



# Nanoscale thermodynamic aspects of plasma catalysis



Erik C. Neyts<sup>a,\*</sup>, Kostya (Ken) Ostrikov<sup>b,c</sup>

<sup>a</sup> University of Antwerp, Department of Chemistry, Research Group PLASMANT, Universiteitsplein 1, 2610 Wilrijk-Antwerp, Belgium

<sup>b</sup> Institute for Future Environments and School of Chemistry, Physics, and Mechanical Engineering, Queensland University of Technology, Brisbane, QLD 4000, Australia

<sup>c</sup> Plasma Nanoscience Laboratories, Industrial Innovation Program, Manufacturing Flagship, CSIRO, P.O. Box 218, Lindfield, NSW 2070, Australia

## ARTICLE INFO

### Article history:

Received 30 December 2014

Received in revised form 7 February 2015

Accepted 10 February 2015

Available online 18 March 2015

### Keywords:

Plasma catalysis

Nanoscale thermodynamics

Nanocatalyst

## ABSTRACT

Plasma catalysis continues to gain increasing scientific interest, both in established fields like toxic waste abatement and emerging fields like greenhouse gas conversion into value-added chemicals. Attention is typically focused on the obtained conversion process selectivity, rates and energy efficiency. Much less attention is usually paid to the underlying mechanistic aspects of the processes that occur. In this contribution, we critically examine a number of fundamentally important nanoscale thermodynamic aspects of plasma catalysis, which are very relevant to these processes but so far have been overlooked or insufficiently covered in the plasma catalysis literature.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

The central idea in catalysis is to facilitate an alternative pathway for a chemical reaction to occur through the use of a catalyst. This alternative pathway is subject to a lower energy barrier, resulting in higher reaction rates. The catalyst will typically lower certain barriers more than others, and stabilize certain intermediates more than others, such that the catalyst also determines the selectivity towards the desired end products [1–3]. Provided that the reactants are supplied and the products are removed efficiently, the catalyst properties ultimately determine the dominant reaction pathways, as well as their selectivity, rates, products and energy efficiency [4–6].

Most of the catalyst materials are nanostructured [7]. This can be achieved by controlling their synthesis, as is the case for nanoparticles and nanoporous materials [3,8]. The catalysts also feature nanoscale roughness, which also plays a role in many catalytic processes [9,10]. Catalyst properties strongly depend on their structure and size [2,6,11]. To make a catalytic process as cost-effective as possible, the total catalyst surface area should be maximized. In this way the exposure of catalytically active sites is maximized while the used amount of catalytic material is reduced.

In heterogeneous catalysis, this is accomplished by dispersing the catalyst over a suitable (most often nanoporous) support and by deliberately allowing the catalyst to form nanofeatures, thereby

dramatically increasing the surface area compared to an atomically smooth surface [12,13]. Clearly, taking into account the nanoscale nature of the catalyst is of prime importance.

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

- 1) arrival and binding (e.g., physisorption or 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.

While catalytic processes are traditionally treated using physical and chemical kinetics approaches, thermodynamics play a crucial role in each of these steps. Thermodynamics is concerned with the description of systems in terms of the exchange of energy and matter with their surroundings, and determines to what extent the reaction can proceed. As the reaction approaches the equilibrium, as determined by the thermodynamic equilibrium constant for a given set of reaction conditions, the reaction rate will drop accordingly. Therefore, a complete description of the catalytic process 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 [14–16]. The thermodynamic complexity of plasma nanocatalysis is further increased by the nanometer length scale of the

\* Corresponding author. Tel.: +32 3 265 23 88.

E-mail address: [erik.neyts@uantwerpen.be](mailto:erik.neyts@uantwerpen.be) (E.C. Neyts).

system. For instance, it is well known that both non-equilibrium and nanoscale effects play very important roles in plasma-based catalyzed growth of nanotubes [17–19]. In this case, fluxes of atomic, radical, molecular, excited, etc. species, as well as ions, electrons and photons impinge on the nano-catalyst, leading to out-of-equilibrium-growth of the (nanoscale) structure. Here we will focus on nanoscale thermodynamic aspects relevant to plasma catalysis.

## 2. Theoretical description of thermodynamics for nanoscale systems

Various approaches to describe the thermodynamics of nanosystems have been developed, including nanothermodynamics by Hill [20], Tsallis thermodynamics [21], nanoscale thermodynamics based on classical thermodynamics [22], and fluctuation theorems [23].

