

Combined effects of evaporation, sedimentation and solute crystallization on the dynamics of aerosol size distributions on multiple length and time scales

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Abstract

We investigate three aspects of aerosol-mediated air-borne viral infection mechanisms on different length and time scales. First, we address the evolution of the size distribution of a non-interacting ensemble of droplets that are subject to evaporation and sedimentation using a sharp droplet-air interface model. From the exact solution of the evolution equation we derive the viral load in the air and show that it depends sensitively on the relative humidity. Secondly, from Molecular Dynamics simulations we extract the molecular reflection coefficient of single water molecules from the air-water interface. This parameter determines the water condensation and evaporation rate at a liquid droplet surface and therefore the evaporation rate of aqueous droplets. We find the reflection of water to be negligible at room temperature but to rise significantly at elevated temperatures and for grazing incidence angles. Thirdly, we derive a thermodynamically consistent three-dimensional diffuse-interface model for solute-containing droplets that is formulated as a three-phase Cahn-Hilliard/Allen-Cahn system. By numerically solving the coupled system of equations, we explore representative scenarios that show that this model reproduces and generalizes features of the sharp-interface model. These interconnected studies on the dynamics of aerosol droplet evaporation are relevant in order to quantitatively assess the airborne infection risk under varying environmental conditions.

1 Introduction

Speaking or coughing produces aerosols of water droplets [1, 2, 3, 4], which, depending on their size, fall to the ground quickly or evaporate and remain suspended in the air for extended times. Accordingly, droplets containing viruses which remain suspended in the air make the environment hazardous. Aerosols are known to be vectors of virus spreading, as shown convincingly for influenza [5, 6, 7, 8, 9]. For SARS-CoV-2, the results of available studies are consistent with virus aerosolization from normal breathing, following several reports indicating that viruses can float in aerosol droplets for hours and remain infectious [10], together with evidence for broad dispersion of RNA in an isolation room, which indicates that viruses can spread via aerosols [11].

Motivated by these observations, our aim is to further investigate droplet evaporation dynamics in connection to airborne infection risk. On the one hand, we study the evolution of the size distribution of droplets due to evaporation and sedimentation, and present an exact solution of the governing equation. This framework allows us to quantify the effect of humidity on the droplet size distribution and shows that increasing humidity drastically reduces the number of virus particles remaining airborne at all times. Furthermore, we use Molecular Dynamics simulations to estimate the molecular interfacial water reflection coefficient, which quantifies the adsorption kinetics of water molecules at the droplet surface. We show that the reflection coefficient depends on the impinging angle of water molecules as well as on the impinging velocity. On the other hand, building on this molecular description, we introduce a three-dimensional, diffuse-interface model formulated as a three-phase Cahn-Hilliard/Allen-Cahn system [12, 13], featuring a liquid, a vapor, and a crystalline phase, to generalize the previously discussed one-dimensional sharp-interface model. The system is coupled with a diffusion equation for a solute concentration inside the droplet. The solute could correspond to salt, so that we are able to study the process of salt crystallization due to precipitation. However, the solute could also correspond to other biologically relevant constituents, such as viruses. In particular, through numerical experiments, we verify that the model is able to reproduce and generalize features of the one-dimensional model. Together, these three approaches describe the evaporation dynamics of a population of droplets and a single droplet under varying environmental conditions on multiple length and time scales.

The paper is organized as follows. The dynamics of the droplet size distribution is discussed in Section 2. In particular, in Section 2.2, we extend the theoretical framework developed in Refs. [14, 15] to describe the evolution of an initial distribution of droplets due to evaporation and sedimentation. In Section 3, we use Molecular Dynamics simulations to estimate the molecular interfacial water reflection coefficient, which quantifies the effect of imperfect accommodation of water molecules at the droplet surface, and addresses a central assumption of the theory developed in Refs. [14, 15]. The diffuse-interface model for evaporation and crystallization of a solution droplet is derived in its general form in Section 4.1, for which we give a weak formulation in Section 4.2. After addressing the choice of free energy in Section 4.3, we proceed to discretize the system and present and discuss meaningful numerical examples in Section 4.4.

2 Evolution of droplet size distribution in presence of evaporation and sedimentation

In terms of length and time scale, the typical size of aerosols produced by speaking is in the tens of micron range [1, 2, 3, 16], and the corresponding sedimentation and evaporation times span several orders of magnitude from milliseconds to hours, depending on the size of the aerosol particles. This question was summarized in terms of the underlying physical mechanisms at the droplet scale in Refs. [14, 15]. In this section, we consider the problem in terms of the distribution of the number of viruses which remain suspended in the air for a given time. We address also the effect of humidity: can one reduce the hazardousness of virus-loaded aerosols by increasing the humidity, and quantify which humidity is required to achieve this. We mention that in the case of Influenza, humidity has been shown to decrease virus transmission [6, 7, 8, 9], an observation which was supported by semi-empirical modeling [16]. We do not consider here any effect of humidity on the virus viability, and only focus on the physical mechanism at play. Droplets evolve due to two main mechanisms: evaporation and sedimentation [14, 15]. The small ones evaporate quickly but remain very long in the air: typically a droplet with diameter $10 \mu\text{m}$ evaporates in 120 ms (for a humidity of 50 %) and takes 11 minutes to fall to the ground [14], while a droplet of diameter $110 \mu\text{m}$ evaporates in 14.5 seconds and takes only 5.6 seconds to fall to the ground. If a droplet evaporates before touching the ground, hence reaching the size of tens to hundreds of nanometers (depending on its initial solute content), it remains in the air for very long times (hours to days) since Brownian motion counteracts gravity for submicron particles. An important remark is that the most dangerous droplets are not the smaller ones in the initial distribution of droplets, but rather the large ones which evaporate before touching the ground. Indeed, the number of viruses in a given droplet is expected to be initially given by $N_v(R) = D^3 n_v \pi / 6$, with n_v the volumetric density of virus (in saliva) and D the droplet diameter. So, for example, between two droplets with initial sizes $1 \mu\text{m}$ and $100 \mu\text{m}$, there is a factor of 10^6 in number of viruses. If the $100 \mu\text{m}$ droplet shrinks to a smaller radius before touching the ground, it will remain suspended in the air indefinitely (say hours), and contain a huge number of virus particles, hence become extremely dangerous compared to the other droplets with much smaller initial size.

2.1 Sedimentation and evaporation dynamics of single droplets

In this section, we briefly summarize some main results of Refs. [14, 15].

2.1.1 Droplet sedimentation without evaporation

The density distribution $p(z, t)$ of droplets at height z and at time t is given by the diffusion equation [14]

$$\partial_t p(z, t) = D_R \partial_z^2 p(z, t) + V \partial_z p(z, t) , \quad (1)$$

where D_R is the droplet diffusion coefficient and V is the stationary drift velocity of the droplets, which is defined as

$$V = \frac{D_R mg}{k_B T} , \quad (2)$$

with m the mass of a droplet, g the gravitational acceleration, k_B the Boltzmann constant, and T the temperature. By balancing the Stokes friction force that acts on a droplet of radius R and mass density ρ with the gravitational force, it is shown in Refs. [14, 15] that the mean sedimentation time is given by

$$\tau_{\text{sed}} = \frac{z_0}{V} = \frac{9\eta z_0}{2\rho R^2 g} = \varphi \frac{z_0}{R^2} , \quad (3)$$

where the droplet diffusion coefficient is given by the Stokes-Einstein relation $D_R = k_B T / (6\pi\eta R)$, the mass of the droplet is $m = (4\pi/3)\rho R^3$, the shorthand notation $\varphi := 9\eta/(2\rho g)$ is used, η is the dynamic viscosity of air, ρ is the water mass density, g is the gravitational acceleration, and z_0 is the initial height of the droplet.

2.1.2 Stagnant droplet evaporation in the diffusion-limited regime

The effect of evaporation decreases the droplet radius R during its descent to the ground, and according to Eq. (3) this increases the sedimentation time. The evaporative flux of a water droplet is derived in Ref. [14] from the molecular diffusion equation for water vapor, which reads in spherical coordinates as

$$\partial_t c(r, t) = r^{-2} \partial_r (r^2 D_w \partial_r c(r, t)) , \quad (4)$$

where $c(r, t)$ is the water vapor concentration at distance r from the center of the droplet at time t , and D_w is the molecular water diffusion coefficient in air. The stationary solution of Eq. (4), *i.e.*, the solution for $\partial_t c(r, t) = 0$, is given by

$$c(r) = c_0(1 + b/r) , \quad (5)$$

where c_0 is the ambient water vapor concentration and b is a constant that remains to be determined. The water flux balance at the droplet surface $r = R$ is given by

$$J = -4\pi R^2 D_w \frac{d}{dR} c(R) = 4\pi R^2 (k_e c_l - k_c c(R)) , \quad (6)$$

where k_e and k_c are the molecular evaporation and condensation rates, respectively, and c_l is the water concentration in the liquid phase. The expression on the left-hand side of Eq. (6) describes the diffusive water flux, while the expression on the right-hand side describes the net flux due to reactive evaporation and condensation at the droplet surface. Both expressions must be equal to ensure mass conservation. Using the stationary solution given in Eq. (5), the constant b can be determined from Eq. (6), which leads to the total water flux

$$J = 4\pi R^2 D_w \frac{k_e c_l - k_c c_0}{D_w + k_c R} . \quad (7)$$

In Eq. (7), the limit of diffusion-limited evaporation is obtained for $k_c R \gg D_w$, which is valid for droplets with radii $R > 70$ nm [14], while the limit of reaction-limited evaporation is obtained for $k_c R \ll D_w$. Note that the molecular condensation rate k_c is defined as

$$k_c = (1 - p_{\text{ref}}) \bar{k}_c , \quad (8)$$

where $\bar{k}_c = \sqrt{k_B T / (2\pi m_w)}$ is the kinetic condensation rate with m_w the mass of a water molecule, and p_{ref} is the molecular reflection coefficient at the droplet surface. In Ref. [14], $p_{\text{ref}} = 0$ is assumed, which is an approximation that we will revisit in Section 3.

In the following, we assume that the evaporation of a droplet at rest occurs in the diffusion-limited regime, which is valid for radii $R > 70$ nm [14], so that Eq. (7) can be written as

$$\frac{d}{dt} \left(\frac{4\pi}{3} R^3(t) \right) = -4\pi R(t) D_w c_g v_w (1 - RH) = -2\pi\theta(1 - RH) R(t) , \quad (9)$$

where D_w is the molecular water diffusion coefficient in air, c_g is the saturated water vapor concentration, v_w is the volume of a water molecule in the liquid phase, $RH = c_0/c_g$ is the relative humidity as the ratio of the ambient water vapor concentration c_0 to the saturated water vapor concentration c_g , and $\theta = 2D_w c_g v_w$ is a shorthand notation. Eq. (9) can be solved to give [14]

$$R(t) = R_0 \left(1 - \frac{\theta(1 - RH)}{R_0^2} t \right)^{1/2} , \quad (10)$$

where R_0 is the initial droplet radius at time $t = 0$. The time needed for evaporation down to a radius at which osmotic effects due to dissolved solutes within the droplet balance the water vapor chemical potential, can be approximated as the time needed to reduce the droplet radius to zero, and is given through Eq. (10) as the evaporation time [14]

$$\tau_{\text{ev}} = \frac{R_0^2}{\theta(1 - RH)} . \quad (11)$$

Combining Eq. (3) and Eq. (11), we can conclude that both sedimentation and evaporation are terminated after a time

$$\tau^* = \min(\tau_{\text{sed}}, \tau_{\text{ev}}) = \min \left(\frac{\varphi z_0}{R_0^2}, \frac{R_0^2}{\theta(1 - RH)} \right) , \quad (12)$$

which is maximized for a droplet radius of $R^* = (\varphi\theta z_0(1 - RH))^{1/4}$, and the corresponding time scale is given by

