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The validity of the kinetic collection equation revisited – Part 3: Sol-gel transition under turbulent conditions

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Abstract

In a coagulating system, a sol-gel transition occurs when a single giant particle (a gel) arises under certain conditions and begins to consume the mass of smaller but higher populated fraction (the sol). This single giant particle (also known as a runaway particle) is detached from the continuous spectrum. Since the kinetic collection equation (KCE) only models the evolution of the continuous size of the spectrum, as the largest particle continue to grow by accretion of smaller ones, the liquid water content predicted by the KCE will decrease.

In this paper, the sol-gel transition is proposed as the mechanism that forms the large droplets that are needed to trigger warm rain development in cumulus clouds. By using a collection kernel enhanced by turbulence and a stochastic simulation method, the formation of a runaway droplet is modeled through the turbulent collection process. The model results show that the sol-gel transition (also called *gelation*) leads to the formation of a droplet with mass comparable to the mass of the initial system. The time when the sol-gel transition occurs is estimated with a Monte Carlo method when the parameter ρ (the ratio of the standard deviation for the largest droplet mass over all the realizations to the averaged value) reaches its maximum value. Moreover, we show that without turbulence, the sol-gel transition will not occur. In the context of theoretical cloud microphysics, gelation can be interpreted as the formation of the "lucky droplet" that grows at a much faster rate than the rest of the droplet population and subsequently becomes the embryo for raindrops.

1 Introduction

The formation process of large droplets that triggers the production of rain in warm cumulus clouds is one of the open problems in cloud physics. Various mechanisms have been proposed in the past (Pruppacher and Klett, 1997); however, there are still major gaps in our understanding of the rapid growth of cloud droplets across the size

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range of diameters from 10 to 50 µm. Some hypotheses explain the formation of these large droplets by enhanced condensation of water vapor molecules onto droplet embryos (Khain et al., 2000). Other studies describe droplet coalescence as the important factor governing the evolution of the droplet spectrum at the early stages of cloud development, mainly by two mechanisms: (i) the collision of large droplets growing on giant and ultra giant nuclei and (ii) the self-broadening of the droplet spectrum by collisions between cloud droplets. Regarding this second mechanism, it has been emphasized by experimental (Vohl et al., 1999) and theoretical studies (Pinsky et al., 1999, 2000) that there is a significant acceleration of droplet growth rate by collisions in a turbulent flow, with collision efficiencies that can be up to 10 times larger than in the pure gravity case.

In this contribution we will focus on a model for the growth of cloud droplets by this second mechanism, i.e. turbulent collision-coalescence at an early stage of cloud development. We will show that this model reveals the sol-gel transition (defined in more detail below) and the formation of runaway droplets.

The kinetic collection or coagulation equation (hereafter KCE) has long been used to model the time evolution of droplet size distributions due to collection events. The discrete variant of this equation has the form (Pruppacher and Klett, 1997):

$$\frac{\partial N(i,t)}{\partial t} = \frac{1}{2}\sum_{j=1}^{i-1} K(i-j,j)N(i-j)N(j) - N(i)\sum_{j=1}^{\infty} K(i,j)N(j) \quad (1)$$

where $N(i,t)$ is the average number of droplets with mass x_i, and $K(i,j)$ is the coagulation kernel related to the probability of coalescence of two drops of masses x_i and x_j. In Eq. (1), the time rate of change of the average number of droplets with mass x_i is determined as the difference between two terms: the first that describes the average rate of production of droplets of mass x_i due to coalescence between pairs of drops whose masses add up to mass x_i, and the second that describes the average rate of depletion of droplets with mass x_i due to their collisions and coalescence with other droplets.

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The collection process is stochastic and therefore more accurately described by the master equation for the joint probability distribution $P(n_1, n_2, \ldots, n_k, \ldots, t)$ where $\bar{n} = (n_1, n_2, \ldots, n_k, \ldots)$ at time t. This equation has the form (Bayewitz et al., 1974):

$$\frac{\partial P(\bar{n})}{\partial t} = \sum_{i=1}^{N} \sum_{j=i+1}^{N} K(i,j)(n_i+1)(n_j+1)P(\ldots, n_i+1, \ldots, n_j+1, \ldots, n_{i+j}-1, \ldots; t)$$

$$+ \sum_{i=1}^{N} \frac{1}{2} K(i,i)(n_i+2)(n_i+1)P(\ldots, n_i+2, \ldots, n_{2i}-1, \ldots; t)$$

$$- \sum_{i=1}^{N} \sum_{j=i+1}^{N} K(i,j) n_i n_j P(\bar{n}; t) - \sum_{i=1}^{N} \frac{1}{2} K(i,i) n_i (n_i - 1) P(\bar{n}; t) \quad (2)$$

