On the timescale of water isotopic equilibration in a raindrop/ambient-air system

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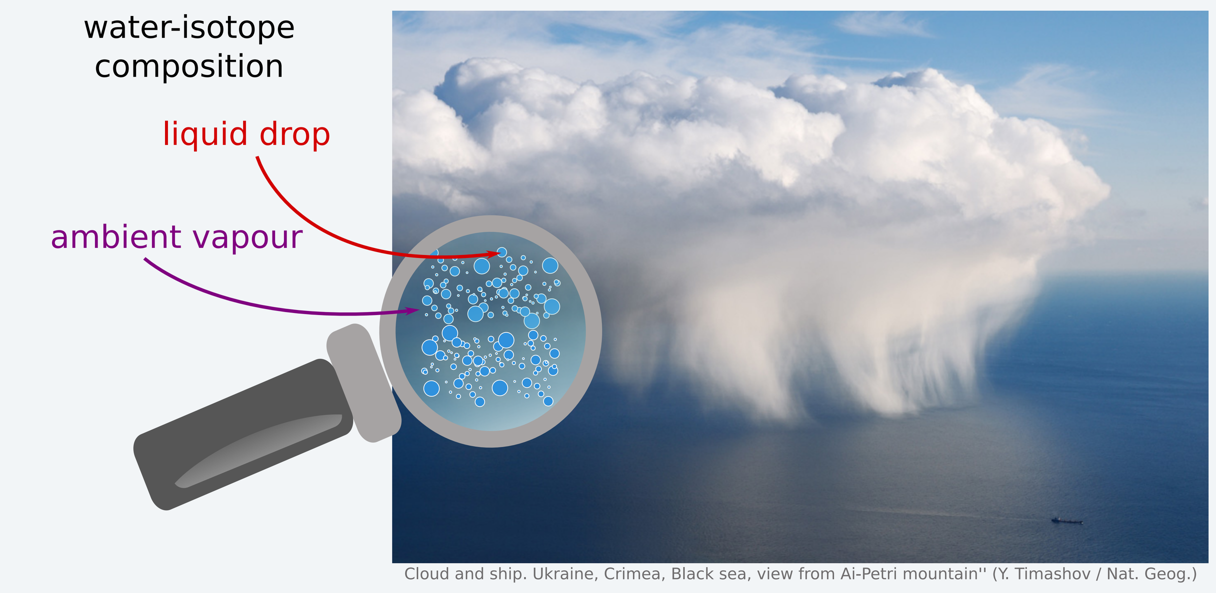
Stable water isotopes such as deuterium, oxygen-18 and oxygen-17 are used as tracers in atmospheric water-cycle analyses. Here, we focus on liquid-water clouds and precipitation. Considering a raindrop/ambient-air vapour diffusion process, the isotopic composition dynamics are driven by the differences in water diffusional coefficients and equilibrium vapour pressures for semi-light (HDO), light (H_2O) and heavy-oxygen ($H_2^{18}O$, $H_2^{17}O$) water. These dynamics lead to isotopic fractionation effects. In the poster, we will discuss approaches to quantify the fractionation effects by analysing the e-folding time scales of mass diffusion. This work is a part of a project aimed at development of particle-based cloud microphysics model capturing the links between the thermodynamic conditions within a cloud and the isotopic composition of surface precipitation.

physical system considered: evaporating ice-free precipitation



Cloud and ship. Ukraine, Crimea, Black sea, view from Ai-Petri mountain" (Y. Timashov / Nat. Geog.)

Maxwell-Mason drop-growth law[1, 2]

Fick's law for moving droplet

$$\frac{dm/dt}{s} = fD\nabla\rho = fD\frac{\rho(T_\infty)-\rho(T_\circ)}{r}, \qquad (1)$$

