Ostwald ripening and the kinetics of rain initiation

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A central problem in cloud physics is understanding the kinetics of the growth of water droplets. It is believed that there exists a 'condensation-coalescence bottleneck' in the growth of intermediate size droplets. Here the Lifshitz-Slezov theory of Ostwald ripening is applied to the kinetics of the growth of rain drops. The analysis shows that kinetic barriers to rain initiation are not significant. It is also shown that Ostwald ripening can greatly enhance the apparent collision efficiency of droplets falling under gravity.

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1. *Introduction.* Clouds are the least well understood aspect of modelling the weather, and their albedo has a stong effect on the radiation balance of the atmosphere [1]. Perhaps the most complex aspect of cloud physics is the removal of moisture from the atmosphere by rainfall. Many different processes may be involved [2–4], and a quantitative understanding of the rainfall cycle has been lacking [5]. One difficulty is that the growth of droplets through the size range $15 - 50\,\mu$m is considered to be a poorly understood 'bottleneck' in the kinetics of rain initiation [5–8]. This bottleneck is partly a consequence of the fact that the collision efficiency of small droplets falling at different rates is believed to be very low, because the streamlines of the flow are deflected around the droplets. It is believed that the effciencies are very low for droplets smaller than $20\,\mu$m radius, but that they are of order unity for droplets of radius $50\,\mu$m or larger [2]. The collision efficiencies of very small droplets are very hard to measure. They are also hard to calculate reliably, because the criterion for droplet coalescence depends upon a breakdown of hydrodynamic equations when the film of air between the droplets becomes very thin [9, 10]. Uncertainties about the collision efficiency are a barrier to making relaiable estimates about the life-cycle of clouds.

Following a suggestion by Saffman and Turner [11] that turbulence can promote collisions of water droplets, there have been extensive efforts to explain how the growth bottleneck might be overcome by the effects of turbulence increasing the relative velocities of water droplets [5, 6, 8, 12]. This paper addresses an alternative mechanism for droplet growth, applying the Lifshitz-Slezov theory of Ostwald ripening [13] to the growth of water droplets. It makes two distinct contributions. First, it is shown that Ostwald ripening can circumvent the apparent bottleneck in rain droplet growth. It is shown that growth of droplets to $50\,\mu$m can occur in approximately ten minutes, independent of the physical parameters of the cloud. In fact, this mechanism is so effective that the emphasis should shift towards explaining the stability of cloud systems. Secondly, it is shown that the non-local interaction involved in the Ostwald ripening effect can lead to 'collision efficiencies' which are greater than unity for very small droplets.

2. *Ostwald ripening.* Ostwald ripening is a process whereby droplets in a supersaturated solution exchange molecules through the solution, resulting in a competitive growth process which favours the growth of the largest droplets at the expense of evaporation of the smallest. The effect is caused by the Laplace pressure, $p = 2\gamma/a$, resulting from surface tension γ acting on the curvature of the surface of a droplet of radius a. The higher pressure inside smaller droplets increases the chemical potential, favouring evaporation. Droplets below a critical radius a_0 evaporate, and the material condenses onto the larger droplets. As the larger droplets grow, the degree of supersaturation s decreases, and the critical size a_0 increases, so that the typical radius of the droplets increases. The first persuasive analysis of the Ostwald ripening effect was by Lifshitz and Slezov [13], which although not rigorous is regarded as essentially correct. The following is a brief summary of the theory which is sufficient to support subsequent arguments. It follows the notation used in [14].

