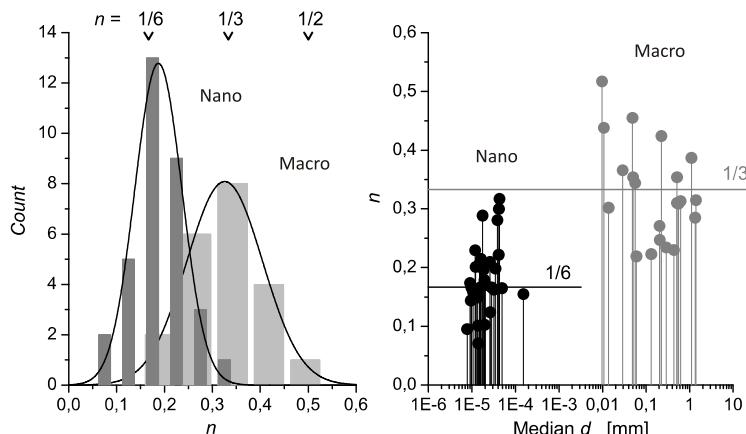


# Failure of Fick's Law at the Nanoscale - an Overlooked Major Nanoeffect

- Previously we demonstrated how a simple classical atomistic view of solid state transformations may prove fruitful for the rationalization of hitherto unexplained nanoeffects (even non-marginal ones). [1]
- Now, adopting a similar view, we shall show that at the nanoscale, the rate at which solid state transformations proceed may be profoundly influenced by a failure of Fick's law. [2]
- We propose that at the nanoscale Fick's 1st law fails because solid state diffusion ceases to be a collective atomistic phenomenon marked by concentration gradients.
- Instead, diffusion at the nanoscale reduces to a discrete process of single-atom random walks at uniform concentration.
- The key factor is that in nanosystems, due to the low reaction temperature and, therefore, low concentration of diffusing species (atoms), the average distance between the latter is larger than that between sources and sinks.

## ● Fick's Law - a Problem:

- Diffusion is a stochastical process - a swarm of atoms swirling around randomly.
- Consider an imaginary plane of area A and (small) thickness  $dx$  anywhere inside this swarm: the randomly moving atoms on the left will occasionally pass through the plane, and so will those on the right.
- If there is a difference in concentration  $dC$  - higher on the right, say - atoms will more often pass from right to left by chance than the other way round: a net mass current  $dm/dt$  (mass  $m$  per time  $t$ ) from right to left results.
- This statistics of swarming atoms is captured by Fick's 1st law of diffusion (with diffusion constant  $D$ ):  
$$dm/dt = D A dC/dx.$$
- Even if the concentration (or pressure in a gas) is very low so that atoms hardly ever collide this mass flow obtains.
- But what if the concentration is so low that at any instant there is only a single atom left in the whole available volume, both left and right?
- Then we have to take into consideration the sources and sinks where atoms emerge or disappear.
- The net mass current is now proportional to the difference in the effective rate of release of atoms (formerly the concentration  $C$ ) between the different sites.
- Every atom released takes a random walk and thus may either return to the source by chance or may find its way to another sink.
- But no longer can concentration gradients build up - the average concentration of diffusing species (atoms) is the same everywhere.
- Thus Fick's law does not govern diffusion any more!
- And this is exactly what happens, we believe, at the nanoscale.
- Why? Because at the nanoscale - due to the higher concentration of sinks and sources and correspondingly shorter paths between them, and the much smaller amounts of substance (volumes) transported - moderate thermal activation at a relatively low temperature is enough to induce sufficient mass flow leading to observable change.
- If one wished to enforce the same scenario at the macroscale a much higher temperature would be required so as to raise the diffusion constant  $D$  (which figures in random walks too, see below) in order for the transport of the enormously increased volume (which scales with the third power of the linear dimension) - over even longer distances - to be accomplishable by discreet random walks at low average concentration  $C$ .
- However, just like  $D$ , the concentration  $C$  of diffusing species (atoms) increases exponentially with the temperature - hence, as the temperature goes up, the average separation of diffusing atoms must dwindle and, therefore, it is not possible to make it larger than that of sources and sinks at the macroscale.



