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What environmental transmission electron microscopy measures and how this links to diffusivity: thermodynamics vs. kinetics

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Introduction to environmental transmission electron microscopy

Environmental or *in-situ* electron microscopy means the observation of material in its native environment, which can comprise pressurised gases or liquids, as compared to more traditional *post-mortem* electron microscopy carried out under (ultra) high vacuum conditions. The idea for this is now 70 years old (Abrams and McBain 1944).

For the observation of bulk material in its native environment so-called environmental scanning electron microscopes (E-SEMs) have been developed in which those components where the electron beam is generated and accelerated and that therefore need to retain ultra-high vacuum, are physically separated from the specimen in the main chamber by a series of diaphragms attached to which are various vacuum pumps to achieve efficient differential pumping. Very good overviews of instrumental aspects of E-SEMs have been provided by one its inventors (Danilatos 1988) and of more recent applications of E-SEMs by Donald (2003).

For observation in transmission electron microscopes the situation is even more complicated as the specimen needs to be thinned and held within that gaseous or liquid environment, all of which needs to be placed within the narrow immersion pole piece of the objective lens to retain high resolution. For reactive gas atmospheres, multiple differential pumping around the objective lens can be applied as well, but for observations in liquids special environmental cells need to be used miniaturised versions of which can now be incorporated directly into the specimen holder (Williams *et al.* 2003), which as a result has become increasingly more complex and difficult to handle. Over the decades the resolution has been gradually improved from 100nm at 20kV (Swift and Brown 1970) to 0.23nm at 300kV (Boyes and Gai 1997) and finally to <0.2nm @200kV (Gai and Boyes 2009) with planar illumination, and most recently, to 0.11nm with raster scanning focused illumination, i.e. scanning transmission electron microscopy (STEM) (Boyes *et al.* 2013). The latter now allows the user to observe single atoms at elevated temperatures and/or in gaseous atmospheres.

The beauty of observing, in real time and in-situ, nano-particles, clusters or even single atoms move, either on the surfaces of thinned material or within a liquid environment, is compelling – but how can we extract physically meaningful numbers from such observations to obtain measurements of real physical parameters?

Strictly speaking, every electron microscopy experiment, by definition, subjects the specimen to irradiation by fast electrons and could thus be considered an *in-situ* experiment on radiation damage, and a microscopist should be aware of beam damage potentially influencing the results of any measurements, even if the damage itself may not be apparent visually: atoms may diffuse and dislocations can move under the influence of the electron beam. Whether or not the result obtained is actually influenced by electron beam damage depends on the material as well as the illumination conditions; and of course the same is true

for *any* form of radiation, whether by electrons, ions, X-rays or visible light: if fluence or dose are too high, any specimen can be damaged.

Solid-state diffusion and segregation measurements

In bulk diffusion experiments, as they are typically conducted in solid state physics laboratories, a solid specimen with some initial planar irregularity (such as an interface, a grain boundary, a free surface etc.) is investigated after anneal at different elevated temperatures for defined durations, and various experimental methods can be used to measure concentration profiles across those interfaces or surfaces. These compositional profiles can then be fitted by models based on the fundamental laws of diffusion (see e.g., Mehrer and Stolwijk 2009). Typical Arrhenius plots are often applied to derive the activation energy for interdiffusion in the bulk (Arrhenius 1889),

$$E_{act, bulk} = E_{bulk,max} - E_{bulk,min} \quad \text{(eqn. 1),}$$

or for diffusion from the surface into the bulk,

$$E_{act,sur} = E_{sur,max} - E_{sur,min}. \quad \text{(eqn. 2),}$$

where the energies have their meanings as sketched in figure 1. Such work relies on the fact that the energy imparted onto the diffusing atomic species by annealing is typically only a few $k_B T$ where k_B denotes the Boltzmann constant and T the absolute temperature. Note that, usually, $k_b T$ is of the order of a few 10meV and therefore $\ll E_{act}$. This is certainly valid up to $T \leq 1000°C$, for which $k_B T \leq 0.11$eV. In summary, ***diffusion experiments measure activation energies which are the energetic barriers to be overcome during atomic movement*** (hence, our indices refer to minima in the band structure; $E_{x,max} - E_{x,min}$, where x=bulk or surface). It should be added that a comparison of the compositional profiles of differently annealed

specimens by analytical transmission electron microscopy of cross-sectioned specimens can also yield the activation energies for bulk interdiffusion if the electron dose is low enough not to promote excessive nucleation of interstitials or surface diffusion (Walther *et al.* 1997).