$$\tau^* = \left(\frac{\varphi z_0}{\theta(1 - RH)} \right)^{1/2} . \quad (13)$$

2.2 Droplet population size distribution dynamics

Let the initial distribution of droplet radii be given by $\tilde{p}_0(R)$. The total initial volume of the droplets is then

$$V_0 = \int_0^\infty dR \tilde{p}_0(R) \frac{4\pi R^3}{3}. \quad (14)$$

For the sake of simplicity, we introduce the droplet volume v as a variable instead of the radius R , where the initial droplet volume distribution $p_0(v)$ is related to the initial radius distribution $\tilde{p}_0(R)$ through $p_0(v)dv = \tilde{p}_0(R)dR$, and the initial total droplet volume is given by

$$V_0 = \int_0^\infty dv v p_0(v). \quad (15)$$

The dynamics of droplet distributions is examined via a balance equation for the time-dependent volume distribution $p(v, t)$, which is given by

$$\partial_t p(v, t) = -\partial_v (vp(v, t)) - \frac{1}{\tau_{\text{sed}}(v)} p(v, t), \quad (16)$$

where the terms on the right-hand side account for evaporation and sedimentation, respectively. The evaporation rate $\dot{v} = d/dt(4\pi R^3/3)$ is given by Eq. (9), and the sedimentation time $\tau_{\text{sed}}(v)$ is given by Eq. (3) with $R = (3v/4\pi)^{1/3}$. Using the expressions given in Eqs. (3) and (9), Eq. (16) can be rewritten as

$$\partial_t p(v, t) = 2\pi\theta(1 - RH) \left(\frac{3}{4\pi}\right)^{1/3} \partial_v \left(v^{1/3} p(v, t)\right) - \left(\frac{3}{4\pi}\right)^{2/3} \frac{v^{2/3}}{\varphi z_0} p(v, t). \quad (17)$$

The initial total number of virions in the air is given by

$$N_v^0 = n_v V_0 = n_v \int_0^\infty dv v p_0(v), \quad (18)$$

where n_v is the initial number of virions per unit volume of droplet fluid. Ultimately, we want to estimate the number of virions $N_v(t)$ that remain in the air at time t . Since droplets, which are created with an initial volume v_0 and number of virions n_v , are subject to evaporation, the density of virions in a droplet increases as the ratio between the initial and the current droplet volume, such that the total number of virions in a droplet stays constant. At any time t , the total number of virions in the droplet is thus given by $n_v v_0$, where v_0 is the initial volume of the droplet, which is in turn a function of the current droplet volume v and time t . The airborne droplets, *i.e.*, those that have not completed sedimentation yet, evolve due to evaporation, and their radius R is related to the initial radius R_0 through Eq. (10), which, rewritten in terms of the droplet volume $v = (4\pi/3)R^3$, defines reversely the number of virions in a droplet of volume v at time t as

$$n_v v_0(v, t) = n_v v \left(1 + \left(\frac{4\pi}{3v}\right)^{2/3} \theta(1 - RH)t\right)^{3/2}. \quad (19)$$

To estimate the total number of virions that remain airborne at time t , one has to take into account that, due to evaporation, there is a growing population of droplets with vanishing volume, which remain airborne indefinitely. It is therefore much simpler to calculate the total number of virions $N_g(t)$ that have reached to ground up to time t . From the distribution dynamics given in Eq. (16), one deduces the rate of virion deposition to the ground as

$$\frac{d}{dt} N_g(t) = \int_0^\infty dv n_v v_0(v, t) \frac{p(v, t)}{\tau_{\text{sed}}(v)}, \quad (20)$$

where n_v is the initial virion density and $v_0(v, t)$ is the initial volume of a droplet with current volume v at time t , given by Eq. (19). Note that, due to conservation of virions, the total number of airborne virions obeys $\dot{N}_v = -\dot{N}_g$.

2.2.1 Exact solution for the time-dependent droplet size distribution

An exact solution of Eq. (17) can be obtained after a suitable change of variables. Consider the distribution $g(x, t)$ of squared radii, *i.e.*, $x = R^2$ and $g(x, t)dx = p(v, t)dv$. Using the definition of the droplet volume $v = (4\pi/3)x^{3/2}$, one finds $x = (3v/4\pi)^{2/3}$, and therefore

$$v^{1/3} p(v, t) = \frac{2}{3} \left(\frac{3}{4\pi}\right)^{2/3} g(x, t). \quad (21)$$

Using this relation, Eq. (17) simplifies to

$$\partial_t g(x, t) = \theta(1 - RH) \partial_x g(x, t) - \frac{x}{\varphi z_0} g(x, t). \quad (22)$$

The general solution of Eq. (22) is known, and is given by

$$g(x, t) = \exp\left(\frac{x^2}{2\theta(1 - RH)\varphi z_0}\right) f(x + \theta(1 - RH)t), \quad (23)$$

where $f(\cdot)$ is a function to be determined by the initial conditions. Using the initial condition $g(x, 0) = g_0(x)$, one finds

$$f(x) = \exp\left(-\frac{x^2}{2\theta(1 - RH)\varphi z_0}\right) g_0(x), \quad (24)$$

so that the exact solution for the droplet distribution reads

$$g(x, t) = \exp\left(-\frac{xt}{\varphi z_0} - \frac{\theta(1 - RH)t^2}{2\varphi z_0}\right) g_0(x + \theta(1 - RH)t). \quad (25)$$

Following Eq. (20), the rate of virion deposition to the ground can be written in terms of the squared radius distribution $g(x, t)$ as

$$\frac{d}{dt} N_g(t) = \frac{1}{\varphi z_0} \int_0^\infty dx n_v v_0(x, t) x g(x, t), \quad (26)$$

where n_v and $v_0(x, t)$ are given via Eq. (19) as

$$n_v v_0(x, t) = n_v \frac{4\pi}{3} (x + \theta(1 - RH)t)^{3/2}. \quad (27)$$

The initial total number of virions is given by the integral over the initial distribution $g_0(x)$ as

$$N_v^0 = n_v \int_0^\infty dx \frac{4\pi}{3} x^{3/2} g_0(x), \quad (28)$$

and we define the fraction of sedimented virions at time t as

$$\phi_g(t) = \frac{N_g(t)}{N_v^0}. \quad (29)$$

Consequently, the fraction of virions still suspended in air at time t is given by

$$\phi_s(t) = 1 - \phi_g(t) = 1 - \frac{N_g(t)}{N_v^0}. \quad (30)$$

2.2.2 Results

Assuming that the initial droplet radii are distributed normally, the droplet distribution can be written as

$$p_0(R) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{(R - R_0)^2}{2\sigma^2}\right), \quad (31)$$

where R_0 is the mean droplet radius and σ is the standard deviation of the distribution. We assume then that the corresponding initial squared radius distribution is then given similarly by

$$g_0(x) = \frac{1}{\sqrt{2\pi}\sigma_g} \exp\left(-\frac{(x - x_0)^2}{2\sigma_g^2}\right), \quad (32)$$

where $x_0 = R_0^2$ and $\sigma_g = 4R_0^2\sigma$.

Experimentally, however, droplet distributions produced by speaking or coughing are best described by log-normal distributions [1], which can be written as a function of the diameter $D = 2R$ as

$$h_0(D) = \frac{dp(D)}{d \log D} = \frac{C_n}{\sqrt{2\pi}\log\sigma_0} \exp\left(-\frac{(\log D - \log D_0)^2}{2(\log\sigma_0)^2}\right), \quad (33)$$

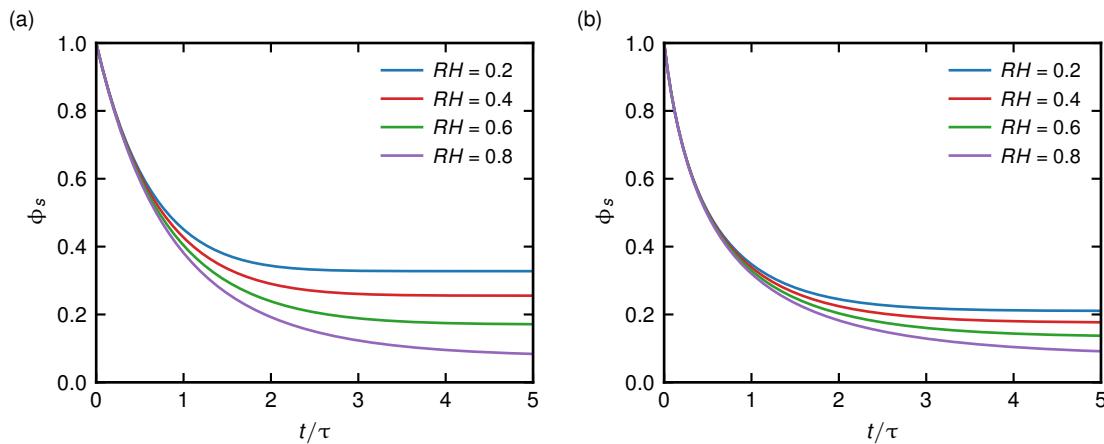


Figure 1: Fraction of suspended virions $\phi_s(t)$ as a function of time t/τ for different relative humidities RH , using initial droplet distributions given by (a) a normal distribution, Eq. (32), and (b) a log-normal distribution, Eq. (34). The characteristic time scale τ is given by $\tau = R_0^2/\theta$.

where the values for D_0 and σ_0 are taken from Ref. [1], and C_n is a normalization constant, which can be chosen arbitrarily in our case since we are only interested in the fraction of suspended virions. The characteristic droplet radius R_0 is then given by $R_0 = D_0/2$, and the initial squared radius distribution for the dimensionless variable $x = (R/R_0)^2$ is given by

$$g_0(x) = \frac{h_0(D_0\sqrt{x})}{2x}. \quad (34)$$

Using the initial distributions, given in Eqs. (32) and (34), together with the exact solution for the time evolution, given in Eq. (25), we can calculate the fraction of suspended virions $\phi_s(t)$, given in Eq. (30), as a function of time via numerical integration of Eq. (26). Following the calculation of $\phi_s(t)$, one can determine the fraction of suspended virions in the long-time limit $\phi_s^\infty = \lim_{t \rightarrow \infty} \phi_s(t)$ as a function of the relative humidity RH . The results are shown in Fig. 1 for both initial droplet distributions. We see that, in both cases and for all relative humidities RH , the fraction of suspended virions ϕ_s decreases considerably after a time τ . Up to this point, the effect of RH on the behavior of ϕ_s is minimal. For longer times $t > \tau$, we observe that, for both initial distributions, ϕ_s asymptotically reaches a plateau at values that depend heavily both on RH as well as on the choice of initial droplet size distribution. We thus conclude that, while the overall behavior of ϕ_s is similar qualitatively for both normal and log-normal distributions, the choice of initial distribution has a significant effect on the long-time behavior of ϕ_s , which is more pronounced for low relative humidities.

3 Molecular interfacial reflection coefficients of water

The molecular reflection coefficient p_{ref} at the droplet surface enters the condensation rate k_c through Eq. (8), and therefore affects the evaporation dynamics of droplets. The reflection coefficient p_{ref} is generally assumed to be small, and in Ref. [14], $p_{\text{ref}} = 0$ is assumed, which corresponds to perfect sticking of water molecules impinging on the droplet surface. Using Molecular Dynamics (MD) simulations, we aim to determine the molecular reflection coefficient p_{ref} as a function of the angle and velocity of impinging water molecules at the vapor-liquid water interface.