The KCE can be obtained from Eq. (2) by taking the mean value of n_k:

$$\langle n_k \rangle = \sum_{\bar{n}} n_k P(\bar{n}; t) \quad (3)$$

and assuming (Bayewitz et al., 1974) that $\langle n_i n_j \rangle = \langle n_i \rangle \langle n_j \rangle$. In general, the average spectrum obtained from Eq. (1), and the ensemble averages spectrum obtained over different realizations of the stochastic collection process are different. The solution to the KCE and the expected values calculated from the stochastic Eq. (2) are equal only if the covariances are omitted from the probabilistic model, as shown in Bayewitz et al. (1974) and Tanaka and Nakazawa (1993). When this condition is fulfilled, the deterministic solution provided by Eq. (1) corresponds to the average value of n_k over many realizations.

The first moment of the distribution of $N(i,t)$ corresponds to the total mass (M_1) in the system and the second moment (M_2), defined as

$$M_2(t) = \sum_{i=1}^{N_d} x_i^2 N(i,t) \quad (4)$$

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(where N_d is the number of drop categories or sizes of the discrete distribution) may become undefined, when the initial number of particles is small or if $K(i,j)$ increases sufficiently rapidly with x_i and x_j.

This is usually interpreted to mean that a macroscopic, "runaway" particle has formed (known as a *gel*) and the system exhibits a phase transition (also called *gelation*). The sol-gel transition occurs when a single droplet much larger than the rest of the system arises and begins to consume the mass of smaller but higher populated fraction of droplets (the sol or continuous spectrum). As a result, this giant droplet becomes detached from the continuous part of the distribution. Consequently, there is a transition from a continuous spectrum to one with a continuous distribution *plus* a massive runaway droplet.

As the KCE only models the evolution of the continuous spectrum, a decrease of the total mass predicted by the KCE is observed. The total mass of the cloud system is obviously conserved, but the KCE is no longer valid to predict the evolution of the system after the sol-gel transition. Then, after the sol-gel transition the mass conservation can be formulated in the form:

$$M_{\text{Total}} = M_{\text{Continuous\_Spectrum (KCE)}} + M_{\text{Runaway\_Droplet}}$$

The former expression reflects the fact that the "missing mass" actually is transferred to the largest droplet that becomes isolated after the phase transition. A detailed analysis of this problem for a collection kernel proportional to the product of the colliding masses can be found in Alfonso et al. (2008).

The term "runaway particle" was coined by the astrophysicists. In astrophysics, the non-conservation of mass after the breakdown of the KCE is usually interpreted to mean that a runaway planet has formed, also known as a gel because of applications in physical chemistry.

The gelation time, T_{gel}, is then defined as the longest time such that the discrete model has a solution with $M_1(t) \equiv M_1(0)$ for $t < T_{\text{gel}}$ and $M_1(t) < M_1(0)$ for $t > T_{\text{gel}}$, where M_1 is the total mass for the continuous spectrum predicted by the KCE. Analytical expressions for the gelation time only exist for very simple kernels; hence, as suggested

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in Inaba et al. (1999), it should be estimated numerically by Monte Carlo simulations (Alfonso et al., 2008, 2010). The numerical algorithm of Gillespie (1975, 1976), which inherently incorporates all stochastic correlations, is used for the stochastic simulation in this work.

2 Simulation results for the turbulent collection kernel

The gelation time, T_{gel}, can be estimated as the time when the maximum of the ratio, ρ, is reached. This ratio is defined as the standard deviation of the largest particle mass over all the realizations to its ensemble average, evaluated from the realizations of the stochastic process:

$$\rho = \sigma(M_{L1})/M_{L1} \tag{5}$$

where M_{L1} is the ensemble mean of the mass of the largest droplet over all the realizations and the standard deviation for the largest droplet mass (σ) is calculated as:

$$\sigma(M_{L1}) = \sqrt{\frac{1}{K}\sum_{i=1}^{K}\left(M_{L1}^{i} - M_{L1}\right)^2} \tag{6}$$

In Eq. (6) M_{L1}^{i} is the largest droplet mass for each realization and K is the number of realizations of the Monte Carlo algorithm.