The interior of a droplet of radius a has a pressure which is higher than the ambient pressure by $p = 2\gamma/a$. This increased pressure implies that water vapour must have a higher concentration at the surface of the droplet: the surface of each droplet is therefore in contact with a layer of air in which the volume fraction of water vapour is $\Phi = \Phi_{\rm e} + \sigma/a$ where σ is a capillary length, defined by:

$$\sigma = 2\gamma V_{\rm m}\Phi_{\rm e}/RT \ . \tag{1}$$

Here D is the diffusion coefficient of water vapour in air, $V_{\rm m}$ is its molar volume, $\Phi_{\rm e}$ its equilibrium volume fraction, and R is the universal gas constant. Lifshitz and Slezov analysed the concentration gradient at the surface of each drop, which leads to a flux of material to or from the surface, and consequently a change in the radius of the droplet, at a rate

$$\frac{{\rm d}a}{{\rm d}t} = -D\frac{\partial\Phi}{\partial r}\bigg|_{r=a} = \frac{D\sigma}{a}\left(\frac{1}{a_0} - \frac{1}{a}\right) \tag{2}$$

with $a_0 = \sigma/s$, s being the supersaturation of the solution. This implies that droplets smaller than a_0 shrink under the effects of the Laplace pressure, and those larger than a_0 grow by absorption of material evaporating from the smaller droplets. The supersaturation decreases as a function of time so that the largest droplets can continue to grow. Lifshitz and Slezov gave a scaling form for the distribution of droplet sizes at time t. Their theory shows that a_0 is comparable to the typical droplet size (in fact $\langle a \rangle = a_0$ [13, 14]) and it predicts that the mean droplet size is

$$\langle a(t) \rangle = \left(\tfrac{4}{9} D\sigma t\right)^{1/3} \ . \tag{3}$$

3. *Kinetics of droplet growth in clouds.* Consider whether Ostwald ripening is relevant to the growth of atmospheric rain droplets. It has been argued [6–8, 20] that there is a 'condensation-collision bottleneck' in the growth kinetics of raindrops at radii in the range $a \approx 15 - 50\,\mu\text{m}$, between smaller droplet sizes where growth by condensation is efficient, and larger sizes where collisions due to gravitational settling become important. Let us consider the growth of droplets to $50\,\mu$m by Ostwald ripening alone. The physical parameters are, at 10°C, diffusion constant for water vapour in air, $D = 2.4 \times 10^{-5}\,\text{m}^2\text{s}^{-1}$, surface tension $\gamma = 7.4 \times 10^{-2}\,\text{Nm}^{-1}$, molar volume $V_\text{m} = 1.8 \times 10^{-5}\,\text{m}^3$, saturation volume fraction $\Phi_\text{e} = 1.2\times 10^{-2}$ [2]. These give a capillary length $\sigma = 1.4 \times 10^{-11}$ m and consequently, using equation (3), the growth law is $a(t) \approx 6\times 10^{-6}(t/\text{s})^{1/3}$ m. This implies that growth to a radius of $50\,\mu$m requires approximately ten minutes. Note that this is a very robust estimate, because it depends only upon physical parameters of the water-air system. In particular, neither the density of the water droplets nor the mass loading of water in the cloud, both of which are highly variable parameters, plays any role. Also, because droplet growth by Ostwald ripening does not involve collisions, the uncertainties in the collision efficiency of droplet coalescence do not affect this estimate. We must, however, ensure that the density of droplets is sufficiently high that water molecules can pass from one to another by diffusion. For typical water droplet densities in clouds of $10^8\,\text{m}^{-3}$ [2, 4], the separation of droplet is of order 1 mm. A water molecule diffuses this distance in a time of order 1 s, so the droplets are indeed sufficiently close to allow Ostwald ripening to occur.

The atmosphere can be either convecting or stable. Convecting atmospheres mix bodies of air with large differences in temperature and saturation, so that the growth of a droplet may occur in an environment with fluctuating supersaturation. According to equation (2), an excess supersaturation can increase the rate of growth of a droplet by a large factor, whereas a reduction in superasaturation causes decrease in radius at a rate which is bounded by $|\dot{a}_\text{max}| = D\sigma/a^2$. These considerations indicate that equation (3) gives a lower limit to the droplet size, if t is interpreted at the time over which the droplet has been in a supersaturated environment. Ostwald ripening is therefore a baseline contribution to the droplet growth, which exists in stable atmosphere and which may be increased by the fluctuating supersaturation in a convecting atmosphere.

