Electronic Supplementary Material (ESI) for Nanoscale.

# Supporting Information

# Ostwald ripening of confined nanoparticles: chemomechanical coupling in nanopores

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## CONTENTS

## I. DERIVATION OF EQ. (10) OF THE MAIN TEXT: KINETICS OF OSTWALD RIPENING

We assume the general situation where the nanoparticles are made up of the element M, which reacts with a molecule A in the environment to form M $A_n$, according to the reaction

$$\mathrm{MA}_n \leftrightarrow \mathrm{M} + n\mathrm{A} \tag{SI–1}$$

The molecule M $A_n$ is the mobile intermediate species that is responsible for Ostwald ripening. Examples of Eq. (SI–1) are the formation/decomposition of $\mathrm{Fe(CO)_5}$ or $\mathrm{Ni(CO)_4}$ for the Ostwald ripening of iron or nickel nanoparticles in presence of carbon monoxide.

The main result of this section is Eq. (SI–25), which applies to any chemical reaction of the type of Eq. (SI–1). In this equation, the effect of particle size and of confining pressure are rigorously accounted for by the factors $\exp[\lambda/R]$ and $\Gamma$ defined in Eqs. (SI–10) and (SI–11).

### A. Equilibrium conditions

At chemical equilibrium, the chemical potentials of the reactants and products in Eq. (SI–1) are equal, which reads

$$\mu_{\mathrm{MA}_n} = \mu_{\mathrm{M}} + n\mu_{\mathrm{A}} \tag{SI–2}$$

where $\mu_{\mathrm{MA}_n}$ and $\mu_{\mathrm{A}}$ stand for the chemical potentials of molecules A and $\mathrm{MA}_n$.

In the particular case where the reactants and products are gaseous, it is customary to express their chemical potentials using the ideal gas expression,

$$\mu_A = \mu_A^0(T) + k_B T \ln(P_A) \tag{SI–3}$$

$$\mu_{MA_n} = \mu_{MA_n}^0(T) + k_B T \ln(P_{MA_n}) \tag{SI–4}$$

where $P_A$ and $P_{MA_n}$ are the partial pressures, and $\mu_A^0(T)$ and $\mu_{MA_n}^0(T)$ are the chemical potentials in the reference state (defined as $P = 1$ with any consistent unit). In that case, the general condition Eq. (SI–2) takes the familiar form

$$P_{MA_n} = K(P_A)^n \tag{SI–5}$$

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where the equilibrium constant $K$ is defined as

$$K = \exp\left(\frac{-1}{k_BT}\left[\mu^0_{MA_n} - \mu_M - n\mu^0_A\right]\right) \tag{SI–6}$$

It is important to stress that the physical meaning of Eq. (SI–2) is the same as Eq. (SI–5), but the former equation is general. In particular, Eq. (SI–2) holds also if the reactants and/or products are adsorbed on either the nanoparticles or the support, rather than gaseous. The only assumption is equilibrium.

In the case of nanoparticles, the chemical potential $\mu_M$ has to be corrected corrected for the Laplace pressure $2\gamma/R$. As an order of magnitude, particles with a radius of $R \simeq 2$ nm and a surface energy about $\gamma \simeq 1$ J/m$^2$ result in a Laplace pressure as large as 1 GPa. In addition, when the particles are confined in the pores of a porous material, there is a possible additional pressure $P$ exerted by the pore wall. The thermodynamic consequences of these two effects are accounted for by the Gibbs-Duhem expressions, which expresses how pressure modifies the chemical potential, namely

$$\left(\frac{\partial\mu_M}{\partial P}\right)_T = \Omega \tag{SI–7}$$

where $\Omega$ is the atomic volume of $M$. The pressure dependence of the equilibrium condition in Eq. (SI–2) can be written explicitly in the following way, in terms of the chemical potential $\mu^0_M$ of the macroscopic (i.e. with no Laplace pressure) and unstressed material

$$\mu_{\mathrm{MA}_n} = \mu^0_{\mathrm{M}} + \Omega\left(\frac{2\gamma}{R} + P\right) + n\mu_{\mathrm{A}} \tag{SI–8}$$

In this equation, we have assumed that $\Omega$ is a constant.

