A Lagrangian particle-based numerical model for surfactant-laden droplets at macroscales

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ABSTRACT

Atmospheric aerosols can consist of inorganic and organic substances, including surfactants at a significant concentration. Importantly, the latter can reduce the surface tension at the liquid–vapor surfaces, where they preferentially adsorb due to their amphiphilic structure. As a result, processes such as droplet coalescence, development of precipitation, and ultimately cloud lifetime may depend on the presence of surfactants in the aerosols. Here, we present a numerical model for cloud droplet formation, which is based on the Lagrangian particle-based microphysics-scheme superdroplet method and takes into account the presence of the surfactant in the droplets. Our results show that surfactant facilitates cloud formation by increasing the number and size of activated droplets, which concentrate at the bottom of the cloud, while the largest droplets are concentrated at the top of the cloud. This indicates a circulation of droplets that involves activation and growth processes from the bottom of the cloud toward the top. Moreover, our conclusions are independent of the particular approach used for modeling the diffusion of Eulerian variables due to the subgrid-scale turbulence. We anticipate that our results will enrich our understanding of the role of surfactants in the behavior of atmospheric aerosols and, importantly, will pave the way for further developments in the numerical modeling of systems with surfactants at macroscopic scales.

I. INTRODUCTION

Pollutants and other atmospheric aerosols play a crucial role in Earth's climate change[1,2] with their study dating back to the 1970s.[3,4] A range of different pollutants have been found to significantly affect cloud development,[5–7] which lead to changes in their properties, such as radiative properties.[8] In particular, humic-like substances (HULIS) play a significant role in decreasing the surface tension of aqueous solutions in the atmosphere and influencing cloud-droplet activation properties.[9] How exactly these effects emerge in these processes still remains a topic of intensive research, which, among others, requires the development of suitable models that can capture in detail the behavior of such systems, thus, providing a deeper understanding of the fundamental underlying processes. Not only will such an understanding allow us to implement better policies that aim at preventing extreme phenomena as a result of climate changes, such as droughts and floods, but it will also enable novel technological developments that require

the numerical modeling of additives in liquid phases, which are relevant in applications, such as atomization, cooling electronic devices, and electricity production (e.g., steam turbines).

Atmospheric aerosols can consist of various inorganic and organic substances, with a part of them being salts and surfactants. The latter are amphiphilic molecules consisting of a hydrophilic and a hydrophobic part in their molecular structure.[10–16] The source of surfactants in the systems can be diverse, for example, biological[17] and anthropogenic.[18] Moreover, due to their amphiphilic character, surfactants preferentially adsorb at the surface of liquids thus lowering their surface tension,[19–22] and in turn affecting key processes, such as droplet coalescence, their populations, as well as the development of precipitation and ultimately cloud lifetime.[23] A more thorough understanding of these processes requires more quantitative descriptions for droplet nucleation and coalescence phenomena, which are involved in these processes.[19] This is crucial as surfactants may affect the activity of cloud condensation nuclei (CCN),[24] that is, small particles on which

water vapor condensates when the supersaturation of air exceeds a critical value. In this case, surfactants can contribute to the mass of a CCN and influence the ability of the aerosol particles to be activated and form clouds.[25] Further studies have shown that the composition of the atmospheric CCN significantly affects the cloud droplet activation, for example, by changing the activation diameter.[26] This takes place by (i) reducing the amount of solute available in the CCN and (ii) decreasing their surface tension.[27] Both effects are expected to play an important role toward a quantitative description of the cloud formation in the presence of surfactants, and they, therefore, should be included in the numerical model. Thus, numerical models might provide an indication on how the amount and probability of generating rain droplets might be affected by the presence/increase in surfactant. Since much surfactant comes from anthropogenic activities, numerical models can provide a clue toward understanding whether the presence of surfactant would favor more or less rain. Models also provide information on which of the properties are expected to be affected by the presence of surfactant, which eventually affects the properties of clouds.

While empirical measurements concerning surfactants in the atmosphere could ideally provide useful insight into the process of cloud formation, numerical studies have emerged as a useful tool to analyze and understand this process.[28,29] For example, such investigations have previously been used to estimate the influence of surfactants on cloud microphysics and clouds formation.[30,31] However, there are currently no available simulations of a cloud as a multitude of surfactant-laden droplets, which could allow for a more detailed description of the relevant mechanisms. Although surfactants are a significant part of the atmospheric aerosol mass, surface tension of aerosol particles and water droplets has remained unexplored in the numerical models of the cloud evolution. In fact, most models traditionally assume a surface tension equal to that of pure water.[32] Hence, a numerical model that incorporates the effect of the surface tension might potentially provide a better understanding of the role of surfactants in the atmosphere and its influence on cloud evolution. Finally, simulating such systems with surfactant at large (macroscopic) scales with molecular or mesoscopic models[33] would be computationally prohibitive.

The goal of our study was to propose a numerical model that incorporates the surfactant effect in the coalescence of droplets at macroscopic scales toward describing phenomena, such as cloud formation and precipitation. Current literature in this area mainly consists of microscopic and global models with the numerical modeling of clouds in the presence of surfactants being at its infancy (see, e.g., Sec. II A). Our numerical model is described in Sec. II with our simulations, suggesting that surfactant may increase the cloud droplet activation (Sec. III). Moreover, the model offers opportunities for further developments of numerical approaches in this area of cloud physics, which aim at incorporating the detail of relevant physical phenomena, as will be further discussed in Sec. IV.

II. MODEL AND METHODOLOGY
A. Background

About 20% of soluble matter in the atmosphere (even up to 70% in some cases) consists of organic compounds.[20] Some of these compounds are surface active and can affect the surface tension of cloud droplets as has been also highlighted by Bzdek

et al.[32] while investigating the coalescence of picoliter droplets. Although such a reduction may depend on the droplet size,[32] this still remains under debate in the context of cloud droplets.[34] A study by Facchini et al.,[19] which is based on measurements on vacuum-evaporated samples of cloud water from the Po Valley in Italy, suggests a large decrease in the surface tension with the concentration of organic solutes that is expected to persist in growing droplets, as a result of droplet condensation. In particular, such large surface-tension changes are crucial in the case of cloud droplets near the critical size of nucleation, since they can lead to an increased droplet population and hence cloud albedo.

