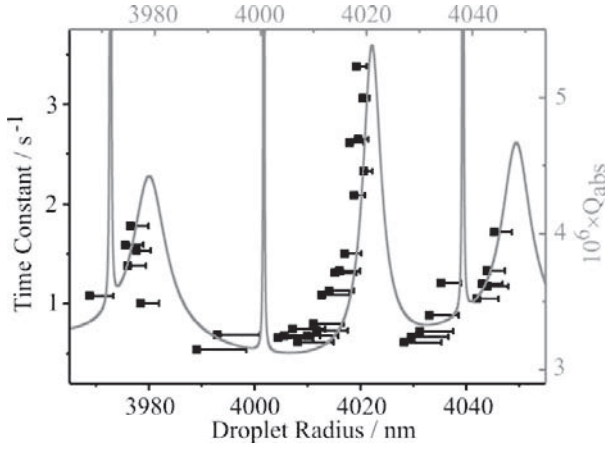


FIG. 2. Example of the dependence of the time constant for condensational growth on the starting size (filled squares, bottom axis). In each event the droplet grows to the size shown by the vertical bar. The variation in the absorption efficiency is shown for comparison (gray line, top axis), shifted by ~ 1 nm to obtain the best comparison. This deviation is likely due to an inaccuracy in the refractive index at the trapping wavelength ($< 0.1\%$) used for the Q_{abs} calculation.

(< 1 nm) as the increased temperature due to increased absorption of the trapping laser counteracts the removal of the heating laser almost entirely. In the figure, the lowest recorded values for the time constant (the slowest growths) correspond to growth events for which the change in Q_{abs} is minimal ($< 1\%$). For these events, it can be assumed that the sole factor responsible for the equilibration is the uptake of water leading to dilution of the solute.

A first approach to interpret the kinetics of mass transfer is to simulate the growth events by using the analytic expression for the rate of condensational growth derived by Kulmala, Vesala, and Wagner [16]. The condensing water mass flux (I , kg s^{-1}) on a droplet of radius r is given by

$$I = 4\pi r(S_{\infty} - S_r) \left[\frac{RT_{\infty}}{M_v \beta_M D p_e(T_{\infty}) A} + \frac{S_r L^2 M_v}{R \beta_T K T_{\infty}^2} \right]^{-1}, \quad (2)$$

where M_v is the molecular mass (kg), D the vapor diffusion coefficient in air, L the latent heat of vaporization of water (J kg^{-1}), K the thermal conductivity of the gas mixture ($\text{W m}^{-1} \text{K}^{-1}$), $p_e(T_{\infty})$ the equilibrium vapor pressure of water at the temperature of the gas phase, T_{∞} , and R the ideal gas constant. A accounts for the influence of Stefan flow on the flux:

$$A = \left(1 + \frac{(S_{\infty} + S_r) p_e(T_{\infty})}{2 p_{\text{tot}}} \right), \quad (3)$$

where p_{tot} is the total gas pressure (Pa). The physicochemical properties D , L , $p_e(T_{\infty})$, and K are calculated in the manner described by Winkler *et al.* [7]. Relative to $p_e(T_{\infty})$, the degree of saturation of water at infinite distance is given

by S_{∞} ; S_r is the corresponding value at the droplet surface. The transitional correction factors for mass and heat transfer are given by β_M and β_T , respectively, and can both be expressed in the form

$$\beta_i = \frac{1 + \text{Kn}_i}{1 + \left(\frac{4}{3\alpha_i} + 0.377 \right) \text{Kn}_i + \frac{4}{3\alpha_i} \text{Kn}_i^2}, \quad (4)$$

where Kn_i and α_i refer to the Knudsen number for either mass or heat transfer and the mass or thermal accommodation coefficients, both of which take values of 1 in the simulations presented here. Kn_M is defined as the ratio of the mean free path of water molecules to the particle radius and Kn_T as the ratio of the mean free path of the components responsible for heat transfer (air and water) to the particle radius. Over the Knudsen range considered in this work, the use of the Fuchs-Sutugin transitional correction factors can be assumed to lead to a molecular flux that is accurate to $\pm 5\%$ [1,3,5]. Equation (2) can be used to simulate the time evolution of the measured growth events by iteratively propagating time. The vapor phase concentration gradient of water at any time is estimated from the offset of the transient size from the final equilibrium size [12].

If the second term in the denominator of Eq. (2) is ignored and the role of Stefan flow is neglected ($A \sim 1$), the equation reduces to the conventional expression for isothermal mass transfer, including the gas-diffusional correction. Including the second term accounts for the suppression of the growth rate due to elevation of the surface temperature by the latent heat produced during condensation. The validity of Eq. (2) has been demonstrated over a wide range of growth conditions by comparing the modeled trends to predictions from the full treatment of the coupled heat and mass transfer [4,17]. However, it should be noted that the assumption is made that the droplet temperature does not change with time (i.e., is in steady state) and that heat dissipation occurs only through conduction into the gas phase [16]. Thus, two limiting treatments can be considered: Neglecting the latent heat is equivalent to assuming that the growth is isothermal, providing an upper limit to the condensation rate; including the latent heat provides a lower limit with dissipation by conduction into the gas phase the only mechanism for its removal. A typical comparison between a measurement and predictions from these models is shown in the inset in Fig. 1. As expected, the former model leads to an equilibration time that is too short, while including the influence of latent heat leads to a time that is too long.