Because the growth predicted by Ostwald ripening is sufficiently rapid that it does not impose any limit on the initiation of rainfall, it is not necessary to consider calculations of the rate of droplet growth due to turbulence-induced collisions in order to explain rain initiation. In fact, the Ostwald ripening mechanism is so efficient for the growth of droplets in clouds that we should ask how a cloud can persist for more than an hour without losing its visible moisture as rainfall. We remark upon two possible explanations for the stability of clouds. One mechanism is that if droplets nucleate on salt grains (or other hygroscopic nuclei) the osmotic potential reduces due to dilution of the salt as the droplets grow, so that small droplets are stabilised. The role of osmotic effects in stabilising small droplets in aerosols was originally discussed by Köhler [15]. A second possibility is that clouds may be dynamic objects, where water droplets grow rapidly at some altitudes, only to evaporate as they fall to lower levels.

Although the effects of droplet curvature (eg. [16, 17]) and hygroscopic nuclei (eg. [18, 19]) on droplet size distributions have been included in complex models for cloud dynamics, these studies have not isolated the role of Ostwald ripening in circumventing the widely perceived droplet growth bottleneck.

4. *Growth by gravitational settling.* As water droplets grow their rate of sinking increases, and eventually the effects of their macroscopic motion dominate over the diffusional growth due to Ostwald ripening. Two effects may be involved. Firstly, the falling drop will be able to 'sweep up' the residual supersaturation of the solution more efficiently than if molecules had to reach the droplet surface by diffusion alone. Secondly, the largest droplets fall at a faster rate than the smaller ones. When a droplet is caught up by a larger and faster droplet, the two droplets may collide and coalesce. The merged droplet will fall at an even faster rate. At the stage where the settling velocity becomes significant, the supersaturation of the air is small enough that most of the moisture is in the form of water droplets, so it is the second mechanism which is most significant. It will be shown that the equation modelling the droplet growth exhibits a finite-time singularity, resulting in a runaway growth of the size of the largest droplets. Other authors have also argued that a runaway growth of droplet sizes occurs in rainfall [20].

The sinking velocity v is estimated by equating graviatational forces and the Stokes formula for the drag on a small sphere: $4\pi(\rho_\text{w} - \rho_\text{a})ga^3/3 = 6\pi\rho_\text{a}\nu a v$ where ν is the kinematic viscosity of the air and where the densities of the air and water are ρ_a and ρ_w respectively. The settling speed is therefore

$$v = \frac{2}{9}\frac{(\rho_\text{w} - \rho_\text{a})g}{\rho_\text{a}\nu} a^2 \equiv \kappa a^2 \ . \tag{4}$$

For water droplets in air at 10°C we have $\nu = 1.4 \times 10^{-5}\,\text{m}^2\text{s}^{-1}$, $\rho_\text{w} = 10^3\,\text{kg}\,\text{m}^{-3}$, $\rho_\text{a} = 1.2\,\text{kg}\,\text{m}^{-3}$ [2], so that $\kappa \approx 1.3 \times 10^8\,\mathrm{m}^{-1}\mathrm{s}^{-1}$.

Gravitational settling allows drops to grow by sweeping up smaller droplets. We can model this process as follows. Assume that a droplet has already grown to a radius a where it is much larger than the other droplets in its path. The settling velocity of the smaller droplets may be neglected. The larger drop moves through a 'gas' of smaller droplets which occupy a volume fraction w, and they cause the lower surface to sweep up a volume of liquid water per unit time $\dot{V} = \pi a^2 v w$. This rate of growth of the volume implies a rate of growth of the droplet radius given by $\dot{V} = 4\pi a^2 \dot{a}$, so that the droplet radius grows by particle accretion at a rate

$$\dot{a} = \frac{\epsilon}{4} w \kappa a^2 \tag{5}$$

where (4) was used to substitute for the sinking speed, and where ϵ is the collision efficiency coefficient. The volume fraction of water droplets is highly variable quantity, but values of the order of $w \sim 10^{-6}$ would be appropriate for a dense cloud [2].