The process of cloud-droplet condensation may be described by Köhler's theory,[35] which includes two basic effects: the Kelvin effect, which expresses the change in the saturation vapor pressure on a curved surface, and Raoult's law, which expresses the change in the saturation vapor pressure in the mixture. More specifically, the Köhler equation for the equilibrium water vapor saturation ratio, S, vs radius, r, of a spherical solution droplet, in Ostwald–Freundlich form is as follows:[36]

$$S \equiv \frac{p_w}{p_w^0} = a_w \exp\left(\frac{2\nu_w \sigma}{RTr}\right), \tag{1}$$

where p_w is the equilibrium partial pressure of water over the solution droplet (actual vapor pressure), p_w^0 is the saturation vapor pressure over a flat surface of pure water, a_w is the droplet solution water activity, ν_w is the partial molar volume of water in the solution, σ is the droplet surface tension, R is the universal gas constant, and T is the Kelvin temperature. The exponential term of Eq. (1) is the Kelvin term. The water activity

$$a_w = \frac{r^3 - r_d^3}{r^3 - r_d^3(1 - \kappa)} \tag{2}$$

in Eq. (1) is Raoult's term, where r_d is the radius of the dry part of a droplet, and κ is the hygroscopicity of the solute. Raoult's law states that $p_w = a_w p_w^0$.

Ovadnevaite et al.[37] have theoretically and empirically proven that the reduction of the surface tension can prevail over the reduction in the Raoult effect in the case of ambient air, which leads to a substantial increase in the cloud droplet concentration. Furthermore, Sorjamaa et al.[21] have shown that the presence of salt in a droplet drives surfactant to the surface, which reduces Raoult's term, while leaving the Kelvin term still considerable. At the same time, Prisle et al.,[31,36,38] by using a global circulation model, have found that if the Köhler theory does not account for surfactant partitioning and only makes use of the reduced surface tension, it underpredicts the empirical critical supersaturation. Moreover, according to Ref. 39, the decrease in the hygroscopicity, due to the presence of surfactant, can partially or fully compensate for the surface tension reduction occurring at the droplet interface. Therefore, both the Kelvin effect and Raoult's law can be considered in a numerical model of a cloud. However, before taking such a step, here, we investigate the role of the surface tension (Kelvin term) and leave a full investigation of Raoult's term for our future work.

Lo and Lee[40] have investigated the influence of surfactants on the droplet evolution. They have used sodium dodecyl sulfate (SDS), a

surrogate of the natural surfactants, and examined its influence on artificial fog droplets in hydrophobic organic compound (HOCs) enrichment reactor. There are also numerous simulation models of a single cloud formation and evolution, for example, see Ref. 28 and references therein. However, none of the above studies have taken into account the presence of surfactants, although these are expected to influence the underlying complex mechanisms.[41] To the best of our knowledge, our endeavor is the first attempt to address this issue by building a simulation model that includes the effect of surfactant in the cloud evolution, such as the formation of clouds and the amount of precipitation.

B. Superdroplet method

Different cloud dynamics models have been thus far proposed in the literature, such as the bulk parametrization method[42] or the spectral (bin) method[43] (see also Ref. 44 and references therein). These models are based on the Eulerian approach, where the cloud properties are continuous in space without considering single cloud droplets. Here, a rather recent approach to accurately model the cloud dynamics will be used, that is, the Lagrangian particle-based microphysics scheme superdroplet method (SDM).[28] Our study extends the capabilities of this model by including the numerical modeling of surfactant effects in the SDM model, thus providing a possible direction for future developments in the area of numerical modeling of systems with droplets at macroscopic scales.

In the Lagrangian approach, computational particles are cloud droplets,[45] which connect the large-scale simulation with the underlying microscopic fluid mechanics. A main advantage of this approach is avoiding the need of representing each individual droplet of the system in the computational model, which would translate into a huge computational cost. Instead, in the SDM, aggregates of single droplets are considered, which are known as superdroplets. Hence, the superdroplet can be treated as an ensemble of many ordinary droplets with the same intrinsic parameters. A multiplicity parameter indicates the number of those single droplets represented by the superdroplet, which is denoted by the positive integer $\xi_i(t)$. The multiplicity parameter can be different in each superdroplet and time-dependent, for example, due to droplet coalescence events. Moreover, each superdroplet has its own position $\mathbf{x}_i(t)$ and attributes $\mathbf{a}_i(t)$, which characterize the $\xi_i(t)$ identical droplets represented by the superdroplet i. For instance, attributes of the superdroplet can include the radius and the solute mass, that is, $\mathbf{a}_i(t) = [R_i(t), M_i(t)]$.[28] In other words, a superdroplet reflects a coarse-grained representation of single droplets both in real and attribute space.

SDM involves a coalescence scheme of superdroplets, which is outlined as follows:

1. If $\xi_j \neq \xi_k$, we can choose $\xi_j > \xi_k$ without losing generality (Fig. 1). Then, the prime variables represent the updated values after coalescence,

$$\xi'_j = \xi_j - \xi_k, \quad \xi'_k = \xi_k, \tag{3}$$

$$R'_j = R_j, \quad R'_k = (R_j^3 + R_k^3)^{1/3}, \tag{4}$$

$$M'_j = M_j, \quad M'_k = (M_j + M_k), \tag{5}$$

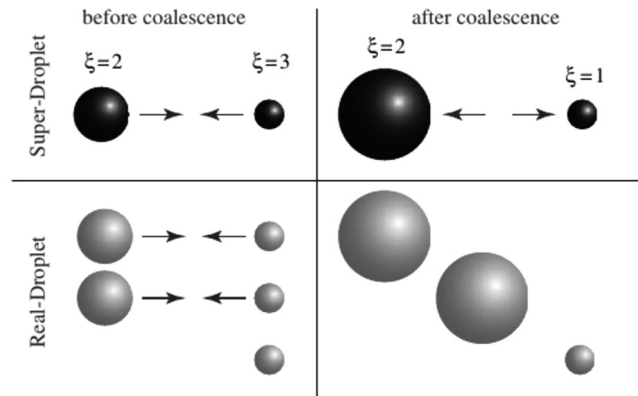$$x'_j = x_j, \quad x'_k = x_k. \tag{6}$$

FIG. 1. Scheme of coalescence for SDM.[28] Top: coalescence of two superdroplets with initial multiplicity 2 and 3. Bottom: the corresponding scheme for the coalescence of real droplets. Left: before coalescence. Right: after coalescence (multiplicities are now 2 and 1).

2. If $\xi_j = \xi_k$,

$$\xi'_j = [\xi_j/2], \quad \xi'_k = \xi_j - [\xi_j/2], \tag{7}$$

$$R'_j = R'_k = (R_j^3 + R_k^3)^{1/3}, \tag{8}$$

$$M'_j = M'_k = (M_j + M_k), \tag{9}$$

$$x'_j = x_j, \quad x'_k = x_k, \tag{10}$$

where $[\cdot]$ is the greatest integer less than or equal to the quantity in the brackets.