The measured dependence of the equilibration time constant on gas pressure is shown in Fig. 3 for condensation events where $\Delta Q_{\text{abs}} \sim 0$. This is compared with predicted values, including the effect of latent heat, for the pressures and size changes observed in the measurements with both α_M and α_T equal to 1. As noted above, the equilibration time scale from the model is longer than the

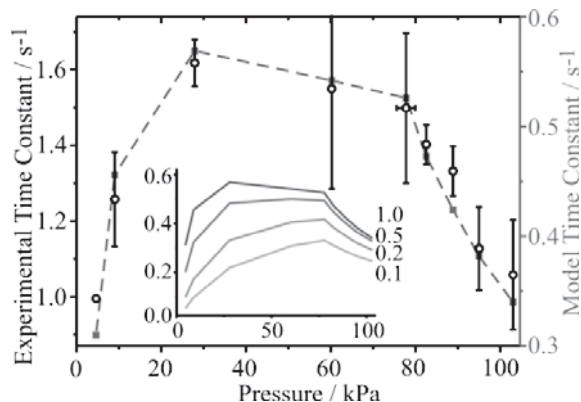


FIG. 3. Pressure dependence of the experimentally determined time constants for equilibration (circles, left axis) and the modeled time constants (dashed gray line to guide the eye, small squares, right axis). The two y axes span the same fractional change in time constant (a factor of 2). The simulated trends in the time constants at the pressures of the measurements are shown in the inset for the indicated values of α_T .

experimental value at all pressures. However, the qualitative dependence and the fractional change with pressure are consistent. The increasing rate from 100 to 80 kPa reflects the increasing rate of gas diffusion. The diminishing rate at low pressure reflects the reduced efficiency with which the latent heat generated at the surface can be conducted away into the gas phase. That the equilibration occurs more rapidly in the measurements than predicted by the model suggests that dissipation of the latent heat into the droplet bulk needs to be better accounted for and that the droplet surface temperature cannot be assumed to be in steady state. Indeed, a bulk value for the latent heat is used to account for the heat deposited at the particle surface during condensation, and this value may be unsuitable given the extremely small droplet size changes in any time step in the theoretical simulation ($\ll 0.1$ nm). The measured trend in the time constant is consistent with predictions that assume $\alpha_T = 1$ (inset, Fig. 3), supporting the conclusion of previous measurements [6,7].

In summary, we have demonstrated that extremely sensitive measurements of the net mass flux (<1 pg/s) during condensation or evaporation can be made on microscopic optically trapped droplets and the time scales for reequilibration explored. Changes in droplet radius of as little as 0.2 nm can be resolved, providing molecular layer resolution of condensational or evaporative processes. An unambiguous interpretation of a growth or evaporation event relies on the isolation of the change in vapor pressure due to a change in solute concentration with droplet size from

changes in temperature due to optical absorption. This process is complicated by the inherent change in the absorption efficiency accompanying the change in particle size. However, we have demonstrated that such a separation is indeed possible for droplet radius changes on the order of several nanometers. A comparison of experimental time constants with predictions over a range of pressures confirms the importance of understanding the impact of the latent heat generated at the particle surface on the equilibration time scale, with the mass transfer slowing as the pressure is reduced due to the ineffectual removal of latent heat into the gas phase. This also demonstrates the necessity to incorporate an accurate treatment of the dissipation of latent heat into the droplet bulk if the kinetics of mass transfer are to be fully understood. It is anticipated that this approach could provide an invaluable new tool in the quest to understand the dynamic coupling between the liquid and gas phases at a liquid surface.

The authors acknowledge the Engineering and Physical Sciences Research Council for financial support for J. P. R. and postdoctoral support for K. J. K. and R. E. H. M. A. M. C. L. acknowledges a Marie Curie Early Stages Training Network. Dr. I. Riipinen, Dr. D. Worsnop, Dr. C. Pfrang and Professors P. Davidovits and E. J. Davis are gratefully acknowledged for helpful discussions.

-
- [1] U. Poschl, Y. Rudich, and M. Ammann, *Atmos. Chem. Phys.* **7**, 5989 (2007).
 - [2] P. Davidovits *et al.*, *Chem. Rev.* **106**, 1323 (2006).
 - [3] E. J. Davis, *Atmos. Res.* **82**, 561 (2006).
 - [4] A. Laaksonen *et al.*, *Atmos. Chem. Phys.* **5**, 461 (2005).
 - [5] X. Qu and E. J. Davis, *J. Aerosol Sci.* **32**, 861 (2001).
 - [6] P. M. Winkler *et al.*, *Phys. Rev. Lett.* **93**, 075701 (2004).
 - [7] P. M. Winkler *et al.*, *J. Geophys. Res.* **111**, D19202 (2006).
 - [8] W. S. Drisdell *et al.*, *Atmos. Chem. Phys.* **8**, 6699 (2008).
 - [9] M. Zientara *et al.*, *J. Phys. Chem. A* **112**, 5152 (2008).
 - [10] Y. Q. Li *et al.*, *J. Phys. Chem. A* **105**, 10627 (2001).
 - [11] L. Mitchem and J. P. Reid, *Chem. Soc. Rev.* **37**, 756 (2008).
 - [12] K. J. Knox and J. P. Reid, *J. Phys. Chem. A* **112**, 10439 (2008).
 - [13] G. Hargreaves *et al.*, *J. Phys. Chem. A* **114**, 1806 (2010).
 - [14] C. H. Chan, *Appl. Phys. Lett.* **26**, 628 (1975).
 - [15] R. E. H. Miles *et al.*, *Phys. Chem. Chem. Phys.* **11**, 7312 (2009).
 - [16] M. Kulmala, T. Vesala, and P. E. Wagner, *Proc. R. Soc. A* **441**, 589 (1993).
 - [17] A. Fladerer, M. Kulmala, and R. Strey, *J. Aerosol Sci.* **33**, 391 (2002).