In the particular case where MA$_n$ and A are vapours, the pressure- and size-corrected relation becomes

$$P_{MA_n} = \Gamma \exp\left(\frac{\lambda}{R}\right) K^0 (P_A)^n \tag{SI–9}$$

with

$$\lambda = \frac{2\gamma\Omega}{k_BT} \tag{SI–10}$$

and

$$\Gamma = \exp\left[\frac{P\Omega}{k_BT}\right] \tag{SI–11}$$

In Eq. (SI–9) the constant $K^0$ is obtained by replacing $\mu_M$ by $\mu^0_M$ in the definition of $K$ (Eq. SI–6). Because the two first actors are larger than one, finite size and confinement can only increase the volatility of the atoms that make up the nanoparticles. Once again, the physical meaning of Eq. (SI–8) is identical to Eq. (SI–9), but the the former is more general than the latter because it does not rest on any assumption about the physical state neither of A nor of MA$_n$.

In the main text, we use the supersaturation $S$ to characterize how far the system is from thermodynamic equilibrium. In terms of the chemical potential, it is defined as

$$S = \exp\left(\mu_{\mathrm{MA}_n} - \mu^0_{\mathrm{M}} - n\mu_{\mathrm{A}}\right) \tag{SI–12}$$

The exponential function in the definition ensures that equilibrium is met for $S = 1$. Using the unstressed chemical potential $\mu^0_M$ in this equation is merely a matter of definition, and it is convenient for further purposes. In the particular case where the reactants and products are ideal vapors, that is when Eq. (SI–5) applies, the definition of $S$ takes form of the following ratio

$$S = \frac{P_{MA_N}}{K^0(P_A)^n} \tag{SI–13}$$

Setting $S = 1$ in this equation, one recovers the familiar expression for the vapour pressures at equilibrium.

### B. Growth rate

In order to model the kinetics of Eq. (SI–1), it is necessary to assume a reaction mechanism. Both A and the mobile species MA$_n$ adsorb on the nanoparticle. We shall assume that the reaction of decomposition of the MA$_n$ species happens via its adsorption on an empty site of the nanoparticle, followed by the subsequent detachment of A, and it adsorption on neighbouring empty sites of the particle. The reverse reaction proceeds via the same steps in reverse order.

Using stars to highlight the fact that the species are adsorbed, the reaction steps are the following for the transfer of an M atom between the particle to the mobile species MA$_n$:

$$\begin{gathered} \mathrm{M\ A}_n^* \leftrightarrow \mathrm{M\ A}_{n-1}^* + \mathrm{A}^* \\ \mathrm{M\ A}_{n-1}^* \leftrightarrow \mathrm{M\ A}_{n-2}^* + \mathrm{A}^* \\ \cdots \\ \mathrm{M\ A}^* \leftrightarrow \mathrm{M} + \mathrm{A}^* \end{gathered} \tag{SI–14}$$

In the last reaction, M is an atom of the nanoparticle. And the adsorption reactions can be written as

$$\begin{gathered} \mathrm{M\ A}_n + * \leftrightarrow \mathrm{M\ A}_n^* \\ \mathrm{A} + * \leftrightarrow \mathrm{A}* \end{gathered} \tag{SI–15}$$

where the symbol $*$ stands for an empty site on the particle surface.

Following the general assumptions of transition-state theory [1], we assume that one of the steps in Eq. (SI–14), say the $i^{th}$ one, is significantly slower than the others. In other words

$$\mathrm{M\ A}_i^* \leftrightarrow \mathrm{M\ A}_{i-1}^* + \mathrm{A}^* \tag{SI–16}$$

is the rate-limiting reaction, with $1 \leq i \leq n$. According to transition-state theory, the forward and backward rates of the reaction, expressed per adsorption site can be written as

$$\dot{f} = \frac{k_B T}{h} \exp\left[\frac{-1}{k_B T}\left(\mu_{\#} - \mu_{MA_i*}\right)\right] \theta_E^2 \tag{SI–17}$$

$$\dot{b} = \frac{k_B T}{h} \exp\left[\frac{-1}{k_B T}\left(\mu_{\#} - \mu_{MA_{i-1}*} - \mu_{A*}\right)\right] \theta_E^2 \tag{SI–18}$$

where $\mu_{\#}$ is the chemical potential of the molecules in their transition state, $h$ is Planck's constant, and $\theta_E$ is the fraction of the adsorption sites that is empty, and therefore available for adsorption.