Now consider a model for the time evolution of the radius of the largest droplets. Their initial growth by Ostwald ripening may be described by the relation $\dot{a} \sim D\sigma/a^2$. Combining this with the relation for growth by sweeping gives the model equation

$$\frac{\mathrm{d}a}{\mathrm{d}t} \sim \frac{D\sigma}{a^2} + \frac{1}{4}\epsilon w \kappa a^2 \tag{6}$$

where ϵ is the collision efficiency. This model indicates that the evolution of the droplets can be divided into two stages, depending upon which term in the expression for $\dot{a}$ is dominant. The first stage, growth by Ostwald ripening, lasts for a time t_1, determined by the condition that the two terms in the right hand side of (6) become equal. This condition is satisfied when the droplets reach a size a_1. From this point on we shall ignore numerical coefficients. The condition for the crossover is $D\sigma \sim \epsilon\kappa w a_1^4$. Using the values quoted above and setting $\epsilon = 1$ and $w = 10^{-6}$ gives $a_1 \approx 40\,\mu$m.

In the second stage of droplet growth, equation (6) for droplet growth may be approximated by $\dot{a}/a^2 \sim \epsilon\kappa w$. With initial condition $a = a_1$ at $t = t_1$, this has the solution $(1/a_1) - (1/a) = \epsilon\kappa w(t - t_1)$. According to this solution, $a(t)$ diverges in a finite time, so that there is a runaway growth of the largest droplets in a time $t_2 \sim (\epsilon w \kappa a_1)^{-1}$. Setting $\epsilon = 1$, $w = 10^{-6}$ and $a_1 = 40\,\mu$m gives $t_2 \approx 200$s.

To summarise, these estimates indicate that if we apply the Lifshitz-Slezov theory of Ostwald ripening, then growth to $50\,\mu$m occurs after approximately ten minutes. Once this size is reached, collisions caused by gravitational settling become significant and there is a runaway growth in a relatively short time. For water droplets formed on osmotically inactive nuclei, there estimates are very robust, because the Ostwald ripening growth law, equation (3), is independent of all of the the physical parameters of the cloud except temperature. The conclusion is that calculations of collision rate enhancement due to turbulence are not required to explain the onset of rainfall, and that attention should shift to explaining the persistence of clouds, which is favoured by condensation onto hygroscopic nuclei.

5. *Ostwald ripening and collision efficiency*. An interesting aspect of the Ostwald ripening mechanism for droplet growth is that it is non-local, in that water is transferred from smaller droplets to larger ones without the necessity for physical contact. The collision efficiency ϵ, (defined in (5) above) cannot be greater than unity if the droplets grow by coalescence upon contact, and in the case of interaction between very small droplets, the collision efficiencies are expected to be very low [2]. It is interesting to consider whether Ostwald ripening can increase the collision efficiencies of very small droplets. It will be argued that this is possible, and that in some circumstances the effective collision efficiency can exceed unity.

A larger droplet falling of radius b falling through a 'gas' of small droplets of radius a will grow at a rate $\dot{b}$, which is proporitional to the volume fraction of the smaller droplets, and by comparison with (5) it is possible to define a 'collision efficiency' ϵ for this growth process. In the following simplified account it is assumed that $b/a \gg 1$. Droplets of radius a are in equilibrium with a air containing a supersaturation $s = \sigma/a$. The supersaturation at the surface of the much larger droplet of radius b is $s' = \sigma/b$, which is negligible because we assume that $b \gg a$. As the larger droplet passes tha smaller ones, it absorbs supersaturated water vapour onto its surface by diffusion, so that the supersaturation drops to a negligible value in a region of dimension R. The influence of the passage of the larger droplet lasts for a time $\tau \sim R/v$, where $v = \kappa b^2$ is the settling speed of the larger droplet. The size of the region of reduced supersaturation is given by $R^2 \sim D\tau$, so that