At the nanoscale, the classical macroscopic laws of thermodynamics no longer hold, and modifications or alternative descriptions are required. Consider for example an icosahedral Ni<sub>147</sub> cluster, which has an apex-to-apex diameter of about 1.5 nm and a surface-to-volume ratio of around 5. As will be shown below, both the melting temperature and adsorption energy on its surface depend on the exact size and structure. Standard equilibrium thermodynamics are not very well suited to describe such a system, because of inherent fluctuations in structure and energy. In fact, due to these fluctuations, definition of static equilibrium becomes rather difficult, if not impossible. This is why structural characteristics in nanoscale systems vary dynamically, in contrast to the quasi-static equilibrium of macroscale objects.

At the nanoscale, modifications or alternative descriptions of classical macroscale thermodynamics are often required. Some authors argue that no such modifications are needed and including a classical size-dependence (as in classical nucleation theory) is sufficient to describe and address the behaviour of nanoscopic systems [24]. Nonetheless, it is obvious that nano-catalysts exhibit modified properties relative to their macroscopic analogues, due to their large surface-to-volume ratio. Hence, standard equilibrium size-independent thermodynamics are not very well suited to describe such systems, because of (1) the finite nature of nanoscale structures, and (2) inherent fluctuations in structure and energy.

Below, we will examine the most important relations between the thermodynamic factors and catalytic effects in nanoscale systems, in particular affected by the plasma.

### 2.1. The Gibbs–Duhem equation at the nanoscale

The first conceptual framework for thermodynamics of nanoscale objects, referred to as “nanothermodynamics” [20,25], was established by Hill. We first consider traditional thermodynamics and then introduce the nanoscale effects [20], keeping the above in consideration. For a macroscopic one-component system the internal energy  $U$  may be expressed as a function of its three natural extensive variables:

$$U(S, V, N) = TS - PV + \mu N, \quad (1)$$

where  $S$  is the conventional entropy (an extensive state function),  $V$  is the volume and  $N$  is the number of particles. The other variables appearing in this equation are the temperature  $T$ , the pressure  $P$  and the chemical potential  $\mu$ . Since the internal energy  $U$  is a state function, the total derivative

$$dU = SdT + TdS - PdV - VdP + \mu dN + Nd\mu \quad (2)$$

can be written as the sum of partial derivatives

$$\begin{aligned} dU &= \left( \frac{\partial U}{\partial S} \right)_{V,N} dS + \left( \frac{\partial U}{\partial V} \right)_{S,N} dV + \left( \frac{\partial U}{\partial N} \right)_{S,N} dN \\ &= TdS - PdV + \mu dN \end{aligned} \quad (3)$$

Eq. (3) expresses conservation of energy, i.e., the first law of thermodynamics. Combining Eqs. (2) and (3) yields

$$SdT - VdP + Nd\mu = 0, \quad (4)$$

which is the well-known Gibbs–Duhem equation for macroscale systems. This equation states that changes in the intensive quantities  $T$ ,  $P$  and  $\mu$  are not independent.

Therefore, at the nanoscale, the internal energy (or any of the other thermodynamic potentials) in principle depends on the exact number of particles  $N$  the structure contains and how they are arranged [20]. As a result, fundamental thermodynamic equations like the Gibbs–Duhem equation are no longer valid. Indeed, in nanoscale systems, the detailed geometry and structure of the system must be taken into account, as well as the fact that surfaces, edges and corners are present and system rotation and translation may occur. According to Hill, the internal energy is now complemented by the so-called subdivision potential  $\varepsilon$ , which takes these factors into account at the ensemble level

$$U = TS - PV + \mu N + \varepsilon, \quad (5)$$

leading to

$$SdT - VdP + Nd\mu + d\varepsilon = 0, \quad (6)$$

which represents the nanoscale version of the Gibbs–Duhem equation. In a macroscopic system, the factors contributing to  $\varepsilon$  become negligible, and Eq. (5) reduces to Eq. (1). Eq. (6) in effect means that the intensive quantities  $T$ ,  $P$  and  $\mu$  may now be varied independently, or stated differently, that  $\varepsilon$  is a function of three independent variables  $T$ ,  $P$ , and  $\mu$ . Nanoscale systems thus have one more degree of freedom compared to macroscale systems.

