Evaporation of water droplets

To remind the basic physics of evaporation, we use water droplets and closely follow ref^3, where the evaporation of a sessile water droplet with a pinned contact line was studied. The droplet was considered as a spherical cap sitting on the substrate as shown in Figure 1. Two parameters, the contact angle $\theta$ and the radius of droplet base, $R$, completely define the droplet shape. Since the contact line of the droplet was not moving, the radius of droplet base $R$ does not change with time while the contact angle $\theta$ does.
Figure 1 Evaporating droplet with the radius of droplet base, $R$. The droplet forms a contact angle $\theta$ with the substrate. Other symbols are defined in the text.

At the droplet surface, the water vapor concentration equals to the saturated vapor concentration $c_v$. Far away from the droplet, the vapor concentration $c(\infty)$ approaches $Hc_v$, where $H$ is the relative humidity in the ambient air ($H<1$). As a result, the water vapor diffuses from the droplet surface where the vapor concentration is greater to the periphery where it is smaller. This causes the shrinkage of the droplet.

The water vapor concentration $c$ is a function of both position $(r, z)$ and time $t$. The temporal and spatial variation of the vapor concentration is governed by the diffusion equation:

$$\frac{\partial c}{\partial t} = D \Delta c,$$  \hspace{1cm} (1)

where $D$ is the diffusivity of the water vapor in the air. Since the substrate is impermeable to the vapor, the vapor flux at the droplet edge is singular. This flux singularity complicates the diffusion problem.

There are two time scales associated with diffusion. The first time scale provides a rough estimate of how fast the vapor diffuses away from the drop. The rate of vapor diffusion depends on the size of the object causing a concentration gradient to occur. In this case, the water droplet sets the spatial scale, $R$, hence this time scale is estimated as: $\tau_d \sim R^2/D$. Another time scale gives a rough estimate of time for the droplet disappearance, $\tau_f$. To find $\tau_f$, we estimate the rate of
droplet evaporation by balancing the rate of change of the volume with the rate of mass change. The latter is limited by diffusion from the droplet surface to the air.

The evaporation flux is estimated as \( J = D|\nabla c| \sim D(1-H)c_v / R \). Using this estimate, the mass loss per unit time is written as \( \frac{dm}{dt} \sim J \cdot A \sim R^2 D(1-H)c_v / R \), where \( A \) is the area of the droplet surface. The total mass of the droplet \( m \) at the time moment \( t \) can be estimated as \( \rho R^3 \), where \( \rho \) is the density of water. As a result, the characteristic time of droplet disappearance is estimated as \( \tau_f \sim m/(J \cdot A) \sim \rho R^2/(D(1-H)c_v) \). The ratio of these two timescales, \( \tau_d / \tau_f \sim (1-H)c_v/\rho \), does not depend on the droplet size and sets up a criterion for selection of different kinetics of drop evaporation. If this ratio is much greater than 1, one expects to observe a diffusion limited kinetics when the drop disappearance is mostly controlled by how fast the water vapor diffuses away from the drop surface. In the opposite case, when the ratio \( \tau_d / \tau_f \) is much smaller than 1, one expects to see a slow kinetics when the concentration field around the drop sets up momentarily at the time scale of droplet shrinkage.

In order to estimate this ratio for water droplets, we take the following physical constants: ambient relative humidity \( H = 30\% \), saturated vapor concentration \( c_v = 2.18 \times 10^{-5} \) g/cm\(^3\) and density of water \( \rho = 1 \) g/cm\(^3\). With these parameters, the ratio \( \tau_d / \tau_f \) is estimated as \( \tau_d / \tau_f \sim 1.53 \times 10^{-5} \ll 1 \). Therefore, the time needed for the establishment of a steady state vapor diffusion is much smaller than the time of droplet disappearance. Consequently, the water evaporation can be considered as a quasi-static process, i.e. the temporal variation of vapor concentration in the left hand side of eq. (1) can be neglected. As a result, to obtain the spatial distribution of vapor, we only need to solve the Laplace equation

\[
\Delta c = 0 \tag{2}
\]

\[\Delta c = 0\]
with the boundary condition at the droplet surface \( c=c_v \), the condition on substrate impermeability to vapor, \( \partial c/\partial z=0 \) at \( z=0 \), and condition at infinity where \( c=Hc_v \). Once the concentration is obtained, the rate of mass loss can be obtained by integrating the vapor flux over the droplet surface as

\[
\dot{m}(t) = -\int (D\nabla c) \cdot ds .
\] (3)