The number of superdroplets decreases due to coalescence only when $\xi_j = \xi_k = 1$; that is, both superdroplets are real droplets. Then, $\xi_j = 0$ and $\xi_k = 1$, and the superdroplet, j, is removed from the system. Therefore, the number of superdroplets (which corresponds to the accuracy of SDM) slowly decreases during the simulation toward an approximate number of superdroplets that provide the flexible response of the model to big changes in the number of real droplets. We define the probability that superdroplets j and k that are present inside a small region ΔV will coalesce in a short time interval $(t, t + \Delta t)$ as

$$P_{jk}^{(s)} = \max(\xi_j, \xi_k)P_{jk}, \tag{11}$$

where P_{jk} is the probability that the (real, single) droplets j and k inside a small region ΔV will coalesce in a short time interval $(t, t + \Delta t)$ [see Eq. (3) in Ref. 28 for the definition of P_{jk} in the SDM]. Such a definition of a coalescence probability ensures that the expectation value of the number of coalescences of real droplets is conserved when we use the SDM. Moreover, for a coalescence process we use a reduced set of non-overlapping pairs of superdroplets, instead of all possible pairs, which further reduces the computational cost of a simulation.[28]

Except for the coalescence process, each superdroplet behaves in just the same way as a droplet. Thus, the condensation/evaporation process of a superdroplet is governed by an appropriate growth equation [specifically, Eq. (2) in Ref. 28, cf. Eq. (1)] and it can move according to the equation of motion:

$$\frac{d\mathbf{r}_i}{dt} = \mathbf{U}(\mathbf{r}_i) - \hat{\mathbf{z}}v_\infty(R_i), \tag{12}$$

where $\mathbf{r}_i$ is the droplet position, $\mathbf{U}(\mathbf{r}_i)$ is the wind velocity, $v_\infty(R_i)$ stands for the terminal velocity,[46] and $\hat{\mathbf{z}}$ is a unit vector in the vertical direction.

Using such a coarse-grained approach makes the simulation of a cloud feasible, without much compromise on the accuracy of the results. Moreover, thanks to the superdroplet method, introducing the changes of the surface tension and their effect on the droplet properties becomes technically more tractable. Also, there are studies, supporting that SDM might be considered a better option than the bin method for investigating nonlinear phenomena, such as turbulence in clouds.[47] Finally, the method might also be generalized to consider ice particles present in the case of a storm-cloud.[48]

Still, in view of the greater detail that SDM provides in our numerical model, this approach might somewhat require more computational resources in comparison with other methods.[48] Moreover, there is an associated computational cost for adding new attributes to a superdroplet as more superdroplets are needed to cover the increased dimensionality of the attribute space without comprising the accuracy of the simulation.[29] A way of addressing this issue has been proposed in Ref. 49, which suggests a simpler and computationally more efficient approach that is based on the Twomey activation scheme.[50] In this case, superdroplets form when a CCN is activated, while they do not exist outside a cloud.

C. Surfactant modeling

Our SDM calculations took place by appropriate modifications of the libmpdata++, libcloudph++, and UWLCM libraries.[51] We have implemented the following changes to the original approach for cloud simulation[45,52,53] in order to incorporate the effects of surfactant: (i) Particles (droplets) contain a particular amount of surfactant and salt, while keeping the ratio of surfactant and salt always the same for each particle. This ratio is a model parameter. (ii) We have derived the formula for the surface tension of a droplet by taking into account the surfactant and salt partitioning, where surfactant covers the surface of a droplet until it saturates, as in Ref. 54. (iii) The modified surface tension is then used for calculating the heat and vapor diffusion equation, which contains the Kelvin term.

The UWLCM library offers two methods for modeling the diffusion of Eulerian variables due to the subgrid-scale (SGS) turbulence:[53] (i) an implicit large-eddy simulation (ILES) method, with no explicit parametrization of SGS mixing, but instead, with numerical diffusion of the advection scheme used to mimic the SGS turbulence; (ii) a Smagorinsky scheme.[55] Hence, we performed the analysis for three varied models of the SGS turbulence to ensure that our conclusions are not model-dependent. These models are as follows: the ILES model, the Smagorinsky model, and the Smagorinsky model with turbulent SGS motion of the superdroplets (obtained by adding a random velocity component u'_{SD}, specific to each superdroplet [cf. Eq. (12), where every component of the velocity perturbation evolves as in Eq. (10) of Ref. 56]. In general, introducing SGS turbulence models should improve the grid convergence characteristics.[48] We also expected that precipitation rate is going to decrease after implementing the influence of the SGS turbulence on the superdroplets.[57] In the code of the simulation of our model, the microphysics of droplets, which was modified for accounting for the presence of surfactant in each droplet, as given

later in this section, is independent of the particular approach for the diffusion of Eulerian variables. Therefore, we were able to apply all three approaches mentioned above in the same manner, without a necessity of any special implementation. For more details about the implementation of three approaches, see Ref. 53.

In our model, we have assumed two types of solute in each droplet: ammonium sulfate [$(NH_4)_2SO_4$] as salt,[53] and sodium dodecyl sulfate (SDS) as surfactant. Moreover, an increase in size of a droplet due to the absorption of water (condensation) reflects a decreasing surfactant concentration.[19] For this reason, we have assumed that a certain percentage of the dry part of the droplet is SDS and the rest is ammonium sulfate.[25] We have also assumed that surfactant can replace the salt in CCN. Hence, the dry radii of the superdroplets statistically remain the same (cf. Westervelt et al.[27]). Further details regarding the concentration of surfactant in the droplets will be discussed below.