Mason's parameterisation of thermal inertia

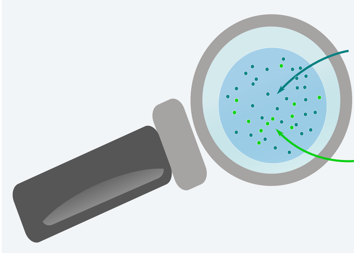
$$\frac{dm/dt}{s} = fkD\nabla\rho = fkD\rho_s\frac{1}{r}\left(\frac{e(T_\infty)}{e_s(T_\circ)}-1\right) \qquad (2)$$

$$k = \left(1 + fD\frac{\rho_{liq}(T_\infty)lv}{T_\infty K}\left(\frac{lv}{R_v^* T_\infty}-1\right)\right)^{-1} \qquad (3)$$

aims of a project

- explore validity and consequences of the assumptions made in isotopic studies
- quantify the timescales for different isotopologues
- derive characteristic length scales (for realistic ambient profiles of relative humidity)
- provide guidance for isotope fractionation numerics in cloud models

light and heavy water isotopologues absolute mass evolution

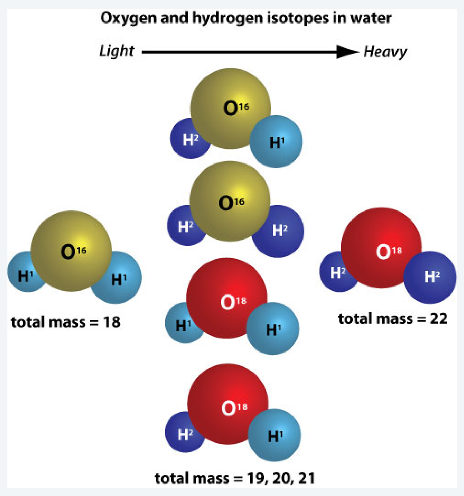


$$\frac{1}{m}\frac{dm}{dt} = \frac{3}{r^2\rho_{liq}}fkD(\text{RH}-1)$$

$$\frac{1}{m'}\frac{dm'}{dt} = \frac{3}{r^2\rho_{liq}}f'k'D'\frac{M}{R_{liq}M'}\left(\frac{e'_\infty}{e'_s(T_\infty)}-1\right)$$

water isotopes considered; isotopic fractionation

We are considering three stable water isotopologues – $^2H^1HO$, $^1H_2\,^{18}O$ and $^1H_2\,^{17}O$, as well as $^3H^1HO$ for comparison with literature.



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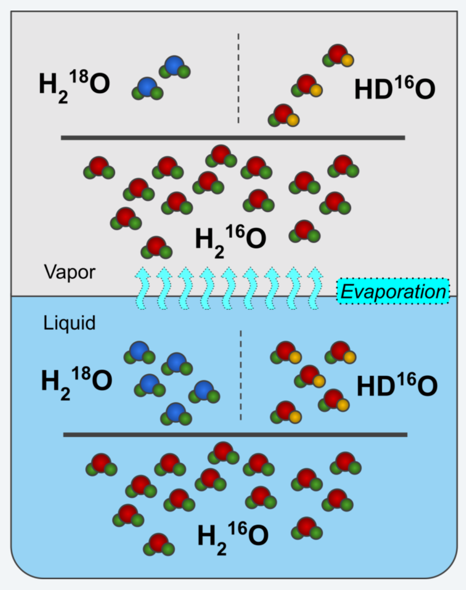

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Bolin '58 assumptions [3]

- no heavy isotopes in the ambient air
- RH=0 in ambient air
- $(T_\circ = T_\infty)$
- $(D = D')$
- $(f = f')$

derived e-folding relaxation timescale for heavy isotopes

$$\tau = \left(\frac{1}{m'}\frac{dm'}{dt}\right)^{-1}, \qquad \tau = \frac{r^2\alpha\rho_{liq}}{3\rho_s f'D'}\left[\text{RH}\left(\frac{\alpha R_{vap}}{R_{liq}}-1\right)+(\text{RH}-1)\frac{1}{1+fDF_k}\right]^{-1}, \qquad F_k = \frac{\rho_{liq}(T_\infty)lv}{T_\infty K}\left(\frac{lv}{R_v^* T_\infty}-1\right) \qquad (4)$$