There is no analytical solution to problem (2)-(3) but Hu and Larson found an approximate solution\(^3\):

\[
\dot{m}(t) = -\pi RD(1-H)c_v(0.27\theta^2 +1.30),
\] (4)

where the contact angle \( \theta \) is measured in radians. If contact angle \( \theta \) changes from 0 to \( \pi/2 \), the contact angle dependent term changes from 1.30 to 1.97 implying that the evaporation rate has a weak dependence on contact angle \( \theta \). This angle is almost constant for a pinned droplet when \( \theta \) is small. To accurately determine the evaporation rate, we have to relate \( \theta \) with the droplet mass:

\[
m(t) = \rho\pi R^3 \frac{2-3\cos\theta(t)+\cos^3\theta(t)}{3\sin^3\theta(t)}
\] (5)

Therefore, eq.(5) provides an implicit relation \( \theta = \theta(m) \). We numerically analyzed eq.(5) to construct a forth order polynomial approximation:

\[
\theta^2 = 17.96\alpha^4 - 33.08\alpha^3 + 19.86\alpha^2 - 0.14\alpha = \frac{m(t)}{\rho\pi R^3}
\] (6)

After substitution this approximation into eq.(4), we simplified the kinetic equation as

\[
\dot{m}(t) = -\pi RD(1-H)c_v(4.848\alpha^4 - 8.933\alpha^3 + 5.361\alpha^2 - 0.039\alpha + 1.300)
\] (7)
Figure 2 The evaporation of a 1.2 μL water droplet in air (ambient relative humidity $H=38\%$, temperature $T=24$ °C). The experimental mass loss (blue circle) was obtained using Cahn DCA-322 analyzer. The theoretical curve is calculated using eq. (7) with $c_v=2.18 \times 10^{-5}$ mg/μL, $D=24.9$ mm$^2$/s, $R=1.02$ mm, $m(0)=1.2$ mg.

To check the validity of eq. (7), we conducted a series of experiments on evaporation of water droplets in air under the ambient relative humidity $H=38\%$ and temperature $T=24$ °C. The experimental mass loss (blue circles in Figure 2) of a 1.2 μL water droplet was acquired using Cahn DCA-322 analyzer. Parameters used in eq. (7) are given in the figure caption. The initial contact angle $\theta=65°$ was measured using KRUSS DSA10 and the radius of droplet base $R=1.02$ mm was then calculated using eq. (5). The saturation vapor concentration and diffusion coefficient of water vapor in the air were taken at $T=24$ °C from Refs. $^4, ^5$. The theoretical curve (the red line in Figure 2) was calculated directly using these parameters without introducing any additional fitting parameters! The theoretical curve shows excellent agreement with the experimental data. Figure 2 also features an almost linear decrease of the sample mass indicating that the evaporation rate of a water droplet is almost constant within such a range of contact angles (0°~65°).

Since both the saturation vapor concentration $c_v$ and diffusion coefficient $D$ depend on temperature, it would be helpful to obtain an empirical relation taking into account the effect of
temperature. This relation would allow one to calculate the rate of water evaporation at different temperatures.

Figure 3 Diffusion coefficient of water vapor in air as a function of temperature (b) the saturation water vapor concentration as a function of temperature.

The data on diffusion coefficient in Figure 3(a) was taken from ref.\(^4\) and was approximated as:

\[
D(T) = 0.171T + 20.8, \tag{8}
\]

where temperature is measured in Celsius and diffusion coefficient \(D\) is measured in mm\(^2\)/s. The data on the saturation vapor concentration in Figure 3(b) was taken from ref.\(^6\) and was approximated as:

\[
c_v(T) = 3.65 \times 10^{-4}T^3 + 4.93 \times 10^{-3}T^2 + 0.377T + 4.81, \tag{9}
\]

where temperature is measured in Celsius and vapor concentration \(c_v\) is measured in mg/m\(^3\).

With this analytical description of the evaporation kinetics of water droplets, one can move further to describe evaporation of more complex aqueous solutions. As seen from this analysis, the evaporation kinetics depends on the materials parameters only through the saturation vapor concentration and density of the material. Therefore, in order to study the evaporation kinetics of complex compounds, one needs to specify these parameters.