Because none of the reactions in Eq. (SI–14) for $n \neq i$ is rate-limiting, they can be considered to occur at equilibrium. As a consequence, the chemical potentials of the reactants and products of the rate-limiting equation satisfy

$$\mu_{MA_i*} = \mu_{MA_n*} - (n-i)\mu_{A*} \tag{SI–19}$$

$$\mu_{MA_{i-1}*} = \mu_M + (i-1)\mu_{A*} \tag{SI–20}$$

For the same reason the adsorption and desorption of MA$_n$ and of A are also equilibrium processes, so that

$$\mu_{MA_n*} = \mu_{MA_n} \tag{SI–21}$$

and

$$\mu_{A*} = \mu_A \tag{SI–22}$$

Using these equalities the rate of reaction $\dot{r} = \dot{f} - \dot{b}$ can be written as

$$\begin{aligned} \dot{r} = \frac{k_B T}{h} \theta_E^2 \exp\left[\frac{-1}{k_B T}\left(\mu_{\#} - \mu_M^0 - i\mu_A\right)\right] \times \\ \left\{ \exp\left[\frac{1}{k_B T}\left(\mu_{MA_n} - \mu_M^0 - n\mu_A\right)\right] - \exp\left[\frac{1}{k_B T}\left(\mu_M - \mu_M^0\right)\right] \right\} \end{aligned} \tag{SI–23}$$

In the context of Ostwald ripening, it is important to keep track of the dependence on the chemical potential of MA$_n$, because this is the mobile species that is eventually responsible for the transport of molecules from the small particles to the large ones. The strongest dependence is in the first exponential factor on the second line, which is equal to $S$ (see Eq. SI–12). Another weaker dependence is via the factor $\theta_E$, which is the fraction of empty sites on the particle surface. Indeed, one can safely assume that $\theta_E$ depends mostly on $\mu_A$, because it is reasonable to assume that molecule A adsorbs more strongly on the surface of the nanoparticle than the larger mobile species $\mathrm{MA}_n$. All put together, the kinetic law takes the form

$$\dot{r} = k\Big\{S - \Gamma \exp\left[\frac{\lambda}{R}\right]\Big\} \tag{SI–24}$$

where $k$ is a kinetic constant that depends notably on the chemical potential of the molecule A, and $\lambda$ and $\Gamma$ have the same meaning as in Eq. (SI–9). The only dependence on the mobile species $\mathrm{MA}_n$ is via the supersaturation $S$.

The rate in Eq. (SI–24) is expressed as the number of molecules that react per site and per unit time. Assuming the number of sites is proportional to the area of the nanoparticle, this can also be expressed in terms of the growth rate of the nanoparticle radius, as follows

$$\boxed{\frac{dR}{dt} = v\Big\{S - \Gamma \exp\left[\frac{\lambda}{R}\right]\Big\}} \tag{SI–25}$$

The main assumption underlying this equation is the existence of a single rate-limiting step in the chemical total reaction converting the atoms M of the nanoparticles into the mobiles species $\mathrm{MA}_n$. As a consequence all non-limiting steps are equilibrated, so that the relevant parameters can be expressed through general thermodynamic concepts.

## II. DERIVATION OF EQ. (15) OF THE MAIN TEXT: ASYMPTOTIC PARTICLE SIZE DISTRIBUTION

We consider the case of free nanoparticles, i.e. the case where the mechanical effect of the support can be neglected. This corresponds to setting $\Gamma = 1$ in Eq. (SI–24). In that case the growth of any nanoparticle is governed by

$$\frac{dR}{dt} = v\left(S - \exp\left[\frac{\lambda}{R}\right]\right) \tag{SI–26}$$

where $v$ is proportional to the kinetic constant $k$.