As previously mentioned, the KCE (Eq. 1) has analytical solutions for only a few selected kernels such as the product kernel $K(i,j)=Cx_i x_j$. The validity of the KCE will break down once gelation occurs. We will demonstrate that the time when the ratio ρ (Eq. 5) reaches its maximum value is a good estimate of the gelation time T_{gel}. The calculations were performed for an initial, mono-disperse distribution of 100 droplets of 14 µm in radius (droplet mass 1.15×10^{-8} g), with $C = 5.49 \times 10^{10}$ cm^3 s^{-1} (Alfonso et al., 2008) in a volume of one cubic centimeter. This initial concentration is

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typical of maritime cumulus clouds and corresponds to a liquid water content of about 1.15 gm^{-3}. The time evolution of ρ was estimated from 1000 realizations ($K = 1000$) of the Gillespie's (1975) Monte Carlo algorithm. The results of this simulation are displayed in Fig. 1 and we observe that the maximum of ρ (solid line) was obtained at $\tau = 1335$ s. Independently, the gelation time can be obtained analytically (Drake and Wright, 1972) from

$$M_2(\tau) = \frac{M_2(t_0)}{1 - CM_2(t_0)\tau} \tag{7}$$

$$T_{gel} = \left[CM_2(t_0)\right]^{-1} \tag{8}$$

and was found to be 1379 s, very close to the time when ρ reaches its maximum value. After this time, the largest droplet continues to grow by accretion of smaller droplets and the total mass M_1 predicted by the KCE starts to decrease (Wetherill, 1990), as seen in Fig. 1. This indicates that the numerical method provides a reliable approximation of the gelation time.

For natural clouds, collisions between droplets under idealized, pure gravity conditions are typically simulated with a collection kernel of the form:

$$K_g(x_i, x_j) = \pi(r_i + r_j)^2 \left|V(x_i) - V(x_j)\right| E(r_i, r_j) \tag{9}$$

The hydrodynamic kernel (Eq. 9) does not take into account the turbulence effects and considers that droplets with different masses (x_i and x_j and corresponding radii, r_i and r_j) have different settling velocities. In Eq. (9), the collision efficiencies $E(r_i, r_j)$ were calculated according to Hall (1980).

In turbulent air, the hydrodynamic kernel can be enhanced due to an increase in relative velocity between droplets (transport effect) and an increase in the collision efficiency (the drop hydrodynamic interaction). These effects were taken into consideration by implementing the turbulence-induced collision enhancement factor $P_{Turb}(x_i, x_j)$ that is calculated in Pinsky et al. (2008) for a cumulonimbus cloud with dissipation

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rate, $\varepsilon = 0.1\,\mathrm{m^2\,s^{-3}}$ and Reynolds number, $Re_\lambda = 2 \times 10^4$, for cloud droplets with radii ≤21 µm. Consequently, the turbulent collection kernel has the form:

$$K_{\mathrm{Turb}}(x_i, x_j) = P_{\mathrm{Turb}}(x_i, x_j) K_g(x_i, x_j) \tag{10}$$

In the simulation for turbulent air, a system corresponding to a cloud volume of $1\,\mathrm{cm^3}$ and a bimodal droplet distribution was considered: 150 droplets of 10 µm in radius and another 150 droplets of 12.6 µm in radius, corresponding to a liquid water content (LWC) of $1.9\,\mathrm{g\,m^{-3}}$. The behavior of the ratio ρ (Eq. 5) was evaluated from 1000 realizations of the Monte Carlo algorithm and, independently, the evolution of the total mass was obtained by solving the KCE (Eq. 1) numerically. Figure 2 shows that the total mass (expressed in % of the initial total mass), calculated numerically from the KCE, is no longer conserved after 1000 s. This time is very close to the time when the ratio ρ, determined from the Monte Carlo realizations, reaches its maximum (1055 s). Given that these results were obtained independently from the numerical solution of Eq. (1) and from the stochastic algorithm, this clearly indicates that the sol-gel transition and the formation of a runaway droplet took place around 1000 s and that the ratio ρ can be used as an estimator of the gelation time when realistic turbulence collection kernels are used.

