On the importance of nanoscale thermodynamic effects in plasma catalysis

E. C. Neyts

1 Research group PLASMANT, Department of Chemistry, University of Antwerp, 2610 Antwerpen-Wilrijk, Belgium

Abstract: Plasma catalysis is envisaged as an efficient method for improved gas stream processing, e.g., in VOC abatement, conversion of greenhouse gases or plasma-assisted deposition of materials. In this contribution, I highlight two nanoscale thermodynamic phenomena of importance for plasma catalytic processes, viz. the Gibbs-Thomson effect and dynamic phase coexistence.

Keywords: plasma catalysis, nanoscale thermodynamics, phase state

1. Introduction

Plasma catalysis is a rapidly emerging field in contemporary science, bridging diverse disciplines such as physical chemistry, materials science, nanoscience and computational chemistry, and can be defined as the acceleration of chemical reactions, enhanced by the synergistic combination of low-temperature plasmas and catalysts with nanoscale structure or features. These reactions are common in plasma- and catalyst-assisted reforming of precursor gases in, for instance, hydrocarbon reforming and nanostructure synthesis such as carbon nanotube growth [1, 2].

Low-temperature plasmas enable a manifold of reactions due to their combination of inherent reactivity, far-from-equilibrium state and low-temperature operation. They typically provide a set of reactants to the catalyst substrate, different from the set of reactants in thermal catalysis. Moreover, the plasma is known to affect many of the catalyst properties, including its workfunction, morphology, oxidation state and other properties. A recent review on these effects can be found in ref. [3].

While catalysts are oftentimes pictured as ideal single-crystal atomically flat surfaces, experimental observations have revealed that any real-life catalyst shows a typically complex nanostructured surface morphology. Deliberate use of these nanofeatures in catalysis – sometimes called “nanocatalysis” – has opened up new avenues towards improved synthesis strategies and processing thanks to the size-dependent catalytic properties of the nanocatalysts involved.

The combination of and the controlled interplay between plasma and nanocatalysts, however, is a relatively new and emerging field of science, holding promise for improved process control, selectivity and/or efficiency. One aspect, however, of such processes that is often overlooked, is the importance of nanoscale thermodynamics. We here highlight two important nanoscale thermodynamic phenomena, viz. the Gibbs-Thomson effect and dynamic phase coexistence.

2. Nanoscale thermodynamic aspects

At the microscopic level, the catalytic process may be divided in three steps:

1) arrival and binding (i.e., physisorption and chemisorption) of the reactants to the catalyst surface;
2) physico-chemical surface processes such as physical diffusion and chemical reactions; and
3) desorption of the catalytic reaction products into the gas phase.

Thermodynamics are crucial in each of these steps. As a chemical reaction approaches its equilibrium for a given set of reaction conditions, the reaction rate will drop accordingly. A complete description of the catalytic process therefore requires considering thermodynamics next to the kinetics of the process.

Classical thermodynamics deal with macroscopic systems under equilibrium conditions where time is not a parameter. Plasma catalysis, however, is typically a far-from-equilibrium process, where large fluxes of energy and matter are continuously delivered to the catalyst. The thermodynamic complexity of plasma nanocatalysis is further increased by the nanometre length scale of the system. Here we focus on two nanoscale thermodynamic aspects very relevant to plasma catalysis: the Gibbs-Thomson effect and temporal dynamic coexistence. Note, however, that other aspects are equally important, including the breakdown of the Gibbs-Duhem equation at the nanoscale, non-extensivity of state functions in nanoscale systems, the dependence of the chemisorption energy on the catalyst size in the nanoregime, and the non-equilibrium nature of plasma catalytic processes. A more thorough description of these effects can e.g., be found in [4].

2.1. Gibbs-Thomson effect

The Gibbs-Thomson effect expresses the change in melting temperature as a function of size:

$$\Delta T_m(d) = T_{m,bulk} \frac{4\sigma_{sl}}{H_f \rho_s d}$$

where $\Delta T_m(d)$ is the decrease in melting temperature for a nanocluster of diameter $d$, $T_{m,bulk}$ is the melting point of the bulk material, $\sigma_{sl}$ is the solid-liquid interface energy, $H_f$ is the bulk heat of fusion, and $\rho_s$ is the solid mass...
density. Note that in this expression the interface energy \( \sigma_{\text{sl}} \) is assumed to be isotropic, and the bulk heat of fusion \( H_f \) and the solid mass density \( \rho_s \) are assumed to retain their bulk values at the nanoscale.