Let the particle size distribution be $n(R,t)$, i.e. the number of particle having at time $t$ a radius in the interval $[R, R + dR]$ is $n(R,t)dR$. Based on Eq. (SI–26) the size distribution obeys the following hyperbolic partial differential equation

$$\frac{\partial}{\partial t} n(R,t) + v\frac{\partial}{\partial R}\left\{n(R,t)\left(S(t) - \exp\left[\frac{\lambda}{R}\right]\right)\right\} = 0 \tag{SI–27}$$

which has to be solved for $n(R,t)$. In this equation, the supersaturation $S(t)$ is an *a priori* unknown function of time. It can be calculated by stating that the volume of all the particles $\int_0^\infty n(R,t)R^3\ d\mathrm{R}$ is preserved. Using Eq. (SI–27) this eventually leads to the following expression

$$S(t) = \int_0^\infty n(R,t)R^2 \exp\left[\frac{\lambda}{R}\right]\ \mathrm{d}R \Big/ \int_0^\infty n(R,t)R^2\ \mathrm{d}R \tag{SI–28}$$

which relates the supersaturation $S$ at any time to the size particle size distribution $n(R,t)$ at the same time.

For dimensional reasons, the asymptotic distribution can only depend on $R$ and $t$ via the dimensionless groups $R/\lambda$ and $tv/\lambda$. Having said that, we look for a self-similar solution of Eqs. (SI–27) and (SI–28) of the type

$$n(R,t) = \left(\frac{vt}{\lambda}\right)^{-\beta} f\left(\frac{R/\lambda}{(vt/\lambda)^{\alpha}}\right) \tag{SI–29}$$

where $f(.)$ is a yet unknown function. It is not *a priori* obvious that a solution of the type of Eq. (SI–29) should be possible at all. If such a solution exists, however, mass conservation demands that the integral

$$\int_0^\infty n(R,t)R^3\ \mathrm{d}R \tag{SI–30}$$

be independent of time. This is possible only if $\beta = 4\alpha$.

Introducing the scaling ansatz Eq. (SI–29) into Eq. (SI–28), one finds the following asymptotic expression for the supersaturation

$$S(t) = 1 + \sigma \left(\frac{vt}{\lambda}\right)^{-\alpha} + \cdots \tag{SI–31}$$

where

$$\sigma = \int_0^\infty f(x) x \ dx / \int_0^\infty f(x) x^2 \ dx \tag{SI–32}$$

is a numerical constant yet to be determined. In order to derive Eq. (SI–31), we have assumed that the distribution $n(R, t)$ took non-vanishingly small values only for $R \gg \lambda$, which is certainly justified in the limit of asymptotically long ripening times. This enabled us to approximate $\exp[\lambda/R] \simeq 1 + \lambda/R$,

Under the same assumptions, the scaling ansatz enables one to transform the evolution equation Eq. (SI–27) into the following form

$$\beta f(x) + \alpha x \frac{df}{dx} = t^{1-2\alpha} \left\{ \left(\sigma - \frac{1}{x}\right) \frac{df}{dx} - \left(\frac{1}{x}\right)^2 f(x) \right\} \tag{SI–33}$$

where $x = (R/\lambda)/(vt/\lambda)^\alpha$ is the argument of $f$. The condition for a self-similar solution of the type of Eq. (SI–29) to exist is that the variables $R$ and $t$ should appear in Eq. (SI–33) only through $x$, which is the argument of $f$ in Eq. (SI–29). The condition is therefore that $\alpha = 1/2$, which entails in turn that $\beta = 2$. Using these values, the following ordinary differential equation is obtained for $f$,

$$\frac{1}{f} \frac{df}{dx} = \frac{1 - 2x^2}{x^3/2 - \sigma x^2 + x} \tag{SI–34}$$

where $x$ is the argument of the function $f(.)$.