To emphasize the importance of the turbulence enhancement in the collection process, an additional simulation was performed for non-turbulent flow under the Earth's gravitational field with the same initial conditions. The total mass at the end of the simulation was found equal to 99.88 % of the initial mass, illustrating mass conservation for this case. Furthermore, the ratio ρ never reaches its maximum, confirming that the sol-gel transition does not take place under these conditions.

3 Discussion and conclusions

One of the outstanding problems in cloud physics is to explain the observations that show that raindrops can grow by condensation and collision-coalescence in times as short as 20 min. In order to form a raindrop with a radius of 1 mm in a warm cloud, a

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total of 10^5 droplets with radius of 10 µm must collide and coalesce. When droplets are small and of uniform size, collisions between them are inefficient and collision events cannot occur at sufficient rates to produce raindrops until some of the droplets grow by condensation to a radius of about 20 µm. The appearance of a runaway droplet after a sol-gel transition is a possible mechanism that explains the rapid formation of raindrops. The stochastic process gives rise to a "lucky droplet" that grows more rapidly than the rest of the droplet population. To further clarify this point, we calculate the time evolution of the mass of the largest and second largest droplets as ensemble means over all the realizations. Figure 4 shows the results for the turbulent case, clearly indicating a significant gap between the mass of the largest and second largest droplets after 1000 s. In contrast, the difference in mass in the non-turbulent, pure gravity case, shown in Fig. 5, remains much smaller with no runaway behavior.

The simulations under the turbulent conditions performed here include a collision enhancement factor for collisions between droplets with radii ≤21 µm, so the role of turbulence in stochastically producing the runaway droplet is likely underestimated in the present study. Since the nucleation and condensation processes are not yet included in this model, future developments will attempt to include the combined effect of turbulent collection and condensation (McGraw and Liu, 2003) on droplet growth.

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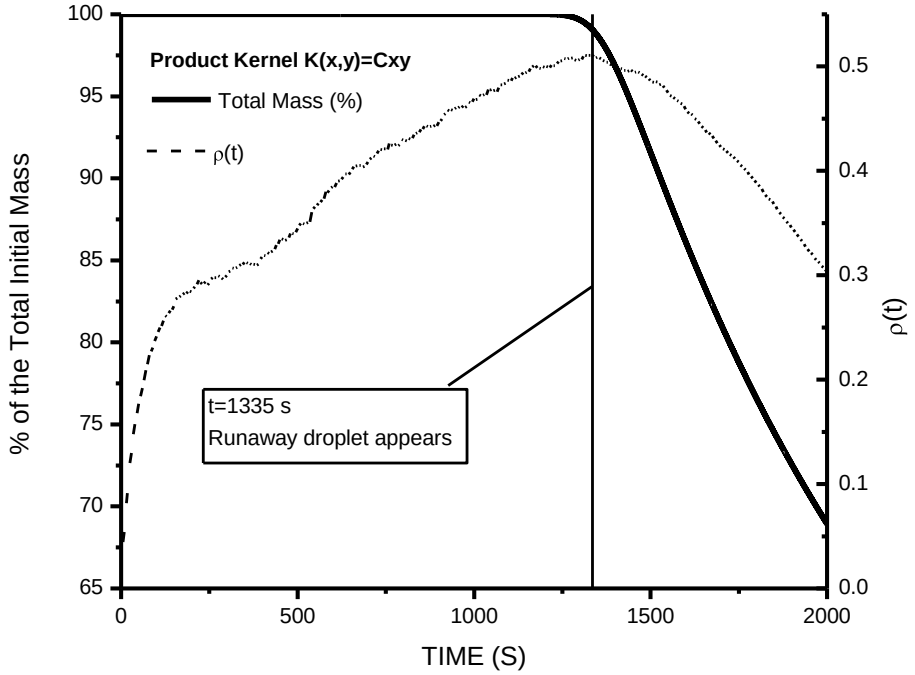

Fig. 1. Time evolution of the statistics ρ defined in Eq. (5) (dashed line and right axis) and the total mass (solid line and left axis) calculated from the numerical solution of the KCE. The results were obtained for the product kernel $K(x,y)=Cxy$, ($C = 5.49 \times 10^{10}$ cm^3 g^{-2} s^{-1}).