3.1 Simulation setup

The simulation box used in all simulations has dimensions of $15 \text{ nm} \times 5 \text{ nm} \times 5 \text{ nm}$ along the x -, y -, and z -axes, respectively, and periodic boundary conditions are applied in all three directions. A block of water measuring $5 \text{ nm} \times 5 \text{ nm} \times 5 \text{ nm}$ is placed in the center of the box, such that its edges are located at $x = 5 \text{ nm}$ and $x = 10 \text{ nm}$, assuming a sharp interface, see Fig. 2 (a) for a simulation snapshot. The TIP4P water model is employed, which consists of two hydrogen atoms, one oxygen atom, and an additional massless site representing the negative charge center. This model was selected because it offers an accurate representation of hydrogen bonding, the dominant intermolecular interaction relevant to this work. All molecular dynamics simulations are carried out using GROMACS 2019 with a 2 fs integration time

step. Temperature coupling is applied using the velocity rescale thermostat with a stochastic term and a time constant of 0.5 ps, maintaining a reference temperature of 300 K. The Lennard-Jones interactions are treated using a cutoff scheme with a cutoff distance of 1.2 nm and a potential-shift modifier. Electrostatic interactions are computed using the particle mesh Ewald (PME) method with a real-space cutoff of 1.2 nm and a Fourier spacing of 0.2 nm. All bonds involving hydrogen atoms are constrained using the LINCS algorithm, and the center-of-mass motion is removed.

3.2 Vapor phase

We define the vapor phase as the region more than 1 nm away from the water slab, *i.e.*, $x > 11$ nm and $x < 4$ nm. This definition was chosen to compensate interfacial fluctuation at the edges of the slab of water. To validate the simulation setup and ensure stability, we calculate the vapor pressure of the system, which is obtained via the ideal gas law as

$$P_{\text{vap}} = \frac{N_{\text{avg}} k_{\text{B}} T}{V}, \quad (35)$$

where k_{B} is the Boltzmann constant, T is the temperature, V is the volume of the vapor phase, and N_{avg} is the average number of water molecules per frame in the vapor phase. The vapor pressure is found to be $P_{\text{vap}} = 63.786$ mbar, which is of the same order of magnitude but larger than the experimental value $P_{\text{vap}}^{\text{exp}} = 35.670$ mbar [17]. The larger vapor pressure is an expected outcome when using the TIP4P model [18].

3.3 Reflection simulations

To determine the molecular reflection coefficient p_{ref} at the vapor-liquid water interface, we perform a series of simulations where a single water molecule is added to the system outside the liquid water slab, and is placed at $x_0 = (1.783, 2.662, 3.161)^T$. In the following, the phrase ‘single molecule’ refers to this externally placed molecule. When a simulation is started, every atom velocity as well as the velocities for the atoms of the single molecule are randomly assigned according to a Maxwell-Boltzmann distribution at 300 K. Consequently, the molecules themselves possess center-of-mass velocities that also follow a Maxwell-Boltzmann distribution at 300 K.

To broaden the range of the analyzed velocities, additional simulations were performed where the velocity of the single molecule was multiplied by a factor of two as well as by a factor of four after drawing it from a Maxwell-Boltzmann distribution at 300 K. This procedure is equivalent to drawing the initial velocity of the added water molecule from a Maxwell-Boltzmann distribution at 1200 K and 4800 K, respectively. For each of these three scenarios, 200,000 simulation runs were performed, leading to a total of 600,000 simulations, each lasting for 30 ps.

A reflection is defined as follows: if a molecule leaves the vapor phase, *i.e.*, its x -coordinate exceeds 4 nm while moving in the positive x -direction, (with $v_x > 0$ nm/ps) or falls below 11 nm while moving in the negative x -direction (with $v_x < 0$ nm/ps), and subsequently reenters the vapor phase within 30 ps, the molecule is considered to have been reflected. Additionally, the initial velocity of each molecule and its angle of incidence is recorded. The angle of incidence β is defined as the angle between the initial velocity vector and the surface normal of the water slab, *i.e.*, $\mathbf{n} = (1, 0, 0)$, see Fig. 2 (a). This information allows for the calculation of the reflection probability as

$$p_{\text{ref}} = \frac{N_{\text{ref}}}{N_{\text{tot}}}, \quad (36)$$

where N_{ref} is the number of reflected molecules within a given velocity or angle range and N_{tot} is the total number of molecules in that range. Only molecules with an initial velocity sufficiently high to leave the vapor phase within the simulation time are considered when calculating N_{tot} .

Each simulation run can be regarded as a Bernoulli trial, with possible outcomes of 1 for a reflected molecule and 0 for an absorbed molecule. This framework allows for the calculation of the statistical uncertainty of p_{ref} : For a given velocity or angle range (*i.e.*, within a single bin), there are N_{tot} independent runs, which leads to the standard error [19]

$$\Delta p_{\text{ref}} = \sqrt{\frac{p_{\text{ref}}(1 - p_{\text{ref}})}{N_{\text{tot}}}}. \quad (37)$$

3.3.1 Results

The results for the molecular reflection coefficient p_{ref} as a function of the initial velocity of the impinging water molecule are shown in Fig. 2(b). The data from all three sets of simulations with different initial velocity distributions are combined in

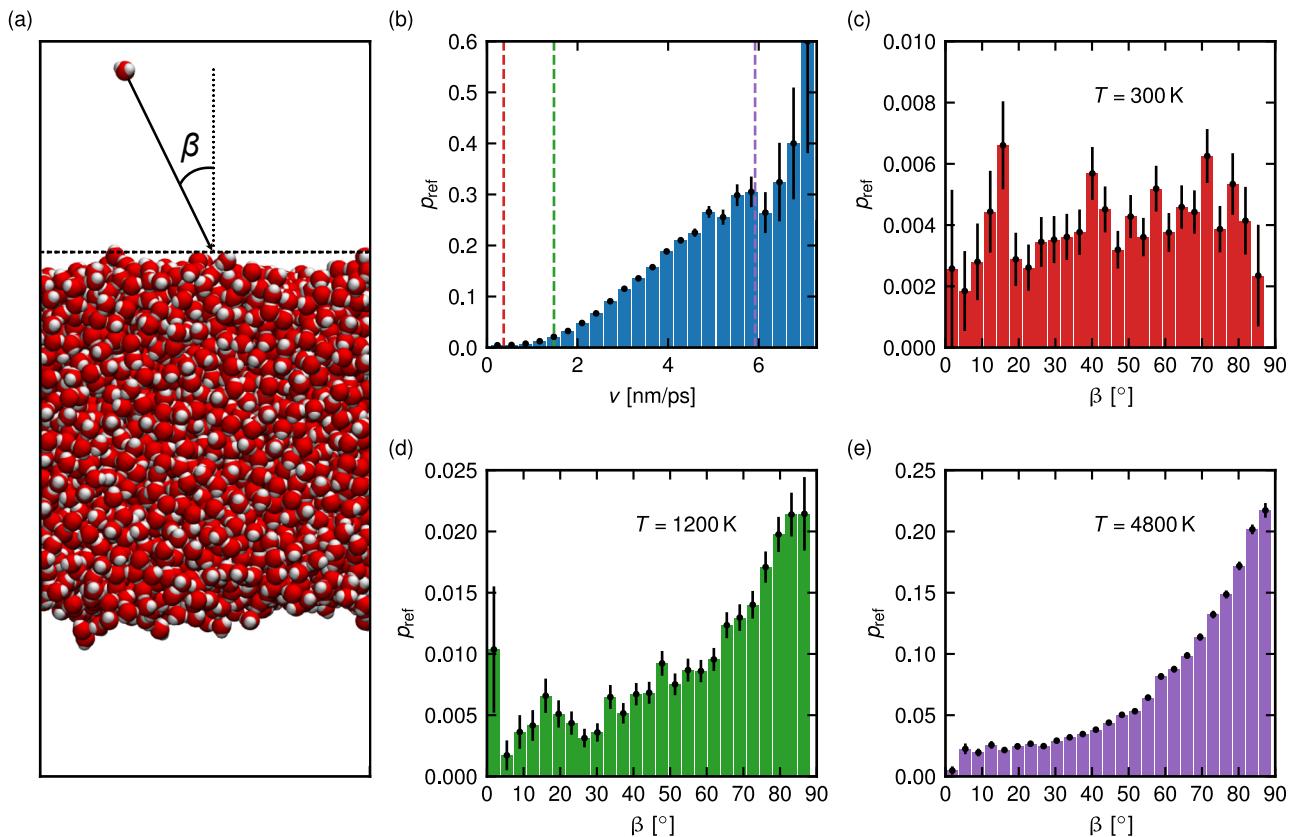


Figure 2: (a) Simulation snapshot. The angle of incidence β is defined as the angle between the initial velocity vector (black arrow) and the surface normal of the water slab (black dotted line). (b) Molecular reflection coefficient p_{ref} as a function of the velocity of the impinging water molecule. The histogram combines data from all three sets of simulations with different initial velocity distributions. Average velocities according to $\sqrt{k_B T / m_w}$ for $T = 300$ K (red), 1200 K (green), and 4800 K (purple) are indicated by vertical dashed lines. (c) Molecular reflection coefficient p_{ref} as a function of the angle of incidence β of the impinging water molecule for initial velocities drawn from a Maxwell-Boltzmann distribution at 300 K. (d) Same as (c) but for initial velocities drawn from a Maxwell-Boltzmann distribution at 1200 K. (e) Same as (c) but for initial velocities drawn from a Maxwell-Boltzmann distribution at 4800 K. Error bars in all panels indicate the standard error given by Eq. (37).

this plot. The reflection coefficient p_{ref} decreases with increasing initial velocity of the impinging water molecule. Average velocities according to $\sqrt{k_B T / m_w}$ for $T = 300$ K, 1200 K, and 4800 K are indicated by vertical dashed lines. We observe that the reflection coefficient p_{ref} increases with increasing velocity of the impinging water molecule. The reflection coefficient p_{ref} as a function of the angle of incidence β of the impinging water molecule is shown in Figs. 2(c)–(e) for initial velocities drawn from a Maxwell-Boltzmann distribution at 300 K, 1200 K, and 4800 K, respectively. In all three cases, the reflection coefficient p_{ref} increases with increasing angle of incidence β , but this increase is more pronounced for higher temperature. This shows that, while the reflection coefficient p_{ref} is small for water molecules impinging onto the liquid phase with velocities typical for room temperature, it can become significant for larger velocities and large angles of incidence. Thus, the assumption of $p_{\text{ref}} = 0$ used in Section 2 is valid at room temperature, as relevant for droplet evaporation at ambient conditions.

4 A multiphase diffuse-interface Cahn–Hilliard/Allen–Cahn model for evaporation and precipitation in droplets containing solutes

In this section we introduce an isothermal phase-field model for the coupled evaporation and crystallization of an aerosol droplet containing dissolved solutes: as the liquid evaporates, the dissolved solute, for example salt, becomes increasingly

concentrated and, once it exceeds a saturation threshold, precipitates by forming a crystalline phase. The model is described by a three-phase Cahn-Hilliard/Allen-Cahn system [12] with phase indicators $\varphi_i : [0, T] \times \Omega \rightarrow \mathbb{R}$, where the index i can represent a liquid phase $i = \ell$, a crystalline phase $i = c$, or a vapor phase $i = v$. The evolution of the phases is coupled with a diffusion equation for the solute concentration $s : [0, T] \times \Omega \rightarrow \mathbb{R}$. We assume that $s = 1$ is the highest possible concentration (or volume fraction) of the pure crystal and $0 \leq s \leq 1$. A central modeling choice is to consider the dissolved or crystalline solute content as a conserved order parameter while allowing the liquid to become supersaturated with solute. The saturation concentration is imposed softly, *i.e.*, supersaturation is permitted but carries an energetic cost that increases smoothly beyond the saturation threshold.

The focus of this section is to derive such a model based on a thermodynamic structure, to discuss suitable free energies, state-dependent mobilities, and reaction rates, and to study the properties of the model in numerical experiments. Our modeling approach is based on the works of Elliot and Luckhaus [13] and Nestler and Wheeler [20]. In this way, in this section we propose a three-dimensional, diffuse-interface model in terms of a three-phase Cahn-Hilliard/Allen-Cahn system to generalize the one-dimensional sharp-interface model discussed in Section 2. Herein, the solute can be seen as a placeholder for any relevant substance, such as salt, proteins or viruses. In particular, with the numerical examples in Section 4.4 we verify that the model is able to capture and generalize features of the one-dimensional model.