The origin of the Gibbs-Thomson effect lies in the large surface-to-volume ratio of nanoparticles, and hence the under-coordination of the surface atoms. As under-coordinated atoms require less energy (heat) to be displaced from their lattice positions, atoms at the surface of the nanocluster become mobile at a reduced temperature.

The importance of the Gibbs-Thomson effect in catalysis and plasma catalysis lies in the associated size- and temperature dependent phase states. Indeed, catalytic processes are often conducted at quite high temperatures. Under such conditions the surface of the nanocatalyst particles may be in a liquid state. This effect is thus very important in any process where the chemical reaction proceeds on a surface of a nanoparticle at elevated temperatures. Non-exhaustive examples include catalysed carbon nanotube growth, ammonia synthesis on nanometre-sized Ru-crystals, Fischer-Tropsch synthesis of hydrocarbons, and many more heterogeneous catalytic processes.

Moreover, not only is the melting point of the nanocluster typically lower than the bulk melting point, nanoclusters also typically show a melting interval rather than a melting point. Indeed, while in a bulk material the derivative of the free energy with respect to temperature shows a discontinuity at the melting point, there is no such discontinuity at the nanoscale. Indeed, due to fluctuations inherent to the nanoscale (see below), phases may coexist over a range of temperatures and pressures, instead of coexistence along sharp lines or points. The Gibbs phase rule is thus not applicable to nanoscale systems, and many phase-like forms may occur that are unobservable in macroscale systems.

2.2. Dynamic coexistence

Bulk systems often demonstrate regions in their phase diagram where liquid and solid states coexist. At the nanoscale, however, such spatial coexistence is (at least below a certain system size) not possible, due to the inherent fluctuations in nanoscale systems. At a given time-averaged temperature, however, a nanocluster may adopt different physical states as a function of time, if at least kinetically permitted. This kinetic condition is typically fulfilled for the solid-liquid phase transition, but is often not for solid-solid phase transitions. Recently, Engelmann et al. [5] proposed assigning an equilibrium constant to this phenomenon

\[
K = \frac{t_{\text{liq}}}{t_{\text{sol}}}
\]

where \( t_{\text{liq}} \) is the time the cluster spends in the liquid state and \( t_{\text{sol}} \) is the time the cluster spends in the solid state, in accordance with classical bulk thermodynamics. Under isobaric conditions, it follows that [5]:

\[
K = \frac{\Delta H}{\Delta f_H - \Delta H} = \frac{\Delta H}{T} = \frac{T \Delta f_H}{\Delta H}
\]

where \( \Delta H \) is the enthalpy of fusion (i.e., the enthalpy change due to complete melting, where the cluster is always liquid) and \( \Delta f_H \) is the enthalpy change due to partial melting (i.e., when the cluster is fluctuating between the solid state and the liquid state). Note, however, that the cluster is in thermal equilibrium and that this fluctuation therefore does not imply an out-of-equilibrium state. Rather, the observed fluctuation in phase state is an emanation of the intrinsic thermal fluctuations in the system made possible by the nanoscale size of the system.

3. Conclusions

We described the importance of two fundamentally phenomena in the thermodynamics of nanoscale systems, which are of particular importance for plasma catalysis: the Gibbs-Thomson effect, describing the depression of the melting point of a nanocatalyst as a function of size, and dynamic coexistence, describing the fluctuation of the phase state of the catalyst nanoparticles at temperatures typically used in plasma catalytic processes. These phenomena determine the morphology and presence of active sites on the catalyst surface as a function of the catalyst size, and hence co-determine the activity of the catalyst.

4. Acknowledgments

This research was carried out in the framework of the network on Physical Chemistry of Plasma-Surface Interactions - Interuniversity Attraction Poles, phase VII (http://psi-iap7.ulb.ac.be/), and supported by the Belgian Science Policy Office (BELSPO).

5. References