Materials segregation, on the other hand, describes the local enrichment of an atomic constituent at either an internal interface (Mc Lean 1957) or at a free surface (Wynblatt and Ku 1979) and, for a simple binary system it can be explained by the contribution of the configurational entropy of the arrangement of atoms in the bulk and the surface or interface to the total free energy of the system.
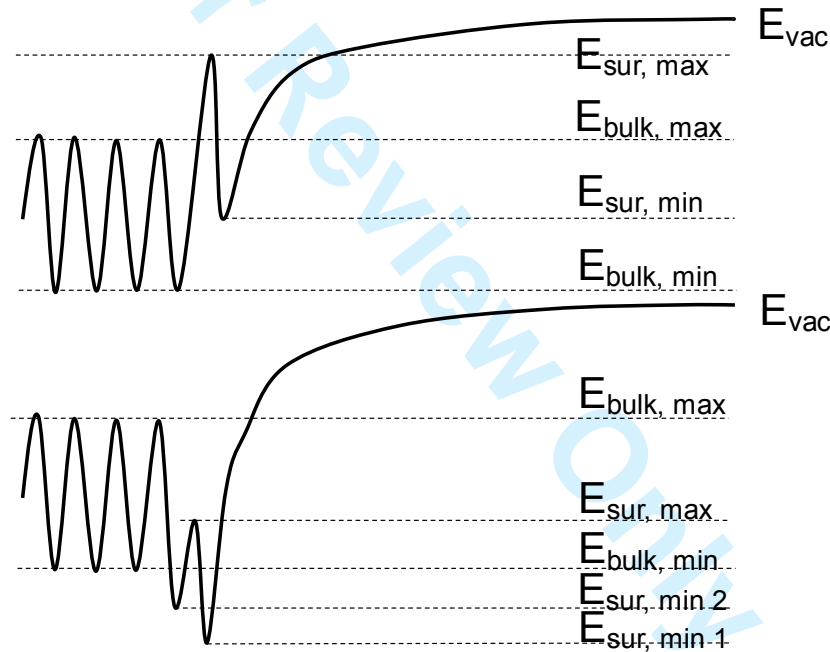
Figure 1: sketch of energies in a bulk crystal (left) and on its surface, relative to the vacuum (right) for the cases of energetically unfavourable surface states (top) and two favourable surface states that lead to surface segregation (bottom).

If we consider the periodic lattice of a bulk crystal, as in the left part of figure 1, then according to Bloch's law the spatial periodicity of the crystal lattice imparts a periodic energy

distribution, where the atoms sit in local minima, separated by maxima, and both these energy levels in the bulk, denoted by $E_{bulk,min}$ and $E_{bulk,max}$ in figure 1, are well below the energy level of the vacuum, E_{vac}.

Surface states in this model can exist either on an elevated level $E_{sur,min}$, between the bulk and the vacuum levels, which means they are thermodynamically less stable than the bulk (meta-stable by comparison), as sketched in the top part of figure 1, or below the minima in the bulk. The latter situation is sketched in the lower part of figure 1 for two such surface states with corresponding energies $E_{sur,min1}$ and $E_{sur,min2} > E_{sur,min1}$. In this case the surface states are energetically more favourable than the bulk states and atoms experience a driving force to occupy them. This is the basic physical model of surface segregation usually applied to describe atomic segregation during epitaxial crystal growth where the surface of the growth front advances with time and atoms that were formerly embedded in the bulk tend to re-emerge at the surface despite continuous coverage by other atoms. From the persistence of those surface states during growth, segregation ratios or segregation lengths can be calculated from chemical analysis of the time evolution of the surface coverage by the corresponding types of atoms and fitting the near-exponential decays. This is conventionally achieved best by employing surface sensitive chemical techniques, such as Auger electron spectroscopy (Wynblatt and Ku 1977), secondary ion mass spectrometry (Muraki *et al.* 1992) or X-ray photo-electron spectroscopy (Moison *et al.* 1989), but again, it can also be achieved by analytical transmission electron microscopy (Walther, Richards and Bastiman 2014). It should be pointed out that at low temperatures, segregation can be kinetically inhibited rather than in thermodynamic equilibrium (Fukatsu *et al.* 1991). Segregation ratios are linked to the ratios of probabilities for atoms swapping bulk and surface sites. These hence allow us to determine segregation energies which are the energetic differences between these meta(stable) states:

$$E_{seg}=E_{bulk,min}-E_{sur,min} \quad \text{(eqn. 3)},$$

We note that ***segregation energies describe differences in energy between two adjacent minima***, and for the case sketched in the lower part of figure 1,

$$E_{seg,2}=E_{bulk,min}-E_{sur,min2} \qquad \text{(eqn. 4)},$$

for the sub-surface and

$$E_{seg,1}=E_{sur,min2}-E_{sur,min1} \qquad \text{(eqn. 5)}$$

for the top surface monolayer. Surface segregation energies can also be calculated using atomic potential models (Ruban, Skriver and Norskov 1999).

If the probability for forward-jumps from the bulk to the surface can be fitted by a model, also the activation energy

$$E_{act,sur2}=E_{sur,max}-E_{sur,min2} \qquad \text{(eqn. 6)},$$

can be determined. For such measurements of activation or segregation energies, different techniques can be used, and indeed quantitative analytical TEM of samples either annealed at different temperatures or deposited under well-defined conditions has been successfully used to measure these quantities (Walther *et al.* 2013).

In summary, *post-mortem* TEM can be used, just like other analytical techniques but with the additional benefit of high spatial resolution, to measure parameters such as activation energies for interdiffusion and segregation energies. The only prerequisite is that it must be verified that free surface effects (i.e. diffusion *on* the specimen surface during the TEM experiment as opposed to *within* the specimen before the experiment) and radiation damage are negligible. This can be ensured by carefully comparing results from thinner and thicker specimen regions (which should be identical) or by repeating the measurements on the same

area (which should give identical results if the specimen has not been altered during examination).

The situation may perhaps be compared to determining the density of a piece of cardboard by tapping it with increasing intensity and recording its mechanical response function, which works well as long as the cardboard is not altered mechanically by the treatment (no holes, no cracks, no significant indentation).

While figure 1 obviously refers to a free surface, i.e. a crystal / vacuum interface, the situation for a crystal / liquid interface is not significantly different on the atomic scale, only with a stronger interaction, as larger densities lead to higher collision rates and thus higher reaction speed. Depending on the material system, energetic barriers may indeed change more gradually, leading to wider interfaces, and faster local atomic rearrangements may roughen the surfaces and make processes much more complicated, but the principles outlined above still apply.

Activation energies can be measured by electron microscopy as long as it can be verified that the specimen is not altered during the experiment, ideally by repeating the measurement in the same area, or another one of different specimen thickness, with (hopefully) the same result.

Energetics in environmental transmission electron microscopy

(i)   Thermodynamic considerations

Environmental TEM measurements differ significantly from the above considerations in that the specimen is now surrounded by a gas or liquid. These atoms are not bonded to a crystal and therefore have high kinetic but lower potential energy. The additional energy of the transmitted electron beam may be high enough to trigger atomic knock-on processes by occasional near head-on collisions with atoms, which can transfer >10 eV energy to an atom in the specimen and therefore knock it off its lattice site (Egerton 2012). While the corresponding scattering cross-sections are small and these processes hence rare, even occasional knock-on processes accumulated over time can mean significant material loss from the specimen (preferential thinning of thin foils, shrinking of nano-particles, hole drilling in thicker specimens). This is usually described as radiation damage and is not due to heating, which remains negligible under most circumstances (Egerton, Li and Malac 2004). For the above application this means that activation energies for interdiffusion or segregation can no longer be measured if the specimen is altered by irradiation because the fundamental assumption that atoms need to gather thermal energy to overcome an energetic barrier has become invalid. Instead, some atoms may gather sufficient energy to move almost anywhere, i.e. they will be in energetic states near E_{vac}, potentially retaining a lot of additional kinetic energy as well. Where they will end up (if not lost entirely from the system) will depend on their diffusion within the environmental cell and on their rate of re-attachment, usually to the surface, of the specimen, along with other atoms from the gas or liquid environment. This can be monitored *in-situ* as formation and growth of new features on the specimen surfaces. At the same time, this desired change of the specimen prevents the microscopist from being able to rule out that irradiation has actually significantly influenced the observation made.