Virus-laden aerosols typically have a complex composition, *e.g.*, solutes or macromolecules, which can induce internal fluid flows and compositional heterogeneities that are not considered here. Nevertheless, for many practical biomedical questions a key factor is the evaporation-driven evolution of aerosol droplet size and resulting particle morphology. We have chosen this theoretical approach because solutes can significantly alter evaporation rates and the morphology of the particles formed when aerosol droplets dry, see *e.g.* [21]. Particle morphologies are hollow spheres, porous spheroids or solid spheres and the particles can be single crystals, polycrystalline or weakly bound agglomerates. These properties of dried particles depend on process parameters such as evaporation rate, solute concentration, humidity, and temperature. Modern single-droplet experiments provide detailed drying and crystallization kinetics and, together with theoretical modelling, allow one to infer internal solute concentration profiles [22]. The onset of crust formation and its impact on drying have been studied theoretically in [23, 24]. The particle formation is also highly relevant for spray drying applications, *e.g.* cf. [25].

4.1 Derivation of the thermodynamically consistent model

Model derivation. We derive the thermodynamically consistent phase-field model by adapting the strategy proposed by Elliott and Luckhaus in [13] to our setting, where source terms in the order parameter equations and a coupling between the order parameter φ and solute concentration s in the free energy density are taken into account.

In a polyhedral, bounded domain $\Omega \subset \mathbb{R}^3$ and for times $t \in (0, T)$ we consider the state vector $\mathbf{q} = (\varphi, s)$, where $\varphi = (\varphi_\ell, \varphi_c, \varphi_v)$ collects the phase-field functions that have to obey the additional constraint

$$\varphi_\ell + \varphi_c + \varphi_v = 1. \quad (38)$$

Here $\varphi_i \approx 1$ means that the i th phase is present and $\varphi_i \approx 0$ means that the i th phase is absent for $i \in \{\ell, c, v\}$. The (isothermal) thermodynamics of these three phases φ and the solute concentration s is modeled by a free energy functional $\mathcal{E}(\mathbf{q}) = \int_\Omega \Psi \, dx$ with free energy density $\Psi = \Psi(\varphi, \nabla \varphi, s)$ of Ginzburg-Landau type. The above constraint Eq. (38) for the phase indicators is taken into account with the aid of the Lagrangian functional $\mathcal{L}(\mathbf{q}, \kappa) = \int_\Omega L \, dx$ with density

$$L(\varphi, \nabla \varphi, s, \kappa) := \Psi(\varphi, \nabla \varphi, s) + \kappa(\varphi_\ell + \varphi_c + \varphi_v - 1). \quad (39)$$

The driving forces of the processes in the droplet and the vapor are thus given by the chemical potentials $\boldsymbol{\mu} = (\mu_\ell, \mu_c, \mu_v, \mu_s)$ determined as the partial derivatives of the functional corresponding to the Lagrangian, *i.e.*,

$$\mu_\ell = \frac{\delta L}{\delta \varphi_\ell} = \frac{\delta \Psi}{\delta \varphi_\ell} + \kappa, \quad \mu_c = \frac{\delta L}{\delta \varphi_c} = \frac{\delta \Psi}{\delta \varphi_c} + \kappa, \quad \mu_v = \frac{\delta L}{\delta \varphi_v} = \frac{\delta \Psi}{\delta \varphi_v} + \kappa, \quad \mu_s = \frac{\delta L}{\delta s} = \frac{\delta \Psi}{\delta s}. \quad (40)$$

The mass balance equation for the order parameters $\varphi = (\varphi_\ell, \varphi_c, \varphi_v)$ reads

$$\frac{d}{dt} \int_\omega \varphi_i \, dx = - \int_{\partial\omega} J_i \cdot \nu \, da(x) + \int_\omega M_i \, dx, \quad i \in \{\ell, c, v\},$$

for any control volume $\omega \subset \Omega$ with outer normal vector ν , where we denoted by J_i the mass fluxes and by M_i the source terms. Hence, it follows

$$\partial_t \varphi_i = - \operatorname{div} J_i + M_i \quad i \in \{\ell, c, v\}. \quad (41)$$

Since we are interested in the case where the solute concentration s is conserved throughout the process, we postulate its mass balance equation to be of type

$$\partial_t s = -\operatorname{div} J_s, \quad (42)$$

for a mass flux J_s .

Let us consider the time derivative of the Lagrangian functional

$$\begin{aligned} \frac{d}{dt} \mathcal{L}(\mathbf{q}, \kappa) &= \int_{\Omega} \left(\mu_{\ell} \partial_t \varphi_{\ell} + \mu_c \partial_t \varphi_c + \mu_v \partial_t \varphi_v + \mu_s \partial_t s + (\varphi_{\ell} + \varphi_c + \varphi_v - 1) \partial_t \kappa \right) dx \\ &= \int_{\Omega} \left(\mu_{\ell} \partial_t \varphi_{\ell} + \mu_c \partial_t \varphi_c + \mu_v \partial_t \varphi_v + \mu_s \partial_t s \right) dx, \end{aligned} \quad (43)$$

where we used that the constraint is satisfied. By substituting Eqs. (41) and (42) and imposing no-flux boundary conditions, we get

$$\begin{aligned} \int_{\Omega} \mu_i \partial_t \varphi_i dx &= \int_{\Omega} (\nabla \mu_i \cdot J_i + M_i \mu_i) dx, \quad i \in \{\ell, c, v\}, \\ \int_{\Omega} \mu_s \partial_t s dx &= \int_{\Omega} (\nabla \mu_s \cdot J_s) dx. \end{aligned}$$

Inserting these relations into Eq. (43), we obtain

$$\frac{d}{dt} \mathcal{L}(\mathbf{q}, \kappa) = \int_{\Omega} \sum_{i \in \{\ell, c, v, s\}} \nabla \mu_i \cdot J_i dx + \int_{\Omega} \sum_{i \in \{\ell, c, v\}} M_i \mu_i dx. \quad (44)$$

We now set $J_c = 0$ (no diffusion of crystalline phase) and otherwise

$$J_i := -m_i(\mathbf{q}) \nabla \mu_i, \quad i \in \{\ell, v, s\},$$

with state-dependent mobilities $m_i(\mathbf{q}) \geq 0$ for $i \in \{\ell, v, s\}$. Therefore, we infer

$$\sum_{i \in \{\ell, v, s\}} \nabla \mu_i \cdot J_i = - \sum_{i \in \{\ell, v, s\}} m_i(\mathbf{q}) |\nabla \mu_i|^2 \leq 0.$$

For the source terms in Eq. (41), we choose

$$\begin{aligned} M_{\ell} &:= h_{\text{cryst}}(\mathbf{q})(\mu_c - \mu_{\ell}) + h_{\text{evap}}(\mathbf{q})(\mu_v - \mu_{\ell}), \\ M_c &:= h_{\text{cryst}}(\mathbf{q})(\mu_{\ell} - \mu_c), \\ M_v &:= h_{\text{evap}}(\mathbf{q})(\mu_{\ell} - \mu_v), \end{aligned}$$

with state-dependent reaction rates $h_{\text{cryst}}(\mathbf{q}), h_{\text{evap}}(\mathbf{q}) \geq 0$. Then, Eq. (44) results in

$$\frac{d}{dt} \mathcal{L}(\mathbf{q}(t)) = - \int_{\Omega} m_{\ell} |\nabla \mu_{\ell}|^2 + m_v |\nabla \mu_v|^2 + m_s |\nabla \mu_s|^2 + h_{\text{evap}} |\mu_{\ell} - \mu_v|^2 + h_{\text{cryst}} |\mu_c - \mu_{\ell}|^2 dx \leq 0, \quad (45)$$

which proves that the Lagrangian functional related to the free energy of the system decreases in time, and hence, that the model is the thermodynamically consistent.

The resulting PDE-system. In summary, with the above choices for the source terms and fluxes the evolution laws Eqs. (41) and (42) describing the diffusion, evaporation and crystallization processes in the solution droplet and the vapor phase thus result in the following coupled PDE-system in $(0, T) \times \Omega$

$$\partial_t \varphi_{\ell} - \operatorname{div}(m_{\ell}(\mathbf{q}) \nabla \mu_{\ell}) = h_{\text{cryst}}(\mathbf{q})(\mu_c - \mu_{\ell}) + h_{\text{evap}}(\mathbf{q})(\mu_v - \mu_{\ell}), \quad (46a)$$

$$\partial_t \varphi_c = h_{\text{cryst}}(\mathbf{q})(\mu_{\ell} - \mu_c), \quad (46b)$$

$$\partial_t \varphi_v - \operatorname{div}(m_v(\mathbf{q}) \nabla \mu_v) = h_{\text{evap}}(\mathbf{q})(\mu_{\ell} - \mu_v), \quad (46c)$$

$$\partial_t s - \operatorname{div}(m_s(\mathbf{q}) \nabla \mu_s) = 0, \quad (46d)$$

$$\varphi_{\ell} + \varphi_c + \varphi_v = 1, \quad (46e)$$

complemented with no-flux boundary conditions and with an initial condition $\mathbf{q}(t = 0) = \mathbf{q}^0$. The mobilities $m_{\ell}, m_v, m_s \geq 0$ and reaction rates $h_{\text{evap}}, h_{\text{cryst}} \geq 0$ for evaporation and crystallization/precipitation are state-dependent functions. Their choice as well as the choice of the free energy density Ψ shall be specified more detailed below in Section 4.3.

Gradient structure of Eq. (46). Following e.g. [26, 27], it can be observed that system Eq. (46) has a gradient structure. For this, we introduce the dual dissipation potential $\mathcal{D}^*(\mathbf{q}; \boldsymbol{\mu}) := \mathcal{D}_D^*(\mathbf{q}; \boldsymbol{\mu}) + \mathcal{D}_R^*(\mathbf{q}; \boldsymbol{\mu})$ with $\mathcal{D}_D^*(\mathbf{q}; \boldsymbol{\mu}) := \int_{\Omega} D_D^*(\mathbf{q}; \nabla \boldsymbol{\mu}) dx$ and $\mathcal{D}_R^*(\mathbf{q}; \boldsymbol{\mu}) := \int_{\Omega} D_R^*(\mathbf{q}; \boldsymbol{\mu}) dx$ the dual dissipation potentials for the diffusion and the reaction processes with densities $D^*(\mathbf{q}; \boldsymbol{\mu}, \nabla \boldsymbol{\mu}) := D_D^*(\mathbf{q}; \nabla \boldsymbol{\mu}) + D_R^*(\mathbf{q}; \boldsymbol{\mu})$,

$$D_D^*(\mathbf{q}; \nabla \boldsymbol{\mu}) := \frac{1}{2} \nabla \boldsymbol{\mu} : \mathbb{M}_D(\mathbf{q}) \nabla \boldsymbol{\mu}, \quad \text{where } \mathbb{M}_D(\mathbf{q}) := \text{diag}(m_{\ell}(\mathbf{q}), 0, m_v(\mathbf{q}), m_s(\mathbf{q})), \quad \text{and}$$

$$D_R^*(\mathbf{q}; \boldsymbol{\mu}) := \frac{1}{2} (h_{\text{evap}}(\mathbf{q})) |\mu_{\ell} - \mu_v|^2 + h_{\text{cryst}}(\mathbf{q}) |\mu_c - \mu_{\ell}|^2$$

for $\boldsymbol{\mu} = (\mu_{\ell}, \mu_c, \mu_v, \mu_s)$. It is easy to see that the potentials are quadratic and positively semidefinite with respect to the variable $\boldsymbol{\mu}$, so that their functional derivatives result in symmetric and positively semidefinite operators. Moreover, one finds that system Eq. (46) is given by the evolution law

$$\partial_t \mathbf{q} = \mathbf{D}_{\boldsymbol{\mu}} \mathcal{D}^*(\mathbf{q}; -\mathbf{D}_{\mathbf{q}} \mathcal{L}(\mathbf{q}, \kappa)). \quad (47)$$