### 2.2. Second law of thermodynamics and extensivity in nano-catalysis

An alternative view on thermodynamics at the nanoscale stems from the second law of thermodynamics. Indeed, the second law of thermodynamics may be violated in nanoscale systems for very short periods of time, due to fluctuations [26,27]. The Boltzmann definition of entropy is:

$$S = k_B \ln \Omega, \quad (7)$$

where  $S$  is the entropy of the system,  $k_B$  is the Boltzmann factor (which can be regarded as the thermodynamic unit of measurement of entropy), and  $\Omega$  is the number of distinct ways of arranging the constituent particles consistent with the overall macroscale properties of the system. The Boltzmann entropy has two fundamental properties: (1) non-decrease, which means that when no heat enters or leaves the system the entropy cannot decrease, and (2) additivity, which means that the entropy of two systems taken together is the sum of the separate entropies. In nanosystems, however, it is impossible to completely satisfy both properties.

Nonextensive thermodynamics is based on a new statistics introduced by Tsallis [21]. Tsallis statistics can be regarded as a modification of generalized Boltzmann–Gibbs statistical mechanics by relaxation of extensive properties to include non-extensive features. This can be seen as follows. In Tsallis thermodynamics, the Tsallis entropy is defined as [21,28]:

$$S = \frac{1 - \sum_j^{\Omega} p_j^q}{q - 1} \quad (q \in \mathbb{R}), \quad (8)$$

where  $p_j$  is the probability of microstate  $j$  and  $q$  is the so-called entropic parameter. In the limit  $q \rightarrow 1$  the standard Gibbs entropy,  $S = -k_B \sum_j p_j \ln p_j$ , is recovered. A key difference between the Gibbs (or Boltzmann) entropy and the Tsallis entropy is the (non-)additivity. The property of additivity for the standard Boltzmann entropy

$$S(\Omega_A, \Omega_B) = S(\Omega_A) + S(\Omega_B), \quad (9)$$

where  $S(\Omega_A, \Omega_B)$  denotes the entropy of the system composed of subsystems  $A$  and  $B$ , and  $S(\Omega_A)$  and  $S(\Omega_B)$  are the entropies of the separate states  $A$  and  $B$ , respectively, is now changed to

$$S(\Omega_A, \Omega_B) = S(\Omega_A) + S(\Omega_B) + (1 - q)S(\Omega_A)S(\Omega_B), \quad (10)$$

where the last term quantifies the non-additivity of the system. Note that additivity should not be confused with extensivity [29]. A quantity is additive if this quantity for a joint state of a composite system may be decomposed as the sum of the separate quantities for the individual states of the system. On the other hand, a quantity is defined as extensive if it scales proportionally with the number of states the system contains. In general, most of the macroscopic physical systems are extensive. One does not imply the other, although in most cases encountered in physics, this is actually the case [29].

At the nanoscale, extensivity no longer holds. Indeed, the notion of extensivity in thermodynamics is based on the requirement that the associated functions (such as the entropy, internal energy, etc.) are homogeneous functions to degree 1 of the system size. This means that a function  $F(x)$  for  $x \mapsto \lambda x$  obeys the mapping  $F(x) \mapsto \lambda F(x)$ . Likewise, quantities such as the pressure and temperature are homogeneous functions to degree 0 at the macroscale, i.e., these are intensive quantities. These functions, however, are only homogeneous in the thermodynamic limit. At the nanoscale, thermal fluctuations render the system inhomogeneous, and the macroscopic notions of extensivity and intensivity are thus not applicable directly to nanoscale systems [30]. This indicates that nanosystems are in principle non-extensive, and non-extensive thermodynamics must be applied.

Hill-nanothermodynamics and Tsallis-thermodynamics (based on non-additivity of entropy) have been established separately. While some authors have presented them as distinct models [22], they are in fact equivalent [31]. Non-additivity in the entropy (Tsallis statistics) and the introduction of the subdivision potential (Hill nanothermodynamics) can as such be seen as two different pathways leading to the consistent thermodynamic description of nanoscale systems [31].

### 2.3. The Gibbs–Thomson effect

Another approach to thermodynamics at the nanoscale is the extension of traditional thermodynamics with finite-size effects. This is one of the oldest approaches to handle finite systems, although the application to nanosystems is still debated. For instance, Wang et al. [22] specifically address metastable phase nucleation at the nanoscale by considering the Young–Laplace equation

$$\Delta P = \frac{2\gamma}{r}, \quad (11)$$

where  $\gamma$  is the surface energy, which determines the pressure difference across a curved surface with radius  $r$ . As nanoscale objects have very high curvatures (i.e.,  $r$  is very small), the internal pressure buildup can be significant. This phenomenon allows metastable phases in the equilibrium macroscale phase diagram to become stable at the nanoscale [22].