$$\frac{R}{b} \sim \frac{D}{\kappa b^3}\ . \tag{7}$$

In cases where $R/b \gg 1$, the effective collision efficiency could exceed unity. To assess this possibility, we must consider the effect of this reduction in supersaturation as the larger droplet passes. Water will evaporate from the smaller droplets of size a. If the time τ is sufficiently large, all of the small droplets in the affected region will evaporate completely and their water content will condense onto the larger droplet, but this could only happen is a is extremely small. For physically relevant values of a, the temporary reduction in the degree of supersaturation will cause a limited evaporation of the smaller droplets, so that their radius is reduced by Δa in the time τ taken for the larger droplet to pass. From (2), the fractional change in radius is estimated as

$$\frac{\Delta a}{a} \sim \frac{D\sigma\tau}{a^3} \sim \left(\frac{D}{\kappa b^3}\right)^2 \left(\frac{b}{a}\right)^2 \frac{\sigma}{a}\ . \tag{8}$$

The evaporated material represents a fraction $O(\Delta a/a)$ of the total volume fraction of the droplets, w, so that the falling droplet sweeps out a cylinder of radius R, which may be much larger than the contact radius $b+a$, with a collection efficiency which is of order $\Delta a/a$. The apparent collision efficiency is therefore

$$\epsilon \sim \left(\frac{R}{b}\right)^2 \frac{\Delta a}{a} \sim \left(\frac{D}{\kappa b^3}\right)^4 \frac{\sigma}{a} \left(\frac{b}{a}\right)^2 . \tag{9}$$

When $D \gg \kappa b^3$ this quantity may be large compared to unity.

For the water-air system at 10° C, we have shown that Ostwald ripening grows droplets to radius of $40\,\mu$m within a few minutes. For $b = 40\,\mu$m, we find $D/\kappa b^3 \approx 3$, so that the range of interaction due to Ostwald ripening is comparable to the size of the droplet. This shows that Ostwald ripening does not substantially enhance the collision effciency of water droplets in clouds.

However, there are other contexts in which phase separation results in nucleated droplets settling due to buoyancy forces, where the condition $R/b \gg 1$ is easily satisfied. One example is in the case of 'test-tube' experiments on phase separation [21, 22], which show phenomena analogous to 'drizzle' when a slow change of temperature reduces the intersolubility of two partially miscible liquids. In the case where the two phases are both liquids with a similar composition, the density difference in the numerator of (4) is orders of magnitude smaller than in the water-air system, resulting in κ being much smaller. Also, when the equilibrium concentration is of order unity, the volume fraction $\Phi_{\rm e}$ and consequently the capillary length σ are much larger than for the water-air system. Both of these effects increase the efficiency, as estimated by (9), to the point where numbers in excess of unity are possible.

6. *Summary.* This paper has discussed the implications of the Lifshitz-Slezov theory of Ostwald ripening for the kinetics of rain formation. It was demonstrated that this theory leads to the growth of water droplets condensed upon an osmotically inactive nucleus to $50\,\mu$m radius in approximately ten minutes by Ostwald ripening alone. This estimate involves only the physical chemistry of the water-air system, and is independent of the mass loading and droplet density in the cloud. After reaching a size of $50\,\mu$m collisions caused by graviationally induced settling become the dominant growth process and lead to a fast runaway growth of the droplet size. This shows that attempts to explain the growth of rain droplets by the effects of turbulence are of marginal relevance. The emphasis must shift to understanding why clouds are so persistent.

Ostwald ripening also provides a mechanism to enhance the collision efficiency for growth of droplets settling under gravity. This effect is of marginal relevance to atmospheric clouds, but it is significant where droplets form in liquids with similar density. It was shown that the apparent collision efficiencies of very small droplets can exceed unity.

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