Testing the gradient system Eq. (47) by $\boldsymbol{\mu} = \mathbf{D}_{\mathbf{q}} \mathcal{L}(\mathbf{q}, \kappa)$ results in

$$\begin{aligned} \frac{d}{dt} \mathcal{L}(\mathbf{q}, \kappa) &= \langle \mathbf{D}_{\mathbf{q}} \mathcal{L}(\mathbf{q}, \kappa), \partial_t \mathbf{q} \rangle = \langle \mathbf{D}_{\mathbf{q}} \mathcal{L}(\mathbf{q}, \kappa), \mathbf{D}_{\boldsymbol{\mu}} \mathcal{D}^*(\mathbf{q}; -\mathbf{D}_{\mathbf{q}} \mathcal{L}(\mathbf{q}, \kappa)) \rangle \\ &= - \int_{\Omega} (\nabla \boldsymbol{\mu} : \mathbb{M}_D(\mathbf{q}) \nabla \boldsymbol{\mu} + h_{\text{evap}}(\mathbf{q})) |\mu_{\ell} - \mu_v|^2 + h_{\text{cryst}}(\mathbf{q}) |\mu_c - \mu_{\ell}|^2 dx \\ &= -2(\mathcal{D}_R^*(\mathbf{q}; \boldsymbol{\mu}) + \mathcal{D}_D^*(\mathbf{q}; \boldsymbol{\mu})) \leq 0, \end{aligned} \quad (48)$$

which is the energy-dissipation estimate Eq. (45) recovered from the gradient structure. In order to address the different dissipative processes separately we also introduce

$$\mathcal{D}_{\text{cryst}}^* := \int_{\Omega} \frac{1}{2} h_{\text{cryst}}(\mu_c - \mu_{\ell})^2 dx, \quad \mathcal{D}_{\text{evap}}^* := \int_{\Omega} \frac{1}{2} h_{\text{evap}}(\mu_v - \mu_{\ell})^2 dx, \quad \mathcal{D}_{m_i}^* := \int_{\Omega} \frac{1}{2} m_i |\nabla \mu_i|^2 dx, \quad (49)$$

for $i \in \{s, \ell, v\}$ such that $\mathcal{D}_D^* = \mathcal{D}_{m_{\ell}}^* + \mathcal{D}_{m_v}^* + \mathcal{D}_{m_s}^*$ and $\mathcal{D}_R^* = \mathcal{D}_{\text{cryst}}^* + \mathcal{D}_{\text{evap}}^*$.

4.2 Weak formulation and saddle point structure

Weak formulation. We rewrite system Eq. (46) in terms of a weak formulation, where we seek $(\mathbf{q}, \boldsymbol{\mu}, \kappa)$ as unknown functions with corresponding test functions $(\mathbf{w}, \boldsymbol{\xi}, w_{\kappa})$ with components $\mathbf{w} = (w_{\ell}, w_c, w_v, w_s)$ and $\boldsymbol{\xi} = (\xi_{\ell}, \xi_c, \xi_v, \xi_s)$. For a.a. $t \in (0, T)$ we thus seek $(\mathbf{q}(t), \boldsymbol{\mu}(t), \kappa(t))$ such that

$$\begin{aligned} \int_{\Omega} \left[m_{\ell}(\mathbf{q}) \nabla \mu_{\ell} \cdot \nabla \xi_{\ell} + \xi_{\ell} \partial_t \varphi_{\ell} + m_s(\mathbf{q}) \nabla \mu_s \cdot \nabla \xi_s + \xi_s \partial_t s + m_v(\mathbf{q}) \nabla \mu_v \cdot \nabla \xi_v + \xi_v \partial_t \varphi_v \right. \\ \left. + h_{\text{evap}}(\mathbf{q})(\mu_{\ell} - \mu_v)(\xi_{\ell} - \xi_v) + h_{\text{cryst}}(\mathbf{q})(\mu_c - \mu_{\ell})(\xi_c - \xi_{\ell}) + \xi_c \partial_t \varphi_c \right] dx = 0, \end{aligned} \quad (50a)$$

$$\int_{\Omega} \mu_{\ell} w_{\ell} + \mu_s w_s + \mu_c w_c + \mu_v w_v dx - \langle \mathbf{D} \mathcal{L}(\mathbf{q}, \kappa), (\mathbf{w}, w_{\kappa}) \rangle = 0, \quad (50b)$$

for all $(\mathbf{w}, w_{\kappa}, \boldsymbol{\xi})$, where we abbreviated the Fréchet derivative of the Lagrange functional in the direction (\mathbf{w}, w_{κ}) by

$$\langle \mathbf{D} \mathcal{L}(\mathbf{q}, \kappa), (\mathbf{w}, w_{\kappa}) \rangle = \int_{\Omega} \partial_s \Psi w_s + \sum_{i \in \{\ell, c, v\}} (\partial_{\varphi_i} \Psi \cdot w_i + (\partial_{\nabla \varphi_i} \Psi) \cdot \nabla w_i + \kappa w_i) + w_{\kappa} (\varphi_c + \varphi_{\ell} + \varphi_v - 1) dx. \quad (51)$$

In this way, Eq. (50b) ensures relations Eq. (40) as well as the constraint Eq. (46e), whereas Eq. (50a) comprises the weak form of the evolution laws Eq. (46). Observe that, by testing Eq. (50b) with $\mathbf{w} = \partial_t \mathbf{q}$, $w_{\kappa} = \partial_t \kappa$ and Eq. (50a) with $\boldsymbol{\xi} = \boldsymbol{\mu}$ we obtain the energy-dissipation estimate Eq. (45).

Saddle point structure. Exploiting the gradient structure Eq. (47), we can introduce the bilinear forms

$$\begin{aligned} a(\boldsymbol{\mu}, \boldsymbol{\xi}) &:= \langle \mathbf{D}_{\boldsymbol{\mu}} \mathcal{D}^*(\mathbf{q}; \boldsymbol{\mu}), \boldsymbol{\xi} \rangle \\ &= \int_{\Omega} \sum_{i \in \{\ell, v, s\}} \left[m_i \nabla \mu_i \cdot \nabla \xi_i \right] + h_{\text{evap}}(\mu_{\ell} - \mu_v)(\xi_{\ell} - \xi_v) + h_{\text{cryst}}(\mu_c - \mu_{\ell})(\xi_c - \xi_{\ell}) dx, \end{aligned} \quad (52a)$$

$$b(\mathbf{w}, \boldsymbol{\mu}) := \int_{\Omega} (\mu_{\ell} w_{\ell} + \mu_s w_s + \mu_c w_c + \mu_v w_v) dx, \quad (52b)$$

and rewrite the weak formulation Eq. (50) in the following saddle-point structure

$$a(\boldsymbol{\mu}, \boldsymbol{\xi}) + b(\partial_t \mathbf{q}, \boldsymbol{\xi}) = 0, \quad (53a)$$

$$b(\mathbf{w}, \boldsymbol{\mu}) = \langle \mathbf{D}\mathcal{L}(\mathbf{q}, \kappa), (\mathbf{w}, w_\kappa) \rangle, \quad (53b)$$

for all $(\mathbf{w}, w_\kappa, \boldsymbol{\xi})$. In this way Eq. (53a) coincides with Eq. (50a) and Eq. (53b) with Eq. (50b). Repeating the test with $\mathbf{w} = \partial_t \mathbf{q}$, $w_\kappa = \partial_t \kappa$, $\boldsymbol{\xi} = \boldsymbol{\mu}$ in Eq. (53) we get

$$\frac{d}{dt} \mathcal{L}(\mathbf{q}(t)) = \langle \mathbf{D}\mathcal{L}(\mathbf{q}, \kappa), (\partial_t \mathbf{q}, \partial_t \kappa) \rangle = b(\partial_t \mathbf{q}, \boldsymbol{\mu}) = -a(\boldsymbol{\mu}, \boldsymbol{\mu}) = -2\mathcal{D}^*(\mathbf{q}; \boldsymbol{\mu}) \leq 0, \quad (54)$$

which is again Eq. (45), recovered from the gradient structure of the coupled system, alike Eq. (48).

4.3 Choice of free energy and dissipation potentials

In the following we specify more detailed a choice for the free energy density and the state-dependent mobilities and reaction rates suited to capture certain effects as evaporation and crystallization progress in the droplet.

Free energy. As discussed in Section 4.1, we consider the free energy and the Lagrange functional

$$\mathcal{E}(\mathbf{q}) := \int_{\Omega} \Psi(\boldsymbol{\varphi}, \nabla \boldsymbol{\varphi}, s) \, dx, \quad \mathcal{L}(\mathbf{q}, \kappa) := \mathcal{E}(\mathbf{q}) + \int_{\Omega} \kappa(\varphi_\ell + \varphi_c + \varphi_v - 1) \, dx. \quad (55)$$

Now we set Ψ as follows

$$\begin{aligned} \Psi(\boldsymbol{\varphi}, \nabla \boldsymbol{\varphi}, s) &:= \sum_{i \in \{\ell, c, v\}} \gamma_i \left[\frac{\varepsilon}{2} |\nabla \varphi_i|^2 + \frac{1}{\varepsilon} W(\varphi_i) \right] + \Pi(\boldsymbol{\varphi}, s), \\ \Pi(\boldsymbol{\varphi}, s) &:= s \ln(s) + (1-s) \ln(1-s) + \varphi_c \beta(s - s_{\text{sat}}) + \lambda \varphi_v s, \end{aligned} \quad (56)$$

where ε denotes the thickness of the interface, γ_i represent the surface tension coefficients, W is the phase-field potential and the potential Π takes into account the coupling between $\boldsymbol{\varphi}$ and s . More precisely, in Π we have the free energy that drives the solute diffusion and keeps $0 < s < 1$ as well as an extra term that for $\beta < 0$ favors crystallization beyond a saturation threshold, *i.e.*, for $s > s_{\text{sat}}$. The classical mixture term with sufficiently large $\lambda > 0$ prevents the solute from entering the vapor phase. Note, the standard quartic double well does not strongly enforce the condition $0 \leq \varphi_i \leq 1$, for which other phase-field energies of logarithmic or double-obstacle type might be better suited (see [28, 29] and references therein). Therefore, in order to better capture the constraint $0 \leq \varphi_i \leq 1$, the phase-field energy $W \in C^1(\mathbb{R})$ is chosen in the form

$$W(\varphi) := \begin{cases} \Lambda \varphi^2 & \varphi < 0, \\ 18\varphi^2(1-\varphi)^2 & 0 \leq \varphi \leq 1, \\ \Lambda(\varphi-1)^2 & \varphi > 1, \end{cases} \quad (57)$$

for a sufficiently large $\Lambda \gg 1$ to additionally penalize values of φ outside the interval $[0, 1]$, see Fig. 3. The terms multiplying γ_i encode the surface tension between the i th and the j th phase via

$$\gamma_{ij} = \frac{1}{2}(\gamma_i + \gamma_j) > 0 \quad \text{for } i, j \in \{\ell, c, v\} \text{ and } i \neq j. \quad (58)$$

Note that this gives the three independent coefficients determined by the values $\gamma_{\ell v}$, $\gamma_{\ell c}$, γ_{cv} , where not all values might be feasible due to the restriction $\gamma_i \geq 0$ of this particular phase-field energy.