The fact that the internal equilibrium pressure increases with decreasing particle size, in turn also elevates the chemical potential. The equation describing this effect is the Gibbs–Thomson equation

$$\mu_r^0 = \mu_\infty^0 + \frac{2\gamma\Omega}{r}, \quad (12)$$

where  $\mu_r^0$  is the standard chemical potential of the particle with radius  $r$ ,  $\mu_\infty^0$  is the standard chemical potential of the infinite bulk material, and  $\gamma$  and  $\Omega$  are the surface energy and atomic volume of the particle, respectively.

It is important to note that in this formulation the surface energy does not depend on the particle size and is assumed to be isotropic. For nanometer sized particles the surface energy is indeed size dependent [32]. Moreover, the surface energy  $\gamma$  is not isotropic for faceted nanoparticles [33].

Another incarnation of the Gibbs–Thomson effect is the depression of the melting point of nanoclusters relative to the melting point of the bulk material. For metallic nanoparticles, this effect can be expressed as:

$$\Delta T_m(d) = T_{m,bulk} \frac{4\sigma_{sl}}{H_f \rho_s d} \quad (13)$$

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  $\sigma_{sl}$  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 Gibbs–Thomson effect has been widely studied both experimentally [34–36] as well as computationally [37–39]. In Fig. 1, the melting point as calculated from classical molecular dynamics simulations of a series of nanoclusters is shown as a function of nanocluster inverse diameter [39], for clusters in the size range of 1–3 nm commonly used in catalysis applications.

The origin of the Gibbs–Thomson effect lies in the large surface-to-volume ratio of nanoparticles, and hence the undercoordination of the surface atoms [40]. As undercoordinated 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

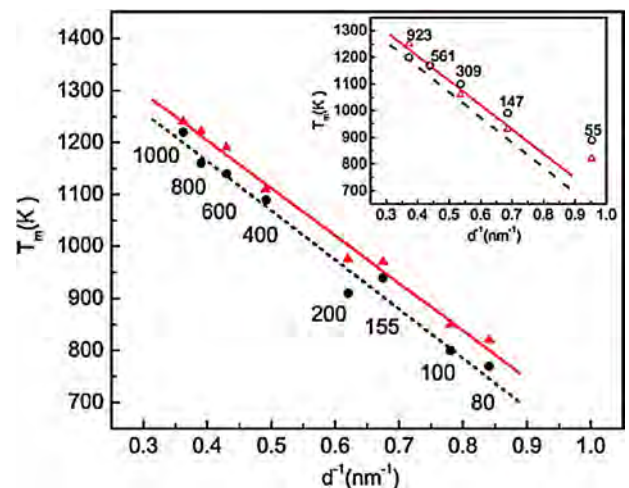


Fig. 1. Calculated melting points of Fe nanoclusters as a function of inverse diameter. Reproduced with permission from [39].

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 catalyzed carbon nanotube growth [41,42], ammonia synthesis on nanometer sized Ru-crystals [43], Fischer–Tropsch synthesis of hydrocarbons [44], and many more heterogeneous catalytic processes [7,45,46].

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 [47].

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. [48] proposed to assign an equilibrium constant to this phenomenon,

$$K = \frac{\tau_{\text{liq}}}{\tau_{\text{sol}}}, \quad (14)$$

where  $\tau_{\text{liq}}$  is the time the cluster spends in the liquid state and  $\tau_{\text{sol}}$  is the time the cluster spends in the solid state, in accordance with classical bulk thermodynamics. Under isobaric conditions, it follows that [48]:

$$K = \frac{\Delta H}{\Delta_f H - \Delta H} \quad (15)$$

where  $\Delta_f H$  is the enthalpy of fusion (i.e., the enthalpy change due to complete melting, where the cluster is always liquid) and  $\Delta H$  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. An example is shown in Fig. 2, for an isolated  $\text{Ni}_{55}$  cluster in vacuum [48]. This cluster has an apex-to-apex diameter of approximately 1.0 nm. It can be seen from the