If there were, for example, only two different surface states of energies $E_{sur,min1}$ and $E_{sur,min2}$, which do not have to lie on top of each other as sketched in figure 1 but could, for instance, represent symmetrically in-equivalent positions within the same surface monolayer (e.g., kink positions vs. free ad-atom positions), or be related to different crystal facets all together, then the rate of re-attachment to each different surface state j, which could be measured experimentally, would be related to a combination of geometric and energetic effects, where the energetically lower state is more favourable and will populate faster if the atoms land on the surface without too much excess kinetic energy. So it should be possible, in principle, to determine which of the two energies $E_{sur,min,j}$, $j=1,2$ is the lower. Whether their energetic difference, expressed in equation (5) can be calculated, remains unclear as long as geometrical constraints (such as steric hindrance to access specific sites, different exposure of facets to the direction of gas/liquid flow etc.) are not quantified and accounted for in detail.

In the above cardboard analogy, our test object has become more fragile and at the same time we are now hitting it hard enough that it partially fragments. The reason for the same intensity of tapping leading to two different types of responses lies in the different boundary conditions: while the piece of cardboard in the first (*post-mortem*) study was rather thick and well clamped in the holder, it is now (*in-situ*) loosely contained within a gas or liquid filled bag and its thinnest parts will quickly disintegrate if touched.

(ii)   Kinetic considerations

If the *thermodynamic* situation is so different, can we at least learn something about growth *kinetics*? This will depend on the degree to which the growth conditions within the environmental cell resemble those typically used in bench-top or clean-room based laboratory experiments in terms of temperature, gas pressure, purity of the gases or liquids used and the flow rates. One major concern will always be that the electron beam can ionise organic matter

easily, and so the gas or liquid in the liquid cell may alter upon electron irradiation significantly by radiolysis, thereby changing its chemical properties and hence the reaction rates observed.

While only a *minority* of atoms take part in diffusion or segregation processes so that transferring high energies to a small sub-set of atoms can be sufficient to invalidate any measurements, phenomena that a *majority* of atoms participate in, such as nucleation of clusters of critical sizes (Abraham 1974) and successive Ostwald ripening of particles (Kalhweit 1975), will be influenced to a far lesser degree by a small fraction of atoms involved in the processes getting some extra energy from the irradiation process. Hence, there probably is still the chance to learn a lot about the kinetics of such processes, while thermodynamic parameters are less accessible. This should be no surprise as nucleation and growth by definition are not thermodynamic equilibrium processes.