Chemical potentials. With the above choice of free energy and Lagrangian functional we observe that the chemical potentials from Eq. (40) take the specific form

$$\begin{aligned} \mu_\ell &= \frac{\delta L}{\delta \varphi_\ell} = -\gamma_\ell \varepsilon \Delta \varphi_\ell + \frac{\gamma_\ell}{\varepsilon} \frac{\partial W}{\partial \varphi_\ell} + \frac{\partial \Pi}{\partial \varphi_\ell} + \kappa, \\ \mu_c &= \frac{\delta L}{\delta \varphi_c} = -\gamma_c \varepsilon \Delta \varphi_c + \frac{\gamma_c}{\varepsilon} \frac{\partial W}{\partial \varphi_c} + \frac{\partial \Pi}{\partial \varphi_c} + \kappa, \\ \mu_v &= \frac{\delta L}{\delta \varphi_v} = -\gamma_v \varepsilon \Delta \varphi_v + \frac{\gamma_v}{\varepsilon} \frac{\partial W}{\partial \varphi_v} + \frac{\partial \Pi}{\partial \varphi_v} + \kappa, \\ \mu_s &= \frac{\delta L}{\delta s} = \frac{\partial \Pi}{\partial s}. \end{aligned} \quad (59)$$

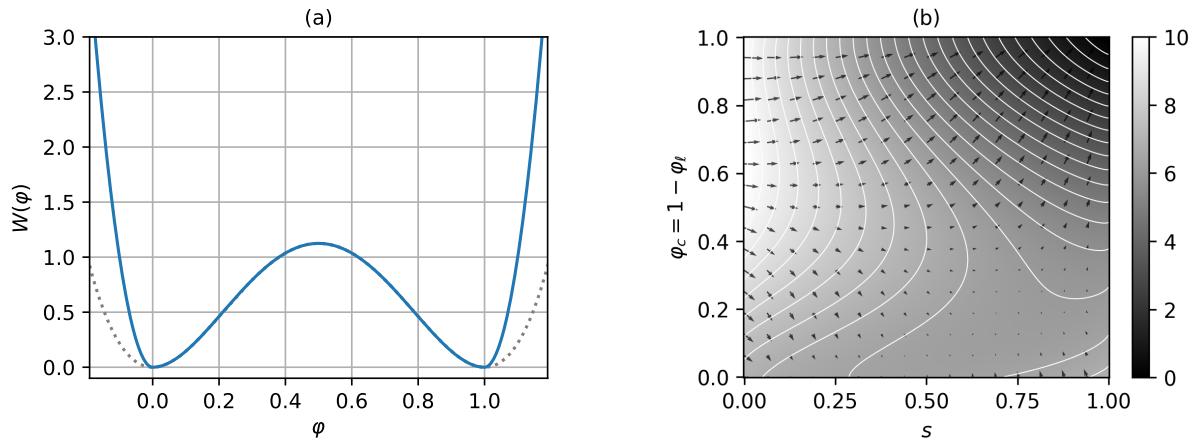


Figure 3: (a) Potential $W(\varphi)$ from Eq. (57) for $\Lambda = 100$ (solid, blue) compared to standard quartic $18\varphi^2(1-\varphi)^2$ (dotted, gray) and (b) energy landscape $(\Psi - \min \Psi)$ with $\lambda = 10$, $\beta = -10$, $\Lambda = 100$, $\gamma_\ell = \gamma_c = 1/8$, $\gamma_v = 2$, $\varepsilon = 0.2$, $s_{\text{sat}} = 0.3$ for a homogeneous solution (no gradients) without vapor $\varphi_v = 0$, i.e., $\varphi_c = 1 - \varphi_\ell$ with isolines and negative gradient vector field.

Mobilities and reaction rates. For the liquid, vapor, and solute diffusive mobilities m_ℓ , m_v , and m_s we use

$$\begin{aligned} m_\ell(\mathbf{q}) &:= (m_{\ell\ell}|\varphi_\ell| + m_{\ell v}|\varphi_v| + m_{\ell c}|\varphi_c|), \\ m_v(\mathbf{q}) &:= (m_{v\ell}|\varphi_\ell| + m_{vv}|\varphi_v| + m_{vc}|\varphi_c|), \\ m_s(\mathbf{q}) &:= (m_{s\ell}|\varphi_\ell| + m_{sv}|\varphi_v| + m_{sc}|\varphi_c|)s(1-s), \end{aligned} \quad (60)$$

for some given constant $m_{ij} > 0$ that set the value of the liquid, vapor, and solute mobility in the pure liquid, vapor or crystalline phase for $i, j \in \{\ell, v, s\}$, respectively. Note that the form of m_s makes sure that diffusion of the solute is confined to regions where $s \in (0, 1)$. For the reaction rates we use

$$h_{\text{evap}}(\mathbf{q}) := h_e^0|\varphi_\ell\varphi_v|, \quad h_{\text{cryst}}(\mathbf{q}) := h_c^0|\varphi_\ell|, \quad (61)$$

for some given constant $h_e^0, h_c^0 > 0$. The form of the evaporation rate makes sure that evaporation is restricted to the liquid-vapor interface whereas the crystallization rate restricts crystallization to the presence of a fluid phase.

4.4 Numerical examples

In the following we carry out numerical simulation using the three-phase model Eq. (46), also making use of the specific form of the potentials discussed in Section 4.3. Based on the weak formulation introduced in Section 4.2 we provide a discrete scheme in space and time in Section 4.4.1. Subsequently, in Section 4.4.2 we present and discuss numerical results for evaporating droplets in different scenarios by varying certain parameter sets, such as the initial solute concentration and the parameters λ and β in the choice of the free energy Eq. (56). The Python code used in this section with the corresponding example parameters is published in [30].

4.4.1 Discretization in space and time.

In order to discretize the weak formulation Eq. (50) in time we introduce $0 = t^0 < t^1 < \dots < t^N = T$ and, for each $k \in \{1, \dots, N\}$ we set $\mathbf{q}^k := \mathbf{q}(t^k) = (\varphi_\ell^k, \varphi_c^k, \varphi_v^k, s^k)$ and correspondingly $\boldsymbol{\mu}^k := \boldsymbol{\mu}(t^k) = (\mu_\ell^k, \mu_c^k, \mu_v^k, \mu_s^k)$ and

the multiplier $\kappa^k := \kappa(t^k)$. For each $k \in \{1, \dots, N\}$ we seek $(\mathbf{q}^k, \boldsymbol{\mu}^k, \kappa^k)$, so that

$$\begin{aligned} \int_{\Omega} m_{\ell}^{k-1} \nabla \mu_{\ell}^k \cdot \nabla \xi_{\ell} + \xi_{\ell} \left(\frac{\varphi_{\ell}^k - \varphi_{\ell}^{k-1}}{\tau^k} \right) + m_s^{k-1} \nabla \mu_s^k \cdot \nabla \xi_s + \xi_s \left(\frac{s^k - s^{k-1}}{\tau^k} \right) + m_v^{k-1} \nabla \mu_v^k \cdot \nabla \xi_v + \xi_v \left(\frac{\varphi_v^k - \varphi_v^{k-1}}{\tau^k} \right) \\ + \xi_c \left(\frac{\varphi_c^k - \varphi_c^{k-1}}{\tau^k} \right) + h_{\text{evap}}^{k-1} (\mu_v^k - \mu_{\ell}^k) (\xi_v - \xi_{\ell}) + h_{\text{cryst}}^{k-1} (\mu_c^k - \mu_{\ell}^k) (\xi_c - \xi_{\ell}) \, dx = 0, \end{aligned} \quad (62a)$$

$$\int_{\Omega} \mu_{\ell}^k w_{\ell} + \mu_s^k w_s + \mu_c^k w_c + \mu_v^k w_v \, dx - \langle \text{D}\mathcal{L}(\mathbf{q}^k, \kappa^k), \mathbf{w} \rangle = 0, \quad (62b)$$

for all $(\mathbf{w}, \boldsymbol{\xi})$. Above we abbreviated $m_i^k := m_i(\mathbf{q}^k)$ and $h_{\alpha}^k := h_{\alpha}(\mathbf{q}^k)$ for $i \in \{\ell, s, v\}$ and $\alpha \in \{\text{react, cryst}\}$ and $\tau^k := t^k - t^{k-1}$. This nonlinear saddle point problem we discretize in space via P^1 finite elements for $\mathbf{q}^k, \boldsymbol{\mu}^k$ and κ^k and solve it via Newton's method. Due to the explicit handling of the mobilities, the nonsmooth state-dependence via $|\varphi_i^{k-1}|$ terms is unproblematic for the Newton solver. For discretization and solution we use the finite element framework FEniCS [31]. We employ an adaptive time step control based on the number of Newton steps per iteration to reach a specified tolerance of the residual. We implement a spherical symmetric setup with radial coordinate $r = \sqrt{x_1^2 + x_2^2 + x_3^2} = |\mathbf{x}|$ and $\mathbf{x} = (x_1, x_2, x_3) \in \Omega$ by replacing in the weak formulation Eq. (62) all integrals as follows $\int_{\Omega} \dots \, dx \rightarrow \int_0^L \dots r^2 \, dr$ to place a spherical droplet of radius $R_0 < L$.

4.4.2 Examples for evaporating droplets

In the following, we present and discuss parameter sets shown in Tab. 1 for a droplet of initial size $R_0 = 3$ and a domain of radius $L = 4$. Throughout the examples, we vary some selected parameters as specified below in Tab. 2. We use the initial data

$$\varphi_c^0(r) = 0, \quad \varphi_v^0(r) = \frac{1}{2} [1 + \tanh(\frac{3}{\varepsilon}(r - R_0))], \quad \varphi_{\ell}^0(r) = 1 - \varphi_v^0(r), \quad s^0(r) = \bar{s}^0 \exp(-\lambda \varphi_v^0(r)), \quad (63)$$

that encode an initial liquid droplet for $r < R_0$ with an adjacent vapor phase for $r > R_0$ but no initial crystalline phase. The initial solute concentration in the liquid is \bar{s}^0 . We solve problem Eq. (46) for $0 < t < T$. The main idea of the following spherical symmetric 3D examples is to drive evaporation via the vapor surface tension, mainly through $\gamma_v = 2$, with smaller values $\gamma_{\ell} = \gamma_c = 1/8$. The main modifications in the examples are the solute concentration \bar{s}^0 in Eq. (63) and the parameters λ , and β in the free energy density Eq. (56). The role of λ is to energetically penalize the solute from entering the vapor phase, whereas β introduces a tilt to the phase-field energy that, for sufficiently negative values, favors the creation of a crystalline phase.

parameter	γ_{ℓ}	γ_v	γ_c	ε	s_{sat}	Λ	$(m_{\ell\ell}, m_{\ell v}, m_{\ell c})$	$(m_{v\ell}, m_{vv}, m_{vc})$	$(m_{s\ell}, m_{sv}, m_{sc})$	h_{ℓ}^0	h_c^0
value	1/8	2	1/8	0.2	0.3	10^2	$(1, 1, 10^{-2})$	$(10^{-2}, 1, 10^{-2})$	$(10^{-2}, 1, 10^{-2})$	1	1

Table 1: General parameters of energy and dissipation

parameter	λ	β	\bar{s}^0
value Ex. (a)	1	-1	10^{-2}
value Ex. (b)	10	-1	10^{-1}
value Ex. (c)	10	-10	10^{-1}
value Ex. (d)	10	-10	10^{-2}

Table 2: Varying parameters throughout Examples (a)–(d)

Example (a): Droplet completely evaporates. For the first example we select a low solute concentration $\bar{s}^0 = 10^{-2}$ and moderately large values $\lambda = 1, \beta = -1$, so that the solute can eventually be dispersed in the vapor phase and the crystalline phase is not strongly favored energetically. The corresponding solution of the phase field model is shown in Fig. 4 over the time interval $[0, 25]$. Starting with a droplet of initial radius 3 the droplet size shrinks over time as can be seen in the plot for φ_{ℓ} . As the radius has shrunk to the size of $R \approx 1.5$ at time $t = 16$ the evaporation process rapidly

accelerates and leads to the extinction of the droplet at time $t \approx 16$. In accordance with the low solute concentration, no crystalline phase is formed, cf. the plot for φ_c in Fig. 4. Accordingly, the vapor phase, depicted in the plot of φ_v in Fig. 4, is the complement of the liquid phase. The evolution of the free energy and dissipation during this process is depicted in the left panel of Fig. 5. One can see that the free energy rapidly decreases due to evaporation, which is the main dissipative process, until the droplet is extinguished at $t \approx 16$ close to the steady state, after which the energy remains (approximately) constant.