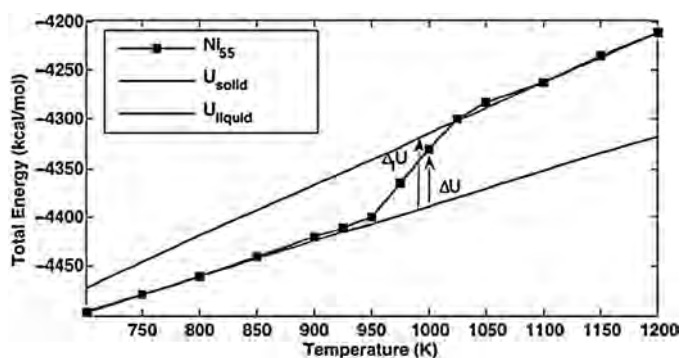


Fig. 2. Total energy curve for a  $\text{Ni}_{55}$  cluster, showing the typical melting interval. Reproduced with permission from [48].

figure that at temperatures below 950 K, the equilibrium constant is close to zero, while it tends to infinity at temperatures above 1025 K.

Because the phase of a nanoscale system depends on its size through the Gibbs–Thomson effect, its phase diagram also changes when additional elements are added. Consider for instance the binary Ni/C system. This system is relevant for, e.g., metal-catalyzed carbon nanotube and graphene growth [49–51], catalytic dry reforming of methane [52,53], Fischer–Tropsch synthesis of hydrocarbons [54], etc. When adding carbon to a nickel nanocluster, the lattice is disrupted, leading to an even lower melting point than expected based on only its size. It has also been demonstrated that this lattice disruption is accompanied by an increase in Ni–Ni and Ni–C bond switching rates, leading to a lowered activation energy for diffusion [55]. As a result, the solubility of carbon in nickel is a function of the cluster size [48,56,57].

#### 2.4. Chemisorption at the nanoscale

The binding (or chemisorption) energy of a reactant to the surface of the catalyst is of prime importance for catalysis. This binding energy is also a function of the nanocatalyst size. The size dependence of the nanocatalyst chemical reactivity has been demonstrated both theoretically [58] (Fig. 3, left panel) as well as experimentally [32] (Fig. 3, right panel). Density Functional Theory (DFT) calculations show that, for instance, CO adsorption on Pd-nanoclusters is weakest (lowest adsorption energy) for clusters containing 30–50 atoms. Below and above this size range, the CO adsorption is stronger. Below this size range, the interaction is stronger because of the decreasing energy gap between the  $2\pi^*$  lowest unoccupied molecular orbital (LUMO) of the CO molecule and the energies of the d-levels of the metal. Above this size, on the other hand, the interaction energy increases due to a decrease in lattice contraction with increasing particle size [58].

#### 2.5. Non-equilibrium thermodynamics and fluctuation theorems

As mentioned above, plasma catalysis is a non-equilibrium process, and in principle non-equilibrium thermodynamics must be applied. Under non-equilibrium conditions, net currents of energy and matter flow across the system. Moreover, nanoscale systems naturally display fluctuations in their properties, both under non-equilibrium as well as under equilibrium conditions, as also described above in Section 2.3.

A general treatment of these fluctuations and the non-equilibrium thermodynamic treatment of small systems is provided by the so-called fluctuation theorems [27]. These fluctuation theorems describe how thermal fluctuations become important at the nanoscale (and on short time scales), and how they lead to deviations from the average macroscale behaviour. Specifically, the fluctuation theorems demonstrate that these thermal fluctuations give rise to a non-zero probability of violating the second law in non-equilibrium systems.

The importance of this for nanoscale systems can be easily understood from e.g. fluctuations in kinetic energy of a system of particles obeying the Maxwell–Boltzmann distribution:

$$\langle E_{\text{kin}} \rangle = \frac{3}{2} N k_B T, \quad (16)$$

for which the fluctuations are of the order of  $\mathcal{O}(1/\sqrt{N})$ , where  $N$  is the number of particles. As the number of particles becomes countable on the nanoscale, it is thus clear that the magnitude of the fluctuations become significant. Because of the presence of these fluctuations, the very concepts of thermal, mechanical and chemical equilibrium, which together constitute (macroscopic) thermodynamic equilibrium, may be hard to define.