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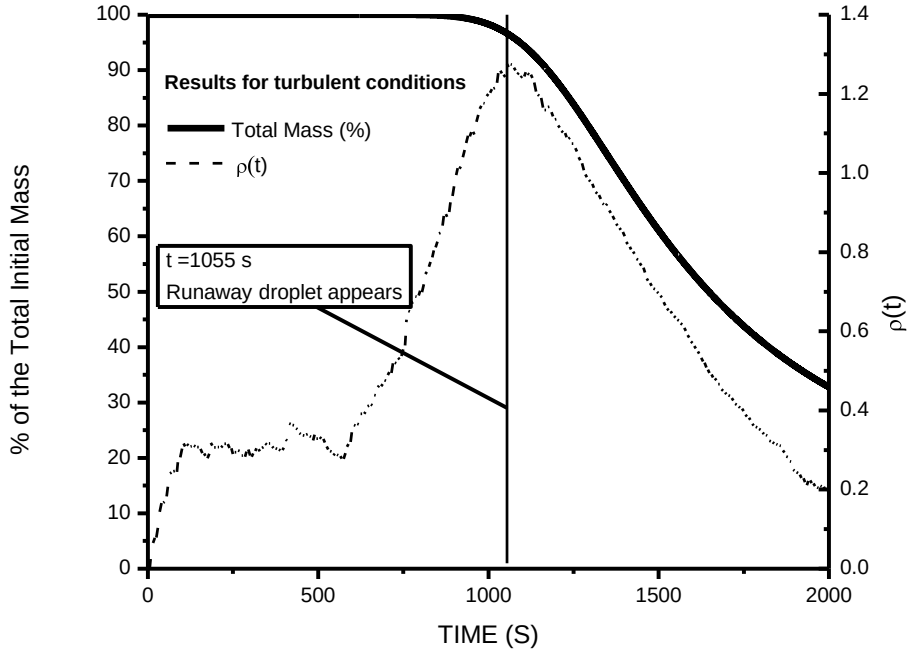

Fig. 2. Time evolution of total mass calculated from the numerical solution of the kinetic collection equation for turbulent collision coalescence (solid line and left axis) and the statistics ρ (dashed line and right axis) estimated from the Monte Carlo algorithm.

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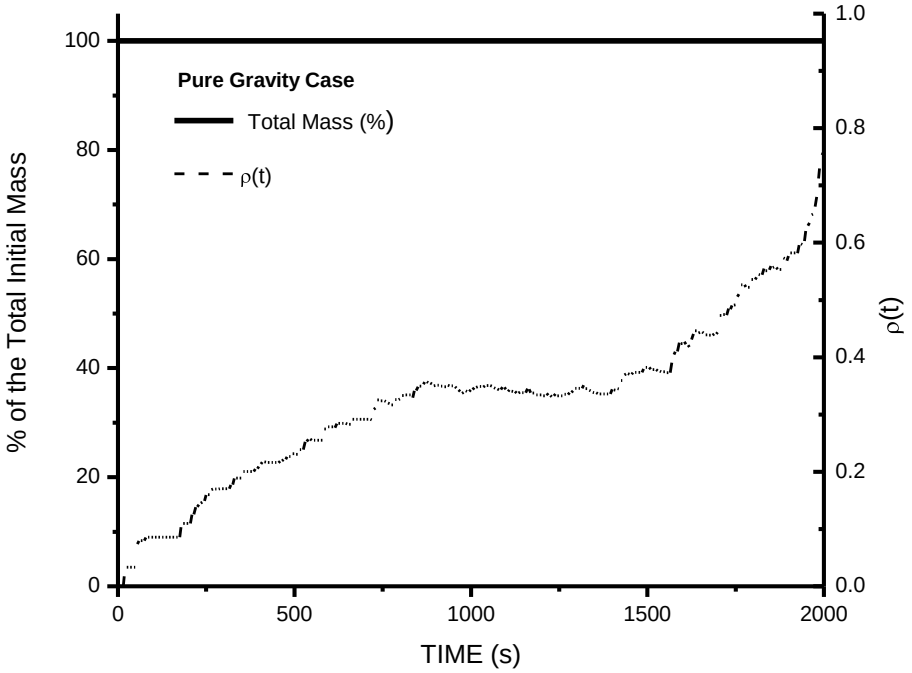

Fig. 3. Same as Fig. 2 but for the gravity only case.