Integrating numerically Eq. (SI–34) for various values of $\sigma$ suggested that Eq. (SI–32) could only be satisfied for $\sigma = \sqrt{2}$. For that particular value, Eq. (SI–34) has the following analytical solution

$$f(x) = \frac{x/\sqrt{2}}{(1 - x/\sqrt{2})^5} \exp\left[\frac{-3}{1 - x/\sqrt{2}}\right] \tag{SI–35}$$

for $x \leq \sqrt{2}$, and $f(x) = 0$ for $x \geq \sqrt{2}$. Although the value $\sigma = \sqrt{2}$ was suggested by numerical evaluation, one can check that Eq. (SI–32) is indeed satisfied by Eq. (SI–36) with $\sigma = \sqrt{2}$. The cumulative distribution is obtained by integrating Eq. (SI–36), yielding

$$F(x) = \frac{1}{(1 - x/\sqrt{2})^3} \exp\left[\frac{-3 \ x/\sqrt{2}}{1 - x/\sqrt{2}}\right] \tag{SI–36}$$

for $x \leq \sqrt{2}$ and $F = 1$ for larger values. The probability that a particle has radius smaller than $R$ at time $t$ is given by $F(R/\lambda/\sqrt{vt/\lambda})$.

Summing up, the Ostwald ripening converges to the following asymptotic solution

$$n(R, t) \simeq \left(\frac{vt}{\lambda}\right)^{-2} f\left(\frac{R}{\sqrt{vt\lambda}}\right) \tag{SI–37}$$

where $f(x)$ is given in Eq. (SI–36), and the corresponding supersaturation is

$$S(t) \simeq 1 + \sqrt{\frac{2\lambda}{vt}} \tag{SI–38}$$

A particular consequence of Eq. (SI–37) is that the most probable radius $R_{mp}$ increases as

$$R_{mp} \simeq \sqrt{\lambda v t/2} \tag{SI–39}$$

## III. CALCULATION OF THE SUPERSATURATION FOR CONFINED PARTICLES

The supersaturation $S$ is a central quantity that controls the growth of the nanoparticles through Eq. (SI–25). Evaluating it through its thermodynamic definition in Eq. (SI–12) would be very cumbersome, and it would also require one to make specific assumptions about the form under which the molecules are present in the system (*e.g.* adsorbed or gaseous).

In the case of free molecules, with no mechanical interaction with the support ($\Gamma = 1$), the supersaturation can be evaluated by expressing that the total number of atoms in the nanoparticles is a constant, *i.e.*

$$\sum_{i=1}^{N} 4\pi R_i^2 \frac{dR_i}{dt} = 0 \tag{SI–40}$$

where the sum is over all the particles. Based on Eq. (SI–25) this leads to the following expression

$$S(t) = \sum_{i=1}^{N} R_i(t)^2 \exp\left[\frac{\lambda}{R_i(t)}\right] / \sum_{i=1}^{N} R_i(t)^2 \tag{SI–41}$$

That enables to calculate $S$ at any given times, starting from the sizes of all existing particles in the system.

The situation is slightly more involved in the case of particles interacting mechanically with a solid support with pore radius $R_p$, possibly undergoing plastic deformation. The conditions for a particle to grow or shrink are discussed in the main text. In terms of radius evolution this can be summarised as follows

$$\frac{dR}{dt} = \begin{cases} v\Big\{S - \exp\left[\frac{\lambda}{R}\right]\Big\} & \text{for} \quad R \leq R_1 \\ 0 & \text{for} \quad R_1 \leq R \leq R_2 \\ v\Big\{S - \Gamma_y \exp\left[\frac{\lambda}{R}\right]\Big\} & \text{for} \quad R_2 \leq R \end{cases} \tag{SI–42}$$

where $R_1$ and $R_2$ are the following saturation-dependent quantities

$$R_1(S) = \max\left\{R_p, \frac{\lambda}{\ln(S)}\right\} \tag{SI–43}$$

and

$$R_2(S) = \max\left\{R_p, \frac{\lambda}{\ln(S/\Gamma_y)}\right\} \tag{SI–44}$$

The overall structure of the $R - S$ space is sketched in Fig. SI–1.

