

**On the Ostwald Ripening process**

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**Abstract**

By using the "off-centre" diffusion theory it is shown that the average radius of the droplets in the precursor regime of the finite volume fraction and of dominance of the large droplets obeys a temporal power law with the exponent  $1/6$  ( $R \sim t^{1/6}$ ). Within the same theory the well-known exponent  $1/3$  is obtained in the asymptotic regime of an infinite time and of a vanishing volume fraction. Transient regimes are characterized by temporal exponents in-between these two limiting values.

It is widely agreed that, under certain conditions, fluctuations in over-saturated binary solutions may lead to a phase separation.[1] The minority phase consists of small, approximately spherical droplets, of various sizes which evolve in time. It has been noticed that the average radius of these droplets increases in time, the large droplets growing at the expense of the small ones, which perish. This phenomenon is known as "Ostwald Ripening", and much attention has been paid to the temporal law governing the evolution of the average radius. The basic explanation of the phenomenon consists in the large curvature of the small droplets, where the concentration of the solute particles is therefore higher, thus leading to a net particles flow from the small,shrinking droplets to the large, growing ones. It has been shown[2] that in the asymptotic limits of an infinite time and of a vanishing volume fraction the average radius  $R$  obeys a  $1/3$ -power law,  $R \sim t^{1/3}$ , which is quasi-universal. Many experiments, both physical and numerical, give support to this power law,[3] while many others disagree.[4] Particularly controversial results have recently been presented and commented in two-dimensional systems.[5, 6] It seems that the asymptotic regime of the  $1/3$ -law is not always reached experimentally, and the precursor stage of a finite volume fraction deserves a special attention.[7, 8] In this regime the solute particles are trasferred directly to a large droplet from the small droplets surrounding it at close ranges. We apply to this process an "off-centre" diffusion theory developed recently,[9, 10] with the result that the average radius goes like  $t^{1/6}$  for the late stages of the direct-transfer regime where large droplets dominate. In the limits of an infinite time and of a vanishing volume fraction, where the growing of a large droplet proceeds from solution, we rederive the exponent  $1/3$  of the temporal law by employing the same theory of "off-centre" diffusion. We argue that the same exponents apply also to the two-dimensional case. Transient regimes appear in-between the two limiting processes mentioned above, with various temporal exponents ranging from  $1/6$  through  $1/3$ .

Suppose that we have a shrinking droplet placed at  $x$  and a growing one placed at  $x + \xi$ . We shall focus on the net flow of solute particles from the former droplet to the latter. According to the "off-centre" diffusion theory[9, 10] the particles may jump (on atomic scale) among  $N$  sites placed on the droplet surface and labelled by  $i = 1...N$ . We denote the frequency of these "on-site"

jumps by  $p_0$ . At the same time the particles may also perform "inter-site" jumps with a frequency  $p$  ( $p \ll p_0$ ) along the  $x$ -axis over the distance  $\xi$ . We denote the particle concentration at each site  $i$  by  $n_i(x, t)$ , and, assuming that these concentrations vary slowly in time, we may write

$$\frac{\partial}{\partial t} n_i(x, t) = p_0 \sum_{j=1}^N [n_j(x, t) - n_i(x, t)] + p \sum_{j=1}^N [n_j(x + \xi, t) + n_j(x - \xi, t) - 2n_i(x, t)] \quad (1)$$

Next, we assume that the concentration functions  $n_i$  vary slowly in space too, so that (1) becomes

$$\frac{\partial n_i}{\partial t} = (p_0 + 2p) n - N (p_0 + 2p) n_i + p \xi^2 \frac{\partial^2 n}{\partial x^2} \quad , \quad (2)$$

where we have denoted

$$n(x, t) = \sum_{i=1}^N n_i(x, t) \quad . \quad (3)$$

By Fourier transforming (2) we obtain immediately the frequency

$$\omega = N p \xi^2 q^2 \quad (4)$$

of the  $q$ -th diffusion mode, and the total number of particles

$$n(x, t) = \frac{1}{2\sqrt{\pi N p \xi^2 t}} \exp\left(-\frac{x^2}{4N p \xi^2 t}\right) \quad , \quad (5)$$

where  $n(x, 0) = \delta(x)$ . We note that (5) is the well-known solution of the diffusion equation in one-dimension (coordinate  $x$ ), and that the "on-site" jumps of the particles on the droplet surface account for the diffusion process along the remaining two local coordinates  $y$  and  $z$ . We note also that the "geometrical factor"  $N$  appears in the effective diffusion coefficient in (5) above, as discussed recently in the "off-centre" diffusion theory.[10]

Further on, we may assume that the solute particles involved in this diffusion process are produced at the shrinking droplet with a dissociation rate which is constant in time. This rate may depend, of course, on the nature of the solute particles and, what is probably more important, it depends on temperature  $T$ . [11] We denote it by  $K(T)$ , therefore, and the total number of particles at  $x$  and  $t$  can be written as

$$N(x, t) = \int_0^t d\tau \cdot K(T) \cdot n(x, t - \tau) = K(T) \int_0^t d\tau \cdot n(x, \tau) \quad . \quad (6)$$

For long times the concentration function  $n(x, t)$  varies slowly, in agreement with the assumptions of the present theory, so that we may write (6) approximately as

$$N(x, t) \cong K(T) \cdot t \cdot n(x, t) = \frac{K(T)}{2\sqrt{\pi N p \xi^2}} \sqrt{t} \exp\left(-\frac{x^2}{4N p \xi^2 t}\right) \quad . \quad (7)$$

Indeed, for large values of time  $n(x, t)$  given by (5) is, up to irrelevant factors,  $n(t) \sim 1/\sqrt{t}$ , and the integral in (6) may be written as

$$\int_0^t d\tau \cdot n(x, \tau) \sim \sqrt{t} = t \cdot n(x, t) \quad , \quad (8)$$

whence (7).