Conclusion

Environmental (*in-situ*) TEM and classical (*post-mortem*) analytical TEM measure complementary phenomena. While in the latter the specimen is in (near) equilibrium and hence thermodynamic parameters such as diffusion or segregation energies can be determined (as long as the influence of free specimen surfaces is ruled out or kept minimal), environmental TEM observes a specimen far away from equilibrium and therefore can measure kinetic parameters such as nucleation and growth rates and can attempt to determine the underlying mechanisms. The experimental conditions need to be carefully controlled to be scalable to growth conditions typically employed in growth chambers for molecular beam, chemical vapour phase or liquid phase epitaxy.
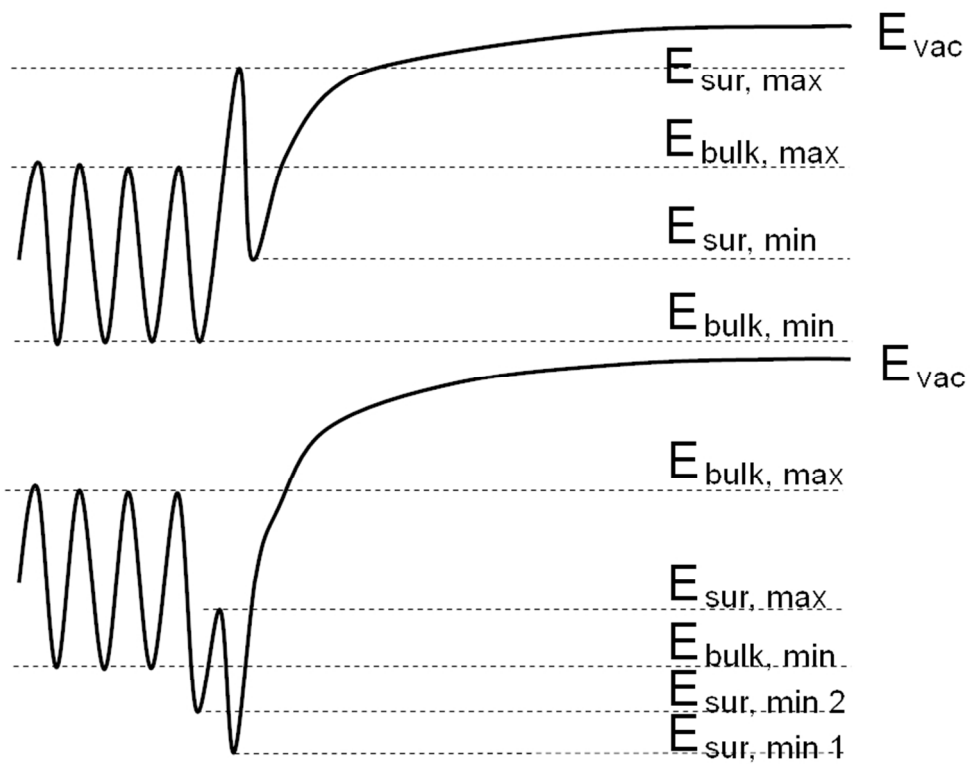
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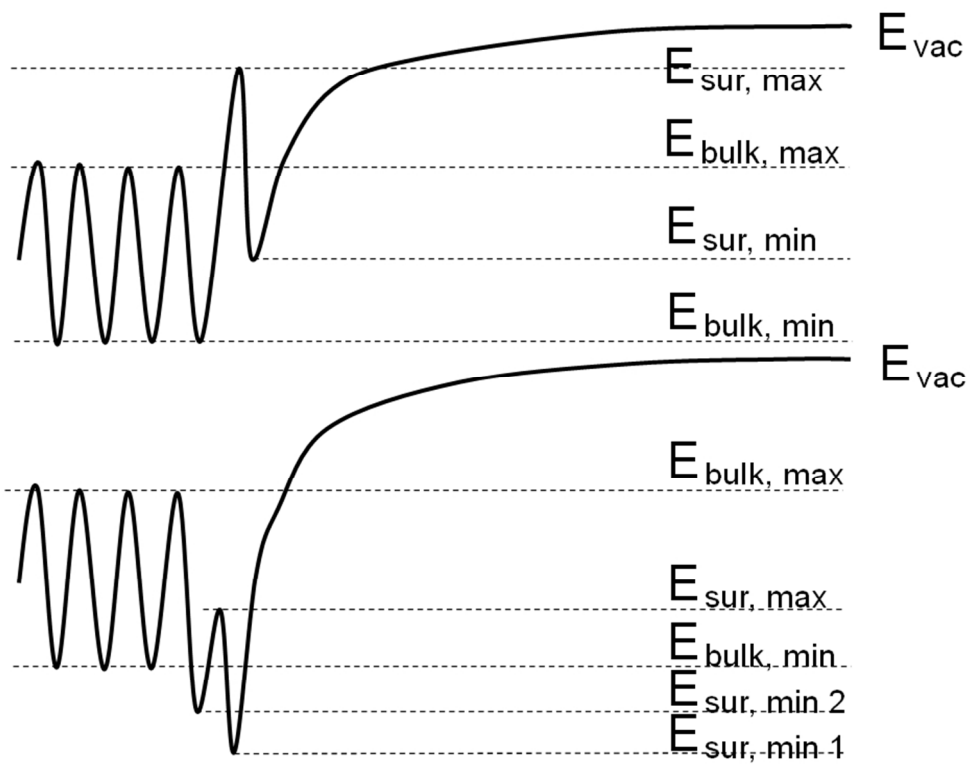
sketch of energies in a bulk crystal (left) and on its surface, relative to the vacuum (right) for the cases of energetically unfavourable surface states (top) and two favourable surface states that lead to surface segregation (bottom).
338x273mm (72 x 72 DPI)

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