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## ● Grain Growth - a Prediction:

- A polycrystal - or any other ensemble of crystallites, no matter whether macro- or nanoscopic - subject to spontaneous (thermally induced) grain growth maintains what is known as statistical selfsimilarity SSS.
- At the nanoscale this SSS applies even to how many sites (atomic kinks or steps which may act as sources or sinks) each crystallite carries, viz. typically one per each facette as previously shown. [1]
- Hence the average distance between sources and sinks scales linearly with the average grain diameter  $d$  and is of comparable magnitude.
- Given a stochastic configuration of sinks and sources, the time it takes to transfer a given amount of substance from one site to another (assuming a constant rate of release at each source) will be proportional to the distance squared.
- This is so because the mean square displacement  $\langle x^2 \rangle$  of every atom taking a random walk scales with the time according to Einstein and Smoluchowski as  $2Dt$  ( $D$ , again, is the diffusion constant).
- Thus, the time needed to transfer a given amount of substance between sites will be proportional to  $d^2$ , the average grain diameter squared. (I)
- The amount of substance which has to be transported in order to accomplish a certain selfsimilar transformation during grain growth - at a particular stage characterized by the average value of  $d$  - scales as  $d^3$ , the third power of the grain diameter, a measure of the volume. (II)
- The difference in the rate of release of atoms from different sites scales as  $1/d$ , the reciprocal grain diameter, due to surface energy (Gibbs-Thomson relation), i.e. the time needed to set free a given amount of substance (number of atoms) is proportional to  $d$ . (III)
- Now, from these three relationships (I-III) we predict that the time it takes to accomplish a certain selfsimilar transformation, say doubling the average diameter  $d$ , will scale as  $d^2$  times  $d^3$  times  $d$ , or  $d^5$ , the average grain diameter to the sixth power - conversely, the proportionality  $d \sim t^n$ , where  $n = 1/6$ , will hold.
- The above reasoning constitutes, in fact, an adaptation of Herring's scaling laws of diffusion - which epitomize Fick's 1st law - to the specific nanoscale conditions, thus underpinning the failure of Fick's law at the nanoscale, for at the macroscale (where Fick's law holds) Herring's laws predict  $n = 1/3$  in stark contrast to the above value of  $1/6$ .
- It is of utmost importance that all the above arguments - just like Herring's original set of laws - apply irrespective of which microscopic mechanisms may be responsible for the solid state transformations considered.
- This is so because these laws are universal scaling relationships based merely on a dimensional analysis (like I-III above) of diffusion.
- It can be shown that such diverse processes as Ostwald ripening in solution, growth by rotation and coalescence, soap froth coarsening and colloidal agglomeration are all in agreement with these laws.
- For this reason the conclusion that Fick's law fails at the nanoscale gains in confidence since it is thus independent of the microscopic details of the experiments from which data are taken.

## ● The Literature - Unmistakable Clues:

- A vast literature exists reporting quantitative results of grain growth experiments both at the macroscale and at the nanoscale.
- For more than a half century now, every two decades or so one or the other investigator would compile and then try to evaluate the reported grain growth exponents  $n$ .
- The reported values of  $n$ , however, are inconsistent partly because every experimentalist has his own way of dealing with the measured data and partly because of the inherent statistical variability of the latter.
- For these reasons we have reevaluated in a uniform way a large amount of virgin raw data digitized from the literature together with results from our own grain growth experiments.
- Both metals/intermetallics (16 different systems) and oxides/mixed oxides (10 different systems) have been considered in our compilation of the experimental values of  $n$ .
- This reappraisal has afforded two important insights:  $n$  is equal to  $1/3$  ( $0.33^\circ/0.02$ ) at the macroscale (contrary to common textbook wisdom according to which  $n = 1/2$ ), and it is indeed quite close to  $1/6$  ( $0.18^\circ/0.01$ ) at the nanoscale, which convincingly confirms the postulated failure of Fick's 1st law.

[For a masterplot of all the data reevaluated in the present study (159 isotherms/1248 data points) see: *Book of Abstracts, ISRS-19, International Symposium on the Reactivity of Solids*, Universität Bayreuth, July 15-18, 2018, Bayreuth, Germany, page P 28.]

*Left:* Unmistakable clues from the literature and our laboratory - 152 isotherms (comprising 1234 data points) of 26 oxides, intermetallics and elements yield statistically reliable (Gaussian) mean values of the grain growth exponent  $n$  confirming the failure of Fick's law at the nanoscale.

## ● References:

- [1] M. Petrik, B. Harbrecht, *ChemPhysChem* **2013**, *14*, 2403-2406.
- [2] M. Petrik, B. Harbrecht, *to be submitted, 2018*.