Part of the particles released by the shrinking droplet (placed at  $x = 0$ ) in this diffusion process condense at  $x = \xi - R$  on the surface of the growing droplet, and quickly distribute themselves uniformly over the whole area of the droplet by "on-site" jumps. We may assume therefore that  $N$  in (7) is proportional to the area of the droplet,  $N \cong R^2/a^2$ , where  $a$  is an atomic length scale. Using (7) we can write now the variation of the droplet radius from  $R_0$  to  $R$  as being given by

$$\rho \cdot \frac{4\pi}{3} (R^3 - R_0^3) \cong \frac{1}{2} a K(T) \int_{R_0}^R dR \cdot \frac{1}{\sqrt{\pi p \xi^2}} \cdot \frac{\sqrt{t}}{R} \cdot \exp\left(-\frac{(\xi - R)^2 a^2}{4R^2 p \xi^2 t}\right) , \quad (9)$$

where  $\rho$  denotes the particle density of the droplet ( $\rho \sim 1/a^3$ ). We can take in (9)  $\xi \cong R$  since the volume fraction is finite and the two droplets are close to each other. In the limit of long times, where the large droplets dominate, we get straightforwardly from (9)

$$R^3 \cong \frac{3K(T)}{8\pi\rho\sqrt{\pi p}} \cdot \sqrt{t} , \quad (10)$$

where  $R_0$  has been identified with  $a$ . From (10) we obtain that the average radius of the droplets increases in time as  $R \sim t^{1/6}$ . Although the above calculations have been done for two droplets it is easy to see that the result holds also for several shrinking droplets surrounding a large, growing one.

The result derived above refers to the direct transfer mechanism between neighbouring droplets, where the volume fraction is finite and the large droplets dominate. This is a precursor regime, which, in principle at least, is followed by the asymptotic regime of vanishing volume fraction. This latter case is an ideal one, where there is only one large droplet growing directly from solution.[2] Therefore it may be described by taking in the exponential in (9)  $\xi \rightarrow \infty$ , replacing  $\xi$  in the denominator by  $R$ , and letting  $R$  go to infinity.. We obtain

$$\rho \cdot \frac{4\pi}{3} (R^3 - R_0^3) \cong \frac{aK(T)}{2\sqrt{\pi p}} \int_{R_0}^R dR \cdot \frac{\sqrt{t}}{R^2} \cdot \exp\left(-\frac{a^2}{4R^2 p t}\right) \cong K(T) \cdot t , \quad (11)$$

*i.e.* the well-known power law  $R \sim t^{1/3}$  for the average radius.

We can apply the same considerations to the two-dimensional systems. For a strictly two-dimensional case the only change in (7) and (9) comes from  $N \cong R/a$ , which leads to a temporal exponent 1/4 in the precursor regime and 1/2 in the asymptotic one. However, the actual flattened islands of the minority phase in two dimensions have the area  $\sim R \cdot l$ , where  $l$  is their thickness, and minimization of energy at equilibrium requires  $l \sim R$ , so that the number of sites  $N$  is actually again proportional to  $R^2$ , as for quasi-spherical droplets in three-dimensions; we are led therefore to the same temporal exponents 1/6 and 1/3. We note in this connection that recent experimental data for thin films of poly-styrene-b-butylmethacrylate deposited on silicon wafers[12] indicate a temporal exponent practically equal to 1/6.

Finally, by comparing (9) for  $\xi \cong R$  and (11) we can see that the crossover between the precursor regime and the asymptotical one can be defined by  $4R^2 p t \gg a^2$ , whence, using (10), we can see that the main factor of delaying the setting up of the asymptotic regime is the low rate of dissociation. Of course, the transition to the asymptotic regime proceeds gradually, being characterized by various transient values of the time exponents in the range 1/6 through 1/3.

In conclusion, we can say that we have identified a precursor regime in the Oswald Ripening process, of finite volume fraction and dominance of the large droplets, where the solute particles

are transferred directly to the large droplets from the small droplets surrounding the former at short distances. The rest of the droplets have an approximately balanced radii, and the net flow of particles between them is relatively small. By using the "off-centre" diffusion theory we derived the 1/6-power law for the temporal increase of the average radius in the precursor regime of the Ostwald Ripening process, and recovered the 1/3-temporal exponent in the asymptotic regime. The transient stages from the former to the latter regime exhibit intermediate values of the temporal exponents. As one can see the two limiting regimes identified here in the Ostwald Ripening process, namely the direct inter-droplet transfer of particles and the growing of a large droplet from solution, have no relevant statistical aspects: the former is a diffusion process to a large, growing droplet from small, shrinking droplets surrounding it at short distances (therefore, essentially a droplet-pair problem), while the latter involves a single, large droplet growing by diffusion directly from solution. The statistical considerations made in Ref.2 are in fact irrelevant for the main result of that work, namely the 1/3-power law. In the inter-droplet direct transfer mechanism the statistical distribution changes only irrelevantly at its two ends, where the small and the large droplets are placed. On the contrary, the statistical aspects are significant, in the sense that the distribution is much and fastly affected, in the transient regimes intervening between the two limiting ones described above.

## References

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