The variations of surface tension, σ, can be calculated by means of the Szyszkowski equation of state.[58] However, this equation is not always appropriate for finite-size droplets, especially for droplet of a rather smaller size.[59] Instead, we can compute the surface tension of a droplet in the following way. We consider an aqueous droplet with a radius, r, which can be divided into a surface monolayer of thickness, δ, and an interior (bulk) with radius, $r - \delta$. The droplet surface tension, σ, depends on the value of the bulk composition $\mathbf{x}^b = (x_1^b, x_2^b, \dots)$ and the surface composition $\mathbf{x}^s = (x_1^s, x_2^s, \dots)$,[59] namely,

$$\sigma(\mathbf{x}^b, T) = \frac{\sum_i \sigma_i v_i x_i^s}{\sum_i v_i x_i^s}, \tag{13}$$

where $x_i^b = n_i^b / \sum_j n_j^b$ is the bulk mole fraction for each species, i, in the droplet, x_i^s is the surface mole fraction, defined in the same manner, and v_i and σ_i are the molecular volumes and surface tensions of each pure component, i, respectively. n_i^s, n_i^b, and $n_i^t = n_i^s + n_i^b$ are the number of particles for the ith species, for the surface, the bulk, and the whole droplet, respectively. The total amount of molecules in the monolayer, n_i^s, is evaluated from the volume of the monolayer, $V^s = 4\pi[r^3 - (r - \delta)^3]/3$, where the thickness, δ, of the monolayer is given from the equation[59]

$$\delta = \left(\frac{6}{\pi}\sum_i v_i x_i^s\right)^{1/3}. \tag{14}$$

In particular, considering the three mole fractions for water (subscript "1"), salt (subscript "2"), and surfactant (subscript "3"), Eq. (13) reduces to

$$\sigma(x_1^b, x_2^b, x_3^b) = \frac{\sigma_1 v_1 x_1^s + \sigma_2 v_2 x_2^s + \sigma_3 v_3 x_3^s}{v_1 x_1^s + v_2 x_2^s + v_3 x_3^s}. \tag{15}$$

Here, we assume that all surfactant is on the surface of the droplet until it covers the whole surface and starts to form aggregates. Moreover, the ratio between salt and water is the same for bulk, as well as for the surface. Therefore, the partitioning formulas for the monolayer are as follows:

$$n_1^s = \frac{V^s - n_3^s v_3}{v_1 + n_2^t v_2 / n_1^t}, \quad n_2^s = n_1^s \frac{n_2^t}{n_1^t}, \quad n_3^s = \min(n_3^t, V^s/v_3), \tag{16}$$

where

$$n_1^t = \frac{4\pi}{3} \cdot \frac{r^3 - r_d^3}{v_1}, \quad n_2^t = (1 - c_{32}) \cdot \frac{4\pi}{3} \cdot \frac{r_d^3}{v_2}, \quad n_3^t = c_{32} \cdot \frac{4\pi}{3} \cdot \frac{r_d^3}{v_3}.$$
$$(17)$$

$c_{32} = n_3^t v_3 / (n_2^t v_2 + n_3^t v_3)$ is the volume fraction of surfactant in the atmospheric CCN particles, and r_d is the dry radius of a superdroplet. For simplicity, in our calculations we assumed that $r_d \ll r_w$, where r_w is the wet radius of a superdroplet. Finally, we used a mass fraction, c, of surfactant, with an appropriate conversion formula:

$$c_{32} = \frac{c m_2 v_2}{c m_2 v_3 - (c - 1) m_3 v_2},$$
$$(18)$$

where m_2 and m_3 are molecular masses of salt and surfactant, respectively.

The model with mass concentrations $c = 0\%$ is the reference model; that is, 100% of the dry part is ammonium sulfate. A simulation with, for example, $c = 20\%$ stands for 20% of SDS and 80% of ammonium sulfate. In Ref. 19, the concentration of surfactant in the atmospheric CCN is about 5%. However, the proportions of particular types of aerosols over the globe may vary.[19,20,36,37,60]

Overall the extent of accuracy of some of the model assumptions for cloud droplets made above are subject to current discussion in the field, but the scheme used constitutes a baseline from which surfactant concentration effects can be incorporated into a previously surfactant-free model. We have used the relative surfactant concentration, c, in the atmospheric water (or a single droplet), as the wet radius of the droplet evolves. In this case, surfactant concentration in droplet's water also evolves and does not remain constant during the simulation.[19] For example, during a droplet growth, the amount of surfactant may initially exceed the critical aggregation concentration (CAC), and then, due to the accumulation of water by the droplet, the concentration may decrease below the CAC level, with the actual amount of surfactant in the droplet remaining the same. However, the amount of salt and surfactant can change due to droplet collisions.

Equation (1) is used to calculate the saturation ratio by using σ as obtained from Eq. (15). In our study, σ was iteratively computed by using Steffensen's method[61] and Eqs. (14)–(17). We used wet, r, and dry, r_d, radii of superdroplets calculated by the UWLCM library. In this way, the effect of the surface tension, as a result of surfactant's presence in the droplets, is taken into account in the numerical model. In turn, the surface tension shall affect the supersaturation curve, which eventually impacts the droplet formation and evolution, as will be further elaborated below.

III. RESULTS

To test the size of the effect produced by the surfactant, we have reproduced drizzling marine stratocumulus[62] simulations using the second Dynamics and Chemistry of Marine Stratocumulus (DYCOMS-II) second research flight (RF02) setup as in Ref. 53, but with the influence of various surfactant concentrations added to the reference model. For each examined concentration of surfactant, we conducted one hundred 6-h 2D simulations to average over multiple cloud evolutions. We used a grid of a size 6.4 km horizontally and 1.5 km vertically, with grid cells 50 × 5 m each, with periodic boundary condition on the left/right boundary of the grid. The time step for our computations was 1 s (see Ref. 53 for more details about choosing appropriate time step value).

Figure 2 shows the snapshots from the example simulation with a concentration of cloud and rain droplets. In general, the implicit LES approach produces more rain than the other two approaches, in line with previous findings.[57] Moreover, to reliably calculate average values for properties, such as the rain-droplet concentration, which are non-linear and sensitive to initial conditions, the realization of a large ensemble of simulations to deal with possible statistical errors for the derived quantities was required. We have found that an ensemble of 100 simulations for each system was enough to yield reliable results for the properties of each system.

Example time evolutions and profiles obtained for the model with and without surfactant are shown in Figs. 3 and 4 (cf. similar results in Ref. 53). Cloud droplets are liquid particles with a radius in the range of $0.5\,\mu m < r < 25\,\mu m$. Cloudy cells are defined as those with a concentration of cloud droplets greater than $20\,cm^{-3}$. The cloud fraction is the ratio of cloudy cells to the total number of cells. The concentration of cloud droplets in cloud grid-cells (Fig. 3) initially grows rapidly, then drops down due to the evaporation process, and finally exhibits slight fluctuations. In the case of the "Smagorinsky + SGS" scheme (SGS motion of superdroplets), we observe a decrease in the concentration of cloud droplets as the simulation progresses, whereas in the case of the Smagorinsky scheme (SGS only for Eulerian variables), there is a slight increase with some fluctuations. The profiles of Fig. 4 indicate the greatest concentration of cloud droplets in the case of the Smagorinsky scheme, in contrast to the lowest values observed in the case of the Smagorinsky + SGS scheme. However, we see almost no visible differences between the different models both in the case of systems with and without surfactant. As for the cloud cover, we have obtained the same result for all schemes, also, independently of the presence of surfactant in the systems. Our results indicate that the effect of surfactant for these properties is negligible, as evidenced by our results in Figs. 3 and 4.