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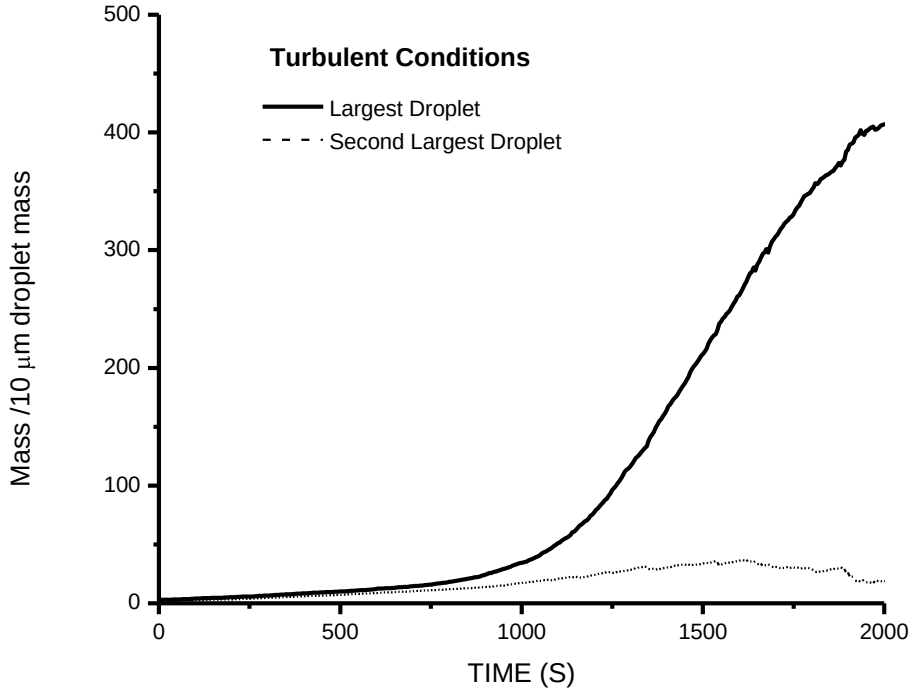

Fig. 4. Time evolution of the ensemble means over all the realizations for the largest (solid line) and second largest (dashed line) droplet masses (expressed in multiples of a 10 μm droplet mass) for the turbulence case.

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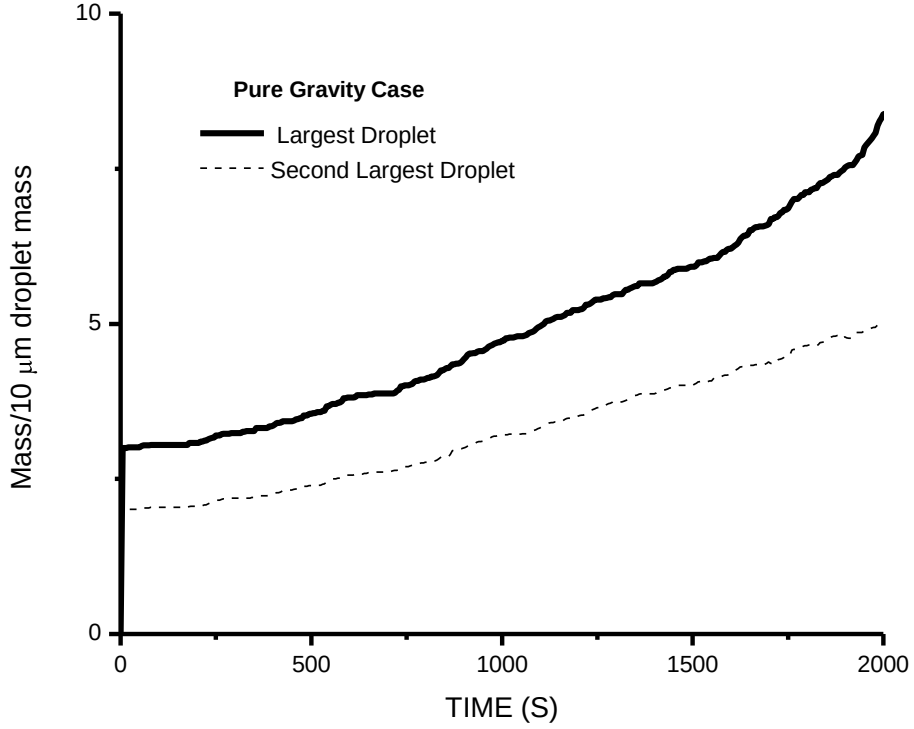

Fig. 5. Same as Fig. 4 but for the gravity only case.

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