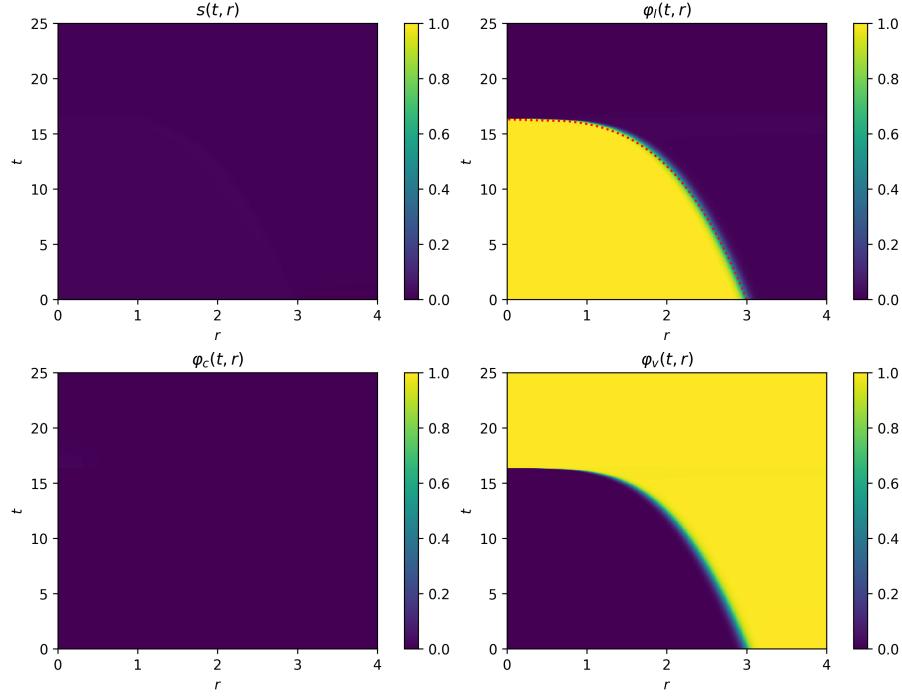


Figure 4: Solute concentration $s(t, r)$ and phase fields $\varphi_i(t, r)$ for $i = \{\ell, c, v\}$ as a function of time t and radius r for different parameters for Example (a) with $\lambda = 1$, $\beta = -1$, $\bar{s}^0 = 10^{-2}$, where the droplet completely evaporates. The dotted red curve indicates the function $R(t) = (R_0^{1/\alpha} - Ct)^\alpha$ for $\alpha = 0.3$.

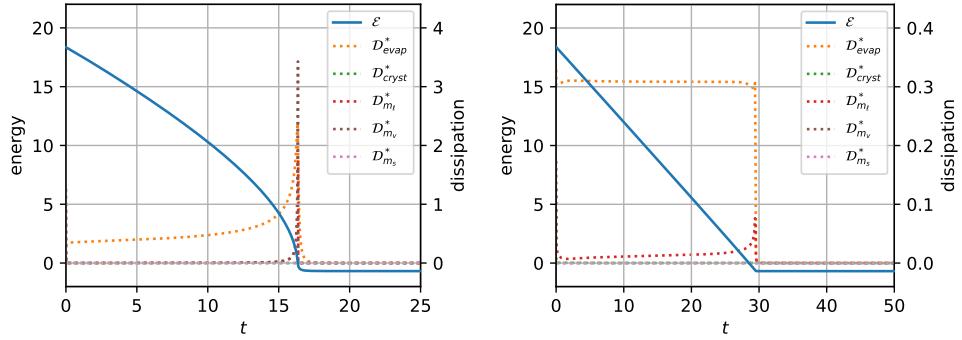


Figure 5: Energy \mathcal{E} and different contributions to the dissipation \mathcal{D}^* for the Example (a) shown in Fig. 4 and Fig. 6 (left) with the mobilities from Tab. 1 and (right) with the reduced liquid mobilities $m_{\ell i} = 10^{-3}$ for $i \in \{\ell, v, c\}$.

In the plot for φ_ℓ in Fig. 4 we show the liquid phase field overlaid with the function $R(t) = (R_0^{1/\alpha} - Ct)^\alpha$ and find that $\alpha = 0.3$ provides a good fit to the simulation. This exponent is close to the expectation $\alpha = 1/3$ for the classical Mullins-Sekerka interface law or the canonical droplet dissolution in the LSW theory [32] reproduced by Cahn-Hilliard phase-field models [33]. In the corresponding study of Section 2.1.2 with the one-dimensional ODE sharp-interface model for droplet evaporation in the diffusion-limited regime, also the complete extinction of the droplet can be observed, but equation Eq. (10) predicts a law for the evolution of the droplet radius with the exponent $\alpha = 1/2$. This exponent rather matches the evolution of the droplet boundary by mean curvature flow, which is the sharp-interface limit of the Allen-Cahn equation

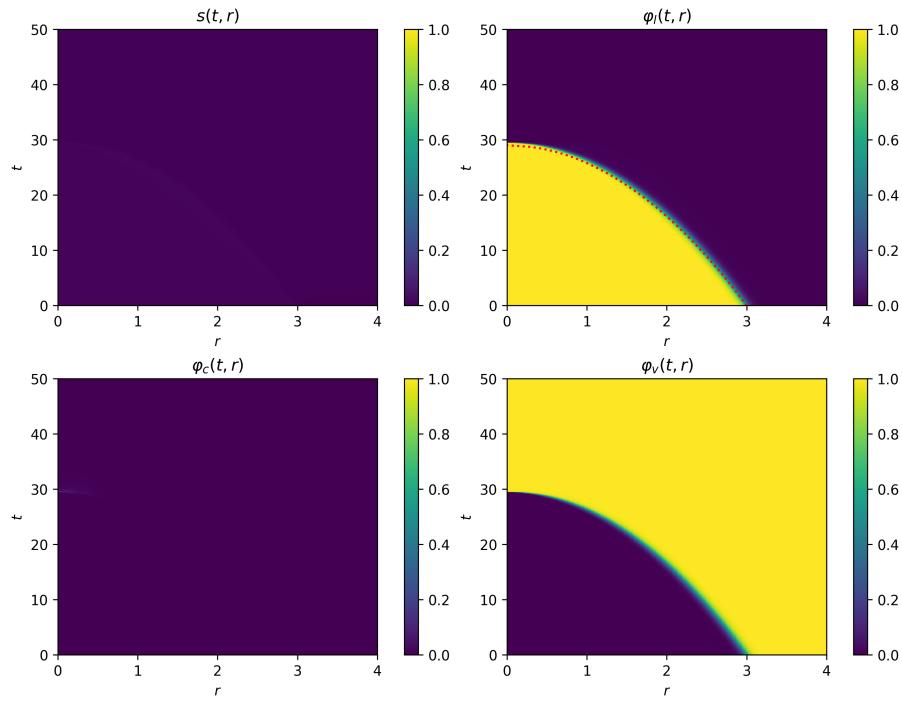


Figure 6: Parameters as Fig. 4 but with $m_{\ell i} = 10^{-3}$ for $i \in \{\ell, c, v\}$, where the droplet still completely evaporates. The dotted red curve indicates the function $R(t) = (R_0^{1/\alpha} - Ct)^\alpha$ for $\alpha = 0.5$, as also predicted in Eq. (10).

[34, 35]. However, if we reduce in our model the mobilities for the liquid phase, e.g., $m_{\ell i} = 10^{-3}$ for $i \in \{\ell, c, v\}$ and run the simulation over a time interval $[0, 50]$, so that the droplet extinction is dominated by h_{evap} and diffusion is practically absent, then the radius follows the above $R(t)$ -law with an exponent close to the prediction of equation Eq. (10) in the diffusion-limited regime, i.e., the red dashed line in Fig. 6 in this parameter setting features the exponent $\alpha = 1/2$. The corresponding energy plot in the right panel of Fig. 5 shows an almost linear descent of the energy with almost constant dissipation dominated by evaporation $\mathcal{D}_{\text{evap}}^*$ with the droplet vanishing at $t \approx 29$.

Example (b): Evaporation stops with a solution droplet. Keeping $\beta = -1$, but using larger parameters λ and \bar{s}^0 , i.e., $\lambda = 10$ and $\bar{s}^0 = 0.1$, results in the droplet evolution depicted in Fig. 7. Due to evaporation, the droplet size shrinks from its initial radius $R_0 = 3$ to the radius $R = 1.5$, which is reached at $t \approx 60$ and then remains constant, cf. the plot for φ_ℓ . Thanks to the large value of λ the solute is confined to the liquid phase, where it diffuses, and, due to the loss in droplet size, the solute concentration is increased over time, cf. the plot for s in Fig. 7. As in Example (a), with $\beta = -1$, also here no crystalline phase is formed, cf. the plot for φ_c , although the solute concentration certainly exceeds the saturation threshold $s_{\text{sat}} = 0.3$. Yet, with $\beta = -1$, it is energetically more favorable to keep $\varphi_c \equiv 0$ during the evolution, cf. Eq. (56). Hence, again, the vapor phase is given by the complement of the liquid phase, cf. the plot of φ_v in Fig. 7. The evolution of the free energy and the dissipative contributions during this process is depicted in Fig. 8. The energy monotonically decreases until the evaporation process stops at $t \approx 30$ and solute diffusion stops at $t \approx 60$ from then on, also the energy remains constant at a positive value.

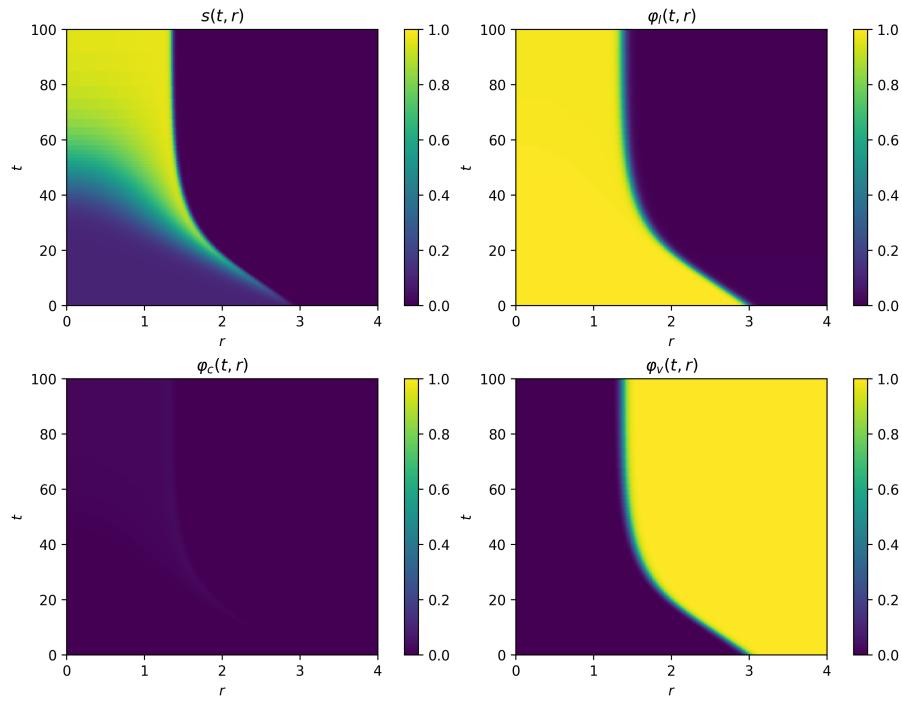


Figure 7: Solute concentration $s(t, r)$ and phase fields $\varphi_i(t, r)$ for $i = \{\ell, c, v\}$ as a function of time t and radius r for Example (b) with $\lambda = 10$, $\beta = -1$, $\bar{s}^0 = 10^{-1}$, where the droplet partially evaporates and stabilizes with homogeneous solute concentration.