There are, however, properties that are significantly affected by surfactant in our model. These properties are the number of activated particles[63] (referring to those with the critical supersaturation exceeded), as well as their size. Both these values increase with an increasing surfactant concentration, independently of the modeling approach (Fig. 5). Although including the SGS motion of the Lagrangian particles (superdroplets) will lead to a decrease in the concentration and size of the activated droplets, we can observe that the same positive dependence on surfactant concentration still remains. Moreover, there is no saturation of this effect with a growing surfactant concentration. Finally, we have observed a slight decrease in the speed of the concentration and the pace of growth for all modeling approaches.

Another key observation from our calculations concerns the biggest difference between the number of activated droplets for the reference model and the model with high surfactant concentration, which occurs at the bottom of a cloud (Fig. 6). In contrast, the largest droplets are concentrated at the top of the cloud (Fig. 6). Hence, our results indicate that "new" droplets are activated at the bottom, and then, they grow moving up the cloud. In a sense, there is a circulation of droplet through an activation and growth process from the bottom of the cloud toward the top.

If "radius activated" droplets were to be identified by checking whether their radius exceeds the critical value for the Köhler curve [Eq. (1)] instead of using the critical supersaturation as the threshold,
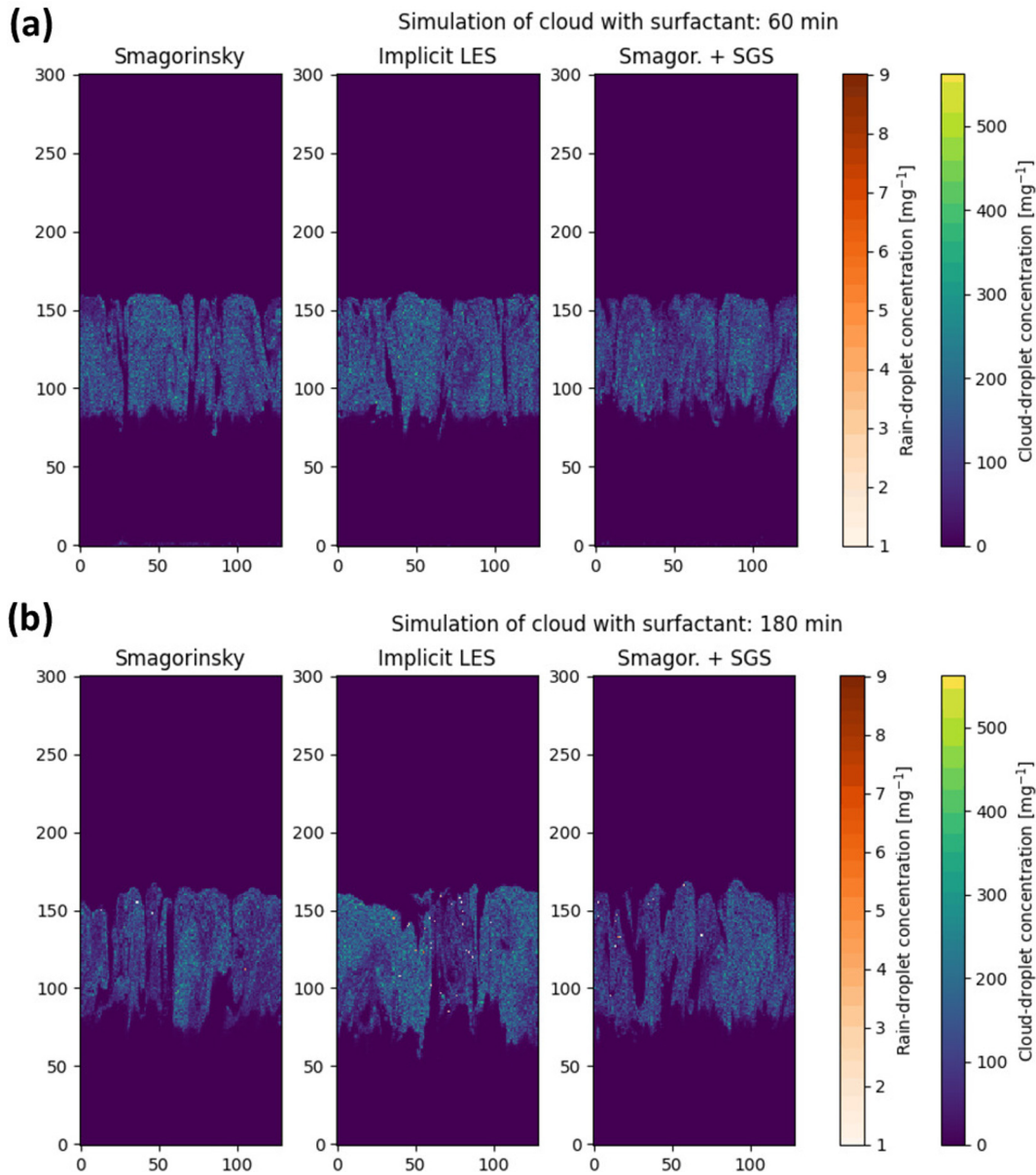
FIG. 2. Cloud-droplet ($0.5 < r < 25 \, \mu m$, purple-yellow scale) and rain-droplet ($r > 25 \, \mu m$, white-red scale) concentration (number of droplets per milligram of dry air) for the snapshots of the SDM simulation with 25% of surfactant (mass of surfactant in the droplet divided by the collective mass of surfactant and salt), for three different modeling approaches and times (a) $t = 60$ min, (b) $t = 180$ min, as indicated. Horizontal and vertical axis values for each subplot are counts of grid cells.

the increase with a growing surfactant concentration becomes smaller (Fig. 7). This is due to the fact that the critical radius is also exceeded by droplets that were activated a long time ago, while critical supersaturation is exceeded usually only once, when the actual activation happens. Therefore, the absolute concentration is larger when the critical radius is exceeded, because it also takes into account the "old" cloud droplets, while when the critical supersaturation is exceeded, only the new cloud droplets are considered. Hence, the relative increase with growing surfactant concentration is bigger in the latter case. We have

also checked that the absolute differences in the number of droplets for these two cases are of the same order of magnitude, which further confirms our conclusions. However, the Smagorinsky scheme produces more radius activated droplets than the ILES scheme, which is opposite to the case of "supersaturation" activated droplets in Fig. 5; the Smagorinsky + SGS scheme still produces the smallest amount of droplets for both measures.