For any collection of particles, the supersaturation $S$ is calculated by imposing that the evolution described by Eq. (SI–42) preserves the total volume of the particles, namely $\sum R^2 dR/dt = 0$. This can be written as

$$S\left(\sum_{R<R_1(S)} R^2 + \sum_{R>R_2(S)} R^2\right) - \sum_{R<R_1(S)} R^2 \exp(\lambda/R) - \Gamma \sum_{R>R_2(S)} R^2 \exp(\lambda/R) = 0 \tag{SI–45}$$

which, unlike Eq. (SI–41), is not explicit in $S$. Starting from the radii $R_i$, the supersaturation can only be calculated numerically because the radii $R_1$ and $R_2$ appear in the limits of the sums. This can be done sequentially using a binary search, by noting that the solution of Eq. (SI–45) has the following lower and upper bounds, respectively

$$S_{lb} = \sum_{i=1}^{N} R_i^2 \exp[\lambda/R_i] / \sum_{i=1}^{N} R_i^2 \tag{SI–46}$$

and

$$S_{ub} = \Gamma_y \sum_{i=1}^{N} R_i^2 \exp[\lambda/R_i] / \sum_{i=1}^{N} R_i^2 \tag{SI–47}$$

The lower bound is the value of $S$ if no nanoparticle is compressed, and the the upper bound is the value if all nanoparticles were compressed exactly by the yield pressure $P_y$. To find a numerical solution to Eq. (SI–45), the

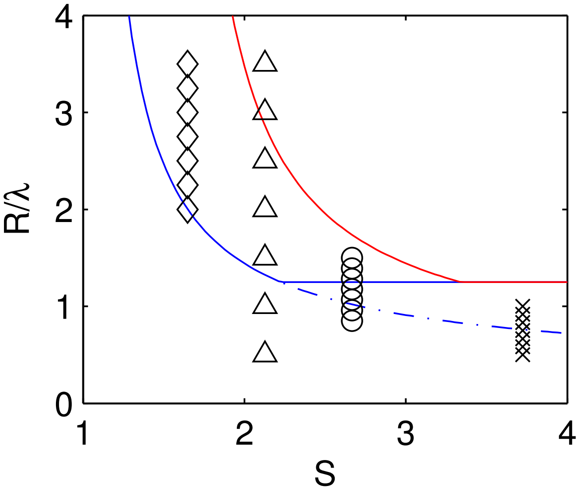

FIG. SI–1. Regions of the $R - S$ space displaying the radii $R_1$ (solid blue) and $R_2$ (solid red) defined in Eqs (SI–43) and (SI–44), in the particular case $R_p = 1.25 \times \lambda$ and $\Gamma = 1.5$. The dashed blue line is $R = \lambda / \ln(S)$, which is the critical size between growing and shrinking for nanoparticles smaller than the pores. Four groups of seven particles with various radii ($\times$, $\circ$, $\Delta$, $\diamond$) are shown together with the corresponding supersaturation calculated following Eq. (SI–45).

bounds are updated sequentially. At each step, either the upper or the lower bound is replaced by the middle value $S_m = (S_{ub} + S_{lb})/2$ depending on whether the left-hand side of Eq. (SI–45) is positive or negative. Because the interval is reduced by a factor of two at each step, about ten iterations are sufficient to reach a numerical accuracy on $S$ of the order of $2^{-10} \simeq 0.1\%$.

The values of $S$ corresponding to four different groups of nanoparticles are shown in Fig. SI–1. If all the particles are smaller than the pores (particles $\times$), then the saturation is given exactly by Eq. (SI–46). In the case of particles $\circ$, the particles larger than the pores fall in the region between $R_1$ and $R_2$, so that their neither grow nor shrink. In the case of particles $\diamond$, all particles are in that situation so that the system does not evolve. Finally, particles $\Delta$ extend over a wide range of radii. The largest two particles are growing larger than the pores, which growth is fed by the smallest two particles. The middle-sized particles neither grow nor shrink.

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[1] I. Chorkendorff and J. W. Niemantsverdriet, *Concepts of Modern Catalysis and Kinetics* (Wiley, 2005).