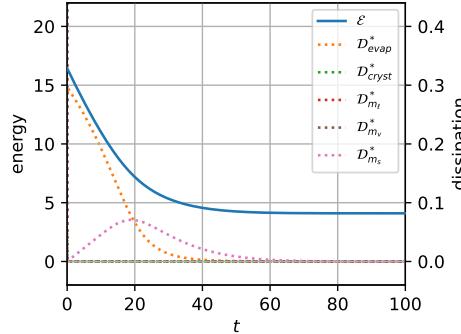


Figure 8: Energy \mathcal{E} and different contributions to the dissipation \mathcal{D}^* for the Example (b) shown in Fig. 7.

Example (c): Droplet with crystalline crust. Here we keep $\lambda = 10$ and $\bar{s}^0 = 0.1$ as in Example (b), but additionally decrease β to $\beta = -10$, which now favors the creation of a crystalline phase. The simulation results are depicted in Fig. 9. As can be seen in the plot of φ_ℓ , evaporation first decreases the droplet radius from initially $R_0 = 3$ to $R = 2.5$ at time $t = 5$. Then, additionally also the crystallization process sets in. The crystalline phase forms at the interface between liquid and vapor, as is favored by $h_{\text{cryst}}(\mathbf{q})$ in Eq. (61) and also by the values of the surface tensions, cf. Eq. (58) and Tab. 1. Observe that the latter equally also allow for a liquid layer between the crystal and the vapor phase, as can be detected in the plot of φ_ℓ from $t \approx 13$ on. Then, also the crystallization process rapidly increases. Since the crystal phase is immobile, i.e., $m_c = 0$ in Eq. (60), it thus creates a crust at the droplet surface. Comparing the plots of s and φ_c in Fig. 9, one can see that this sudden increase of the crystal phase goes along with a high amount of solute significantly exceeding the saturation threshold. Due to the formation of a crust at the droplet surface, the evaporation process is significantly slowed down after $t \approx 13$, but does not come to a halt. This behavior can also be confirmed by the evolution of the free energy and dissipative contributions over time as depicted in Fig. 10. Here one sees a first decrease in energy due to evaporation, clearly followed by a sudden energy drop due to a rapid formation of a crystalline crust at $t \approx 13$, which then continues with a moderate energy decrease due to the solute diffusion.

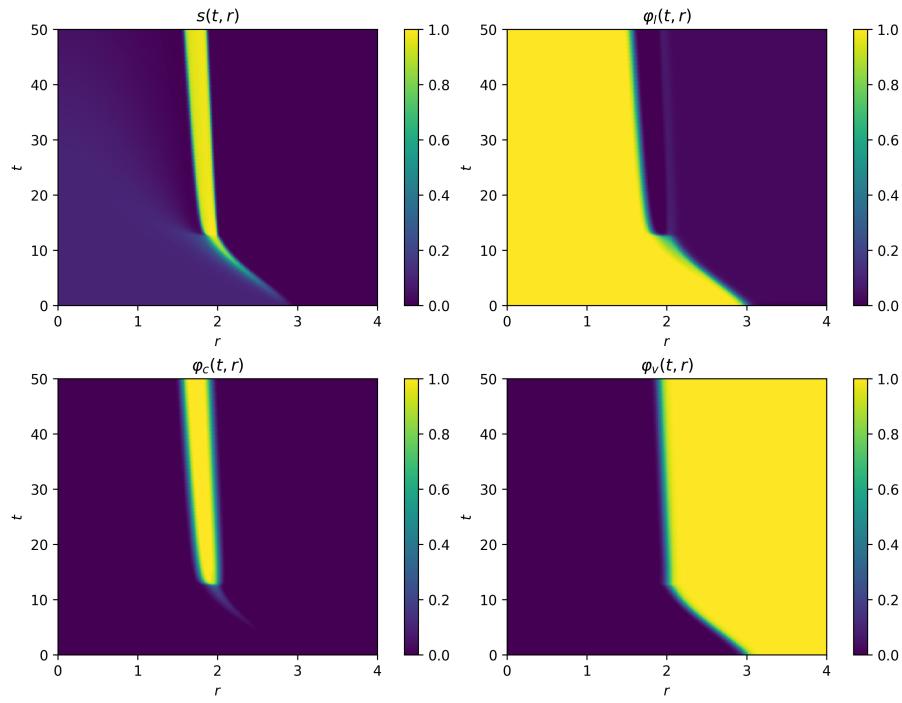


Figure 9: Solute concentration $s(t, r)$ and phase fields $\varphi_i(t, r)$ for $i = \{\ell, c, v\}$ as a function of time t and radius r for Example (c) with $\lambda = 10$, $\beta = -10$, $\bar{s}^0 = 10^{-1}$, where the droplet evaporates and forms a crystalline crust.

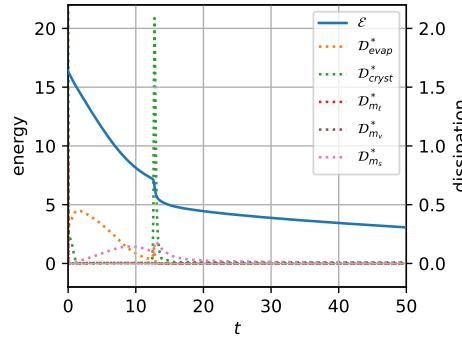


Figure 10: Energy \mathcal{E} and different contributions to the dissipation \mathcal{D}^* for the Example (c) shown in Fig. 9.

Example (d): Droplet evaporating and forming a crystal. Here we again choose $\lambda = 10$, $\beta = -10$, but a low solute concentration $\bar{s}^0 = 10^{-2}$. The low value of β again favors the formation of a crystal phase. However, due to the lower solute concentration the crystal phase forms slower, cf. plot of φ_c in Fig. 11, and evaporation progresses, first quickly, till a radius of $R \approx 0.8$ is reached at $t \approx 11$, cf. the plot of φ_ℓ . Then it slows down, but progresses till complete evaporation of the liquid phase is reached at $t = 30$. The slowing-down of the evaporation process is due to a speed-up of crystallization, which first primarily takes place at the interface between the liquid and the vapor phase. The solute is confined to the crystal and the liquid phase, but due to the lower initial concentration, it can just slow down the evaporation process, but not bring it to a halt. Therefore, evaporation continues, so that at $t = 30$ a crystal is left. The profiles of the free energy and the dissipative contributions depicted in Fig. 12 also show a rapid decrease of the free energy due to the fast evaporation till $t \approx 11$, followed by a slow energy decrease due to crystallization and slow evaporation. The energy reaches the value approximately 0 at $t \approx 30$, when the droplet has fully crystallized and the liquid phase has disappeared.

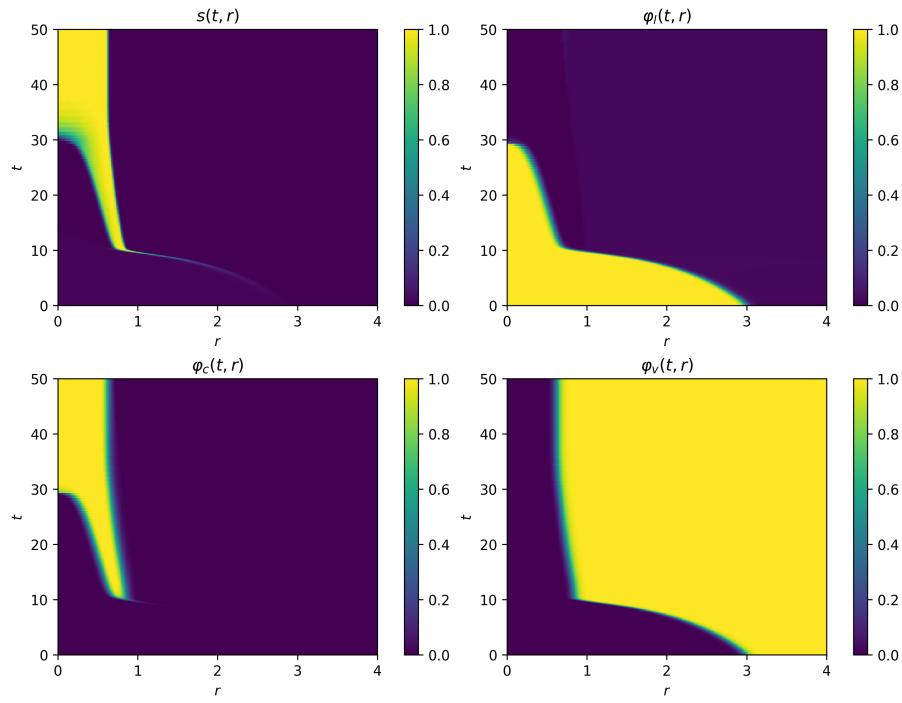


Figure 11: Solute concentration $s(t, r)$ and phase fields $\varphi_i(t, r)$ for $i = \{\ell, c, v\}$ as a function of time t and radius r for Example (d) with $\lambda = 10$, $\beta = -10$, $\bar{s}^0 = 10^{-1}$, where the droplet evaporates, reaches $s = 1$, and then precipitates with liquid phase vanishing.

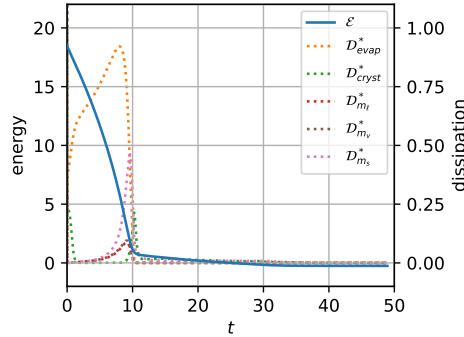


Figure 12: Energy \mathcal{E} and different contributions to the dissipation \mathcal{D}^* for the Example (d) shown in Fig. 11.

5 Conclusions

We treat three aspects of aerosol-mediated air-borne virus transport on different length and time scales. In Section 2, we have presented a theoretical framework to describe the coupled dynamics of evaporation and sedimentation of airborne droplet ensembles in terms of their size distribution, which allows to calculate the fraction of virions that remain suspended in air as a function of time and relative humidity. An exact solution of the underlying population dynamics equation is derived, which can be evaluated numerically for arbitrary initial droplet distributions. The results show that the droplet size distribution has a significant effect on the fraction of virions that remain suspended in air. In Section 3, we have employed Molecular Dynamics simulations to determine the molecular reflection coefficient of water molecules at the vapor-liquid water interface as a function of the angle and velocity of impinging water molecules. The molecular reflection coefficient is a key input parameter for the calculation of the water evaporation rate in Section 2. The results show that the reflection coefficient is small for water molecules impinging onto the liquid phase with velocities typical for room temperature, but can become significant for larger velocities and large angles of incidence.

Subsequently, in Section 4 we have derived a thermodynamically consistent three-phase diffuse-interface model in terms of a coupled Cahn-Hilliard/Allen-Cahn model, featuring a liquid, a vapor, and a crystalline phase, where a solute species diffuses in the liquid and may crystallize. We discussed the gradient-flow structure of the model and provided a weak formulation. Based on this, we introduced a discretization in space and time, and carried out numerical simulations in physically meaningful scenarios. In this way, we showed that the diffuse-interface model is able to capture features that were also observed with the one-dimensional model of Section 2 and to generalize it to the process of crystallization and crust formation. The phase-field framework captures a broad range of experimentally relevant droplet-drying scenarios. A natural next step is a more systematic calibration of free-energy and mobility parameters for the Cahn-Hilliard/Allen-Cahn model from Molecular Dynamics simulations to capture the drying dynamics more realistically.

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