The concentration of cloud droplets remains almost identical as in the case of the droplets with radius exceeding the critical radius,
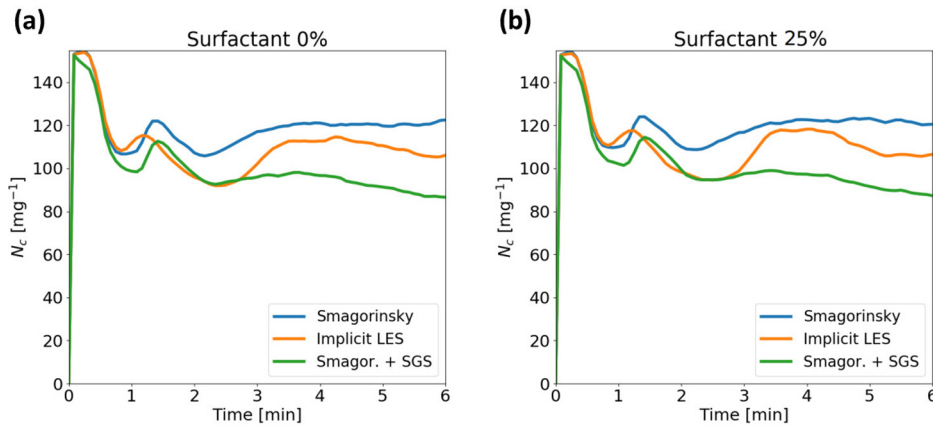
FIG. 3. Time evolution of concentration of cloud droplets in cloudy grid cells, N_c, averaged for 100 simulations: original model from Ref. 53 reproduced (a) and our model with 25% mass ratio of surfactant (b).
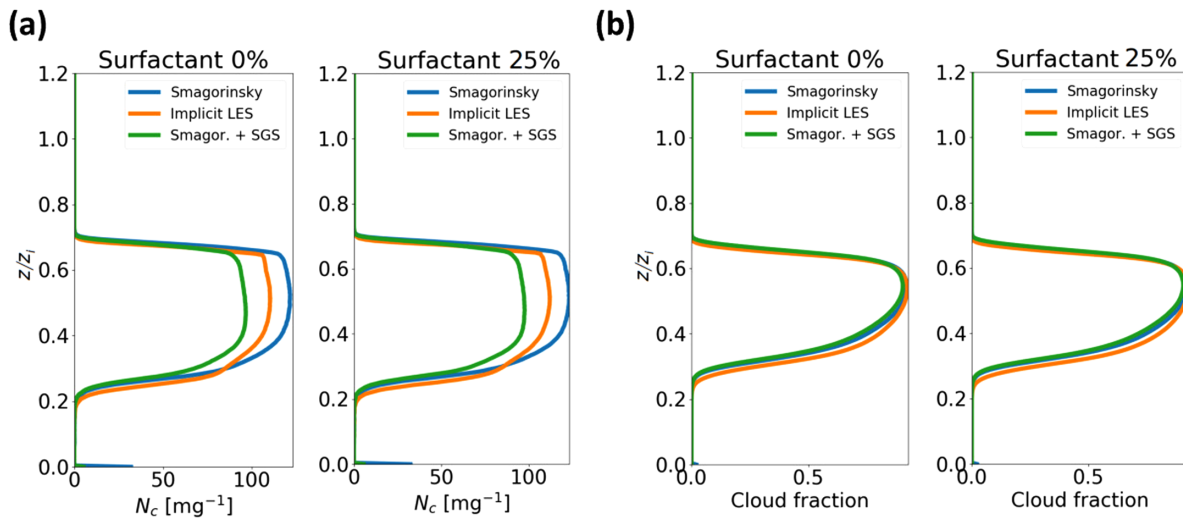

FIG. 4. Vertical profiles of: (a) concentration of cloud droplets in cloudy grid cells for the original model without surfactant;[53] concentration of cloud droplets in cloudy grid cells for our model with 25% of surfactant, as indicated; (b) cloud fraction for the original model; cloud fraction for our model with 25% of surfactant, as indicated. The plotted results are averages of 100 simulations for the whole simulation grid, and the scaled height z/z_i is defined as in Ref. 53.
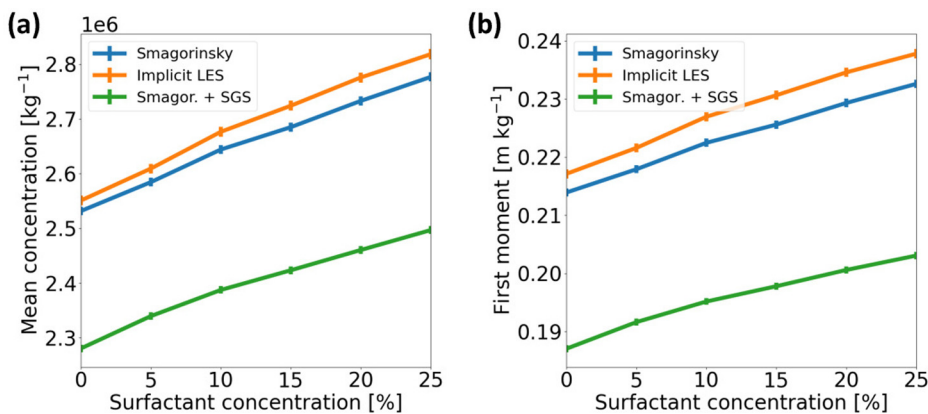