isotope relaxation timescales in literature

- Bolin (1958) for tritium
$$\left[c_1\frac{1}{m}\frac{dm}{dt}\right]^{-1},$$
where $c_1 = \alpha\frac{\rho_s}{\rho}$
- Friedman et al. (1962) eq. (2), A - experimentally determined factor for ventilation
$$\frac{4\pi r^2}{3\alpha\rho_s(T_\circ)DA}$$
- Booker (1965) eq. (1) for tritium
$$\frac{r^2\rho_{liq}}{3\alpha fD\rho_v}\left(1+\frac{D}{\alpha rN}\right),$$
where N-1/4 of absolute mean speed of water-vapour molecules,
- Miyake et al. (1968): eq. (28)
$$\frac{r^2\alpha\rho_s R_v^* T}{3e_s fD}$$
- Stewart (1975) eq. (7)
$$\frac{\alpha mRT}{4\pi re_s k(D')^n},$$
where N-experimental turbulence parameter
- Jouzel (1986) eq. (7)
$$\frac{\alpha r^2\rho_{liq}}{3D'f'\rho_s}$$
- Gedzelman and Arnold (1994) eq. (24)
$$\frac{\alpha r^2\rho_l}{3D_i f_i\rho_s}$$
for $S = 1$
- Bolot et al. (2013) eq. (B5)
$$\frac{r^2\rho_{liq}\alpha}{3\rho_s D'f'}\left((S+A(1-S))-\alpha\frac{Df}{D'f'}A(1-S)\right)^{-1},$$
where $A = (1+fDF_k)^{-1}$
- Hiron and Flossmann (2020) eq. (13)
$$\frac{\alpha_k r^2\rho_{liq}}{3D_i f_i\rho_s}$$

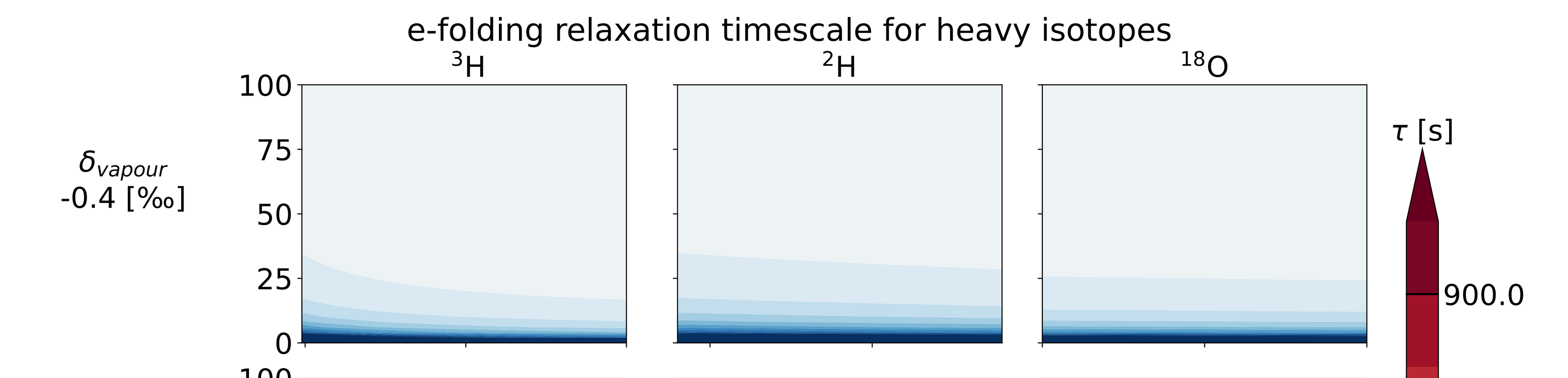

Figure: Relaxation timescales calculated with eq. (4)

Figure description

Plots are representing e-folding relaxation timescales τ for heavy isotopes (^{3}H, ^{2}H, ^{18}O) and changing $\delta_{vapour} \in (-0.4, -0.12, -0.075, -0.03, 0, 0.5)$‰, droplet radius $r = 0.1$mm, temperature of the environment $T_\infty = 283.15$K (same as in Bolin'58). Ranges of the liquid isotopic content δ are taken from [12].

variables

- α – isotope equilibrium fractionation factor,
- α_k – kinetic fractionation factor,
- D – diffusional coefficient,
- e, e_s – partial vapour pressure/partial saturation vapour pressure,
- f – ventilation factor,
- F_k – thermal inertia factor,
- K – heat conduction coefficient,
- lv – latent heat of vapourisation,
- m, m' – heavy and light isotopologue mass,
- M, M' – molar mass of heavy and light isotopologue
- r – radius of a drop,
- ρ, ρ_s – water vapour density/saturation vapour density,
- ρ_{liq} – liquid water density,
- RH – relative humidity,
- R_v^* – specific gas constant,
- R_{vap}, R_{liq} – heavy to light isotopic ratio for vapour and liquid,
- s – surface of a droplet,
- $T_\circ$ – drop temperature,
- T_∞ – environment temperature,

Questions

❓ How the n-turbulence factor is related to the f-ventilation factor?

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