FIG. 5. Number of activated droplets (critical supersaturation exceeded) per kilogram of dry air vs surfactant concentration c (a), and 1st moment of the dry spectrum [defined by Eq. (29) in Ref. 45, (b)] vs surfactant concentration c, averaged over 100 six-hour simulations, for three different modeling approaches, as indicated. Error bars (vertical) show the statistical errors of the calculated mean quantities for each surfactant concentration.
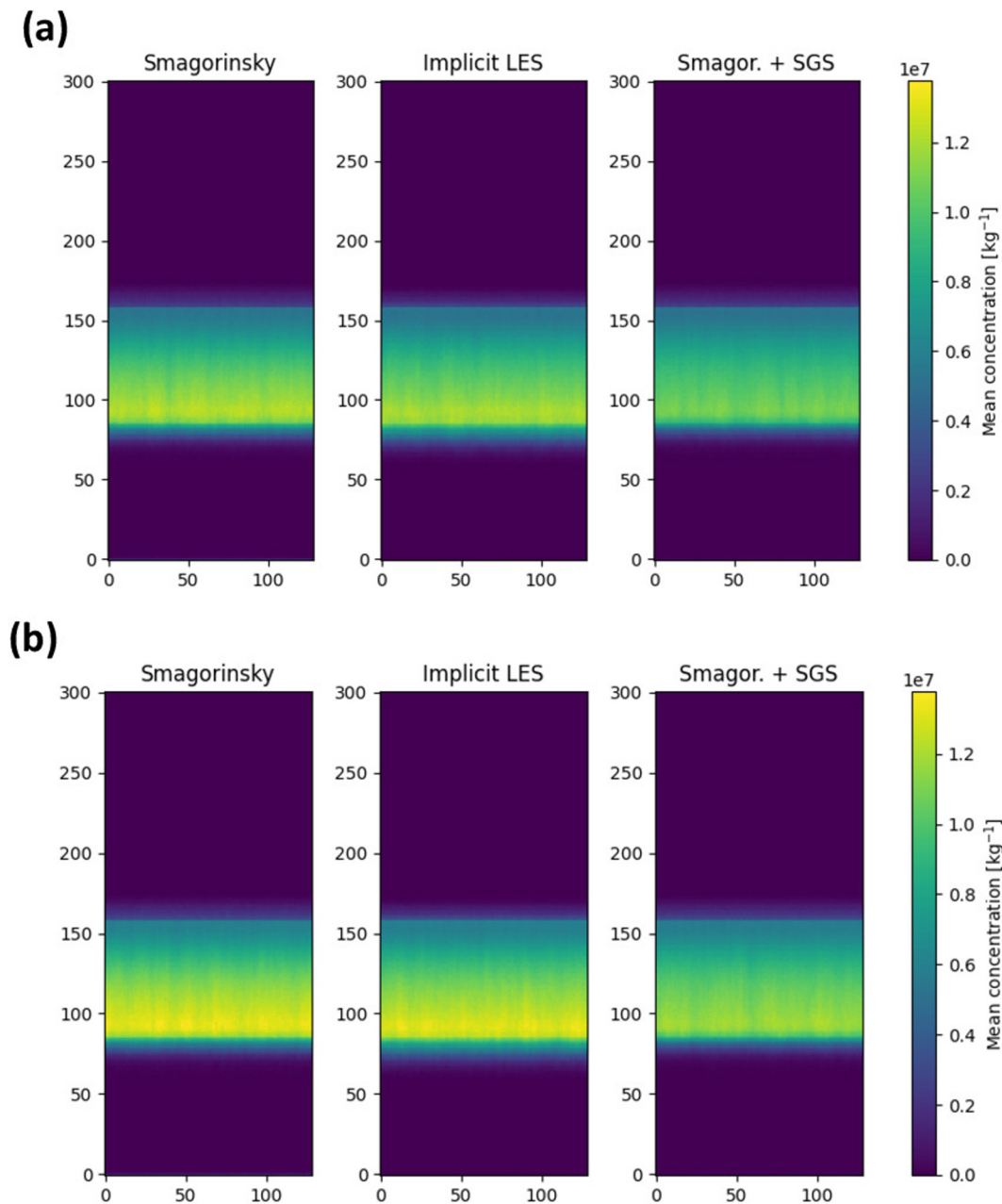
FIG. 6. Maps of the number of activated droplets per kilogram of dry air for the whole simulation grid, averaged over 100 simulations for the same sets of the model parameters and over six-hour time of each simulation, for three different modeling approaches, as indicated. (a) Reference model (without surfactant). (b) Model with 25% of surfactant. Note that the maps are expanded by ten times in a vertical direction, for a better view.

because activated droplets are converted into cloud droplets (Fig. 8). There is also a decrease in aerosol concentration as surfactant concentration increases (Fig. 8, lower panel). Such an effect can be explained by the fact that aerosol particles transform into cloud droplets, which leads to an anti-correlation between the latter two effects. However, the differences between the Smagorinsky and the ILES schemes are negligible for the concentration of aerosol particles, while for the

concentration of cloud particles, the Smagorinsky scheme yields more particles.

Finally, we have found that the amount of water in the cloud and the concentration of rain drops do not change with the concentration of surfactant in the case of all different models (Fig. 9). Still, the implicit LES approach produces more water and rain droplets in the cloud than the other two approaches. Moreover, there is a big
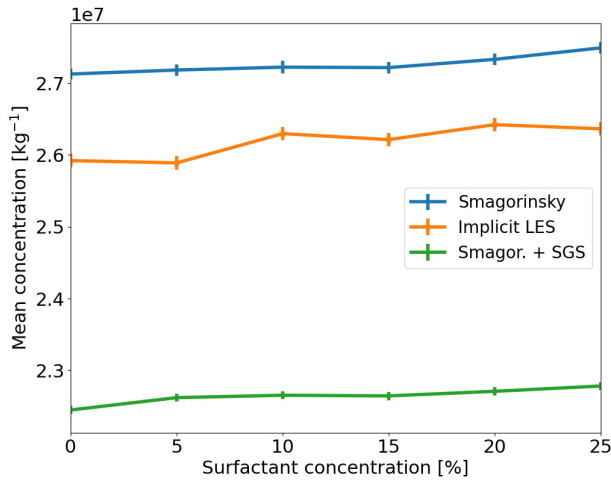
FIG. 7. Concentration of droplets that exceed the critical radius for the Köhler curve ("radius activated") per kilogram of dry air vs surfactant concentration c, averaged over 100 six-hour simulations, for three different modeling approaches, as indicated. Error bars (vertical) show the statistical errors of the calculated mean quantities for each surfactant concentration.

discrepancy between the precipitation results for different approaches. Such differences have also been previously reported in Ref. 53. In the case of ILES, a decrease in the concentration of rain droplets with a growing surfactant concentration is observed. However, in view of the large statistical errors, this effect deserves further investigation.

The quantities shown in Figs. 7–9 do not appear to show as strong a change with concentration as Fig. 5, but this is partly due to an optical effect caused by the large differences in values predicted by the three particular models that we used (Smagorinsky, implicit LES, and Smagor. + SGS), which are shown together on the same plots. The effects of the growing surfactant concentration relative to 0% concentration show the same dependence for all three models that we have used. We did not plot other quantities that showed no clearly discernible surfactant effect. The uncertainty in the data points is primarily statistical. It is caused by the large shot-to-shot fluctuations in the quantities between particular simulation runs that have different noise histories. The data points shown are calculated after averaging the results over different noise realizations. Other sources of errors are smaller and can be neglected.

IV. CONCLUSIONS AND DISCUSSION

In this study, we have proposed a model for a cloud consisting of surfactant-laden droplets, which is based on the Lagrangian
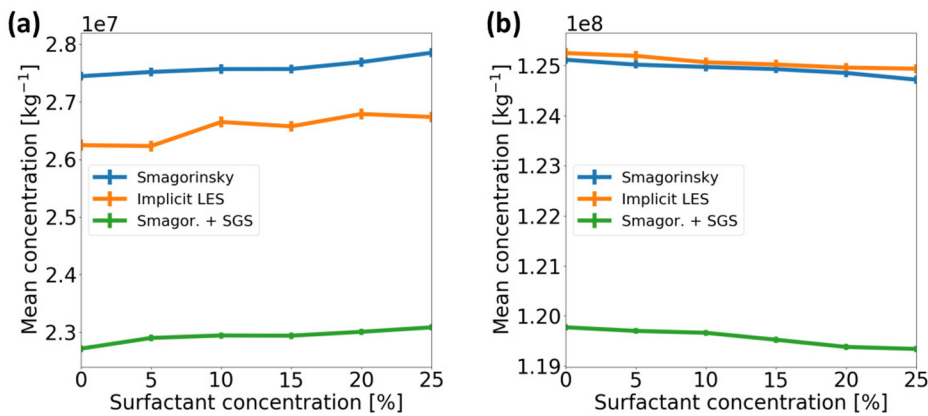

FIG. 8. Concentration of cloud droplets ($0.5 < r < 25\,\mu$m, a) and aerosol particles ($r < 0.5\,\mu$m, b) vs surfactant concentration c, averaged over 100 six-hour simulations, for three different modeling approaches, as indicated. Error bars (vertical) show the statistical errors of the calculated mean quantities for each surfactant concentration.

FIG. 9. Liquid water path (a) and concentration of rain drops [$r > 25\,\mu$m, (b)] vs surfactant concentration c, averaged over 100 six-hour simulations, for three different modeling approaches, as indicated. Error bars (vertical) show the statistical errors of the calculated mean quantities for each surfactant concentration.
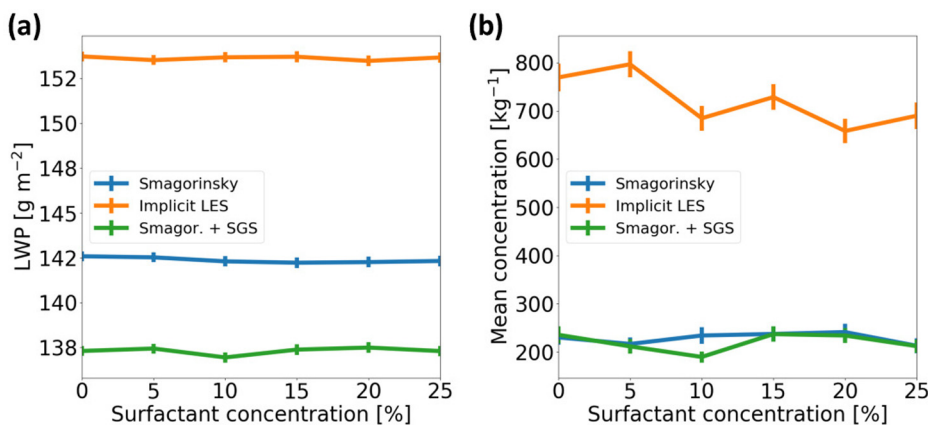
particle-based microphysics scheme superdroplet method.[28] The model is based on the modification of the Kelvin term (the term responsible for the droplet surface behavior) in Köhler's equation (1) by introducing Eq. (15) to calculate surface tension, σ, with the presence of surfactant in the droplet. We have shown that atmospheric surfactants influence the cloud formation process by increasing the concentration and size of activated droplets. This result is in accordance with previous studies, suggesting that a decrease in the surface tension of cloud droplets due to surfactant might lead to an increase in the population of the smaller-size droplets,[18] especially in the bottom of the clouds. Although the decrease in the surface tension due to surfactant is limited by CAC, we have not observed a saturation of the effect of the droplet concentration increase. However, it might be the case that such saturation occurs for higher surfactant amounts than what has been assumed here, which calls for further studies. We have also found no clear link between the presence of surfactant in the system and the amount of rain. This is also a point that might require further investigations in the future. In this direction, further developments of the current model are essential to obtain a more comprehensive picture of the underlying phenomena. Possible extensions might include: (a) improving surfactant partitioning or the interpolation between partial surface tensions in (13) (these details remain an active topic of investigation in the field); (b) adding the influence of surfactant to the Raoult term (e.g., see Ref. 39); (c) introducing coalescence efficiency that changes in the presence of surfactant;[64,65] (d) other types of surfactants than SDS; (e) the presence of ice particles and other types of clouds;[29,48] (f) examination of other grid sizes and time steps, with a possibility to apply a substepping procedure;[53] and (h) study other properties of clouds than those shown in the paper. Such developments might lead to a more comprehensive model of a cloud in the presence of surfactant, which will enable the modeling of various aspects of Earth's climate, for instance, regional changes in precipitation, or the exact role of aerosols in cloud formation.

Our numerical model offers new opportunities for investigating the role of surfactants at macroscopic models that involve topological changes of droplets (e.g., coalescence of surfactant-laden droplets). In this context, such models can be further refined based on information from molecular-scale models.[33,66–69] Hence, the SDM holds promise for further developments in the area of numerical modeling for large-scale systems consisting of droplets with different properties, as has been shown here in the case of a cloud with surfactant-laden droplets. We anticipate that our study will motivate further work in this direction.

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AUTHOR DECLARATIONS
Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Mateusz Denys: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Software (equal); Validation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal). **Piotr Deuar:** Conceptualization (supporting); Investigation (supporting); Supervision (equal); Writing – original draft (equal); Writing – review & editing (equal). **Zhizhao Che:** Conceptualization (equal); Funding acquisition (supporting); Supervision (equal); Writing – original draft (equal); Writing – review & editing (equal). **Panagiotis Theodorakis:** Conceptualization (equal); Data curation (equal); Funding acquisition (equal); Methodology (equal); Project administration (equal); Resources (equal); Supervision (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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