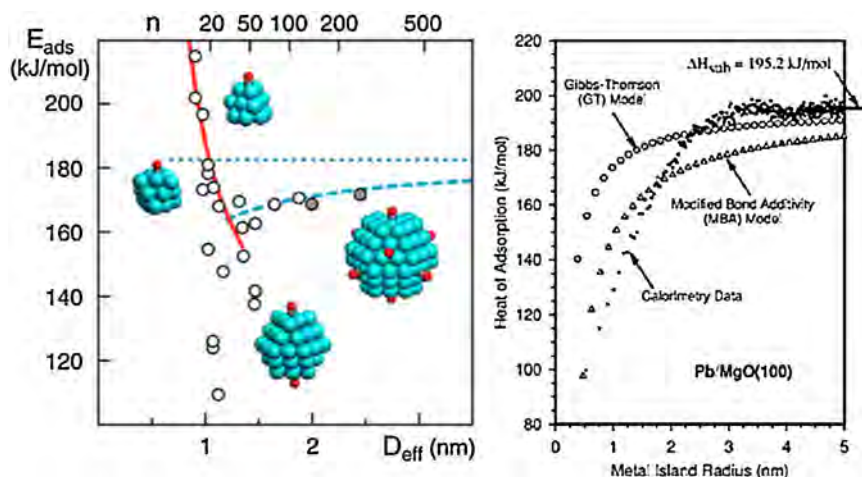


Fig. 3. Size dependence of the heat of adsorption of CO on Pd (left panel, reproduced with permission from [58]), and Pb on MgO (100) (right panel, reproduced with permission from [32]).

To fully appreciate the fluctuation theorems, it is instructive at this point to recall Loschmidt's objection from 1876 to the statistical definition of entropy by Boltzmann. Loschmidt argued that since the microscopic laws of motion are time-reversible (which means that for every forward trajectory, there exists a conjugate, backward trajectory that is an equally valid solution to the equations of motion), it must also be possible that a system evolves towards a lower entropy state. This, however, is in apparent contradiction with the second law of thermodynamics, which states that the entropy must increase monotonically. This paradox may be understood from the fluctuation theorems.

The fluctuation theorem derived by Evans and Searles [23,59]

$$\frac{P(\Omega_t = A)}{P(\Omega_t = -A)} = \exp(A) \quad (17)$$

relates the probabilities of forward and backward trajectories. In this equation,  $\Omega_t$  is the dissipation function, which is in general a dimensionless dissipated energy, and which corresponds to the entropy production  $\sigma = Q/T$  for ergodic temperature-stabilized (thermostatted) time-reversible dynamical systems, with  $Q$  being the heat exchanged between system and thermostat bath at temperature  $T$ . Because the dissipation function is an extensive property, which scales with time, Eq. (17) shows that the probability of backward trajectories becomes exponentially rare as the system size or the observation time increases. Thus, for sufficiently large systems and sufficiently long time scales, the classical second law of thermodynamics is recovered. This, in turn, is the solution to Loschmidt's paradox. Clearly, as plasma nanocatalysis deals with nanoscale systems which are far from equilibrium, fluctuation theorems are of great importance in understanding the thermodynamics of these systems.

Another fluctuation theorem was presented by Crooks [60]. This theorem relates the distributions of trajectories from an equilibrium state  $A$  to another equilibrium state  $B$  to the distributions of reverse trajectories, from state  $B$  to state  $A$ . The relation between both distributions

$$\frac{p_f(W = A)}{p_r(W = -A)} = \exp[\beta(A - \Delta F)] \quad (18)$$

is determined by the work  $W$ . The trajectories may be crossed at an arbitrary rate and thus be far from equilibrium. For reversible trajectories the work associated with the forward trajectories is equal but of the opposite sign to the work associated with the reverse

trajectories, such that the ratio of distributions is unity and  $A = \Delta F$ . Taking the ensemble average

$$\exp(-\beta\Delta F) = \langle \exp(-\beta W) \rangle_f \quad (19)$$

yields the Jarzynski equality [61], where the ensemble average is taken over the forward trajectories  $A \rightarrow B$ . This equality is very important, as it allows to determine the free energy change in going from state  $A$  to state  $B$  by measuring or calculating the work done along the irreversible trajectories connecting both states. As recently pointed out by Sevcik et al. [62], this equality (and fluctuation theorems in general) is required for understanding molecular-scale processes, which are critical in plasma catalysis.

### 3. Summary of relation between thermodynamics and nanoscale systems

Following the above analysis, the relation between thermodynamics and nanosystems can be summarized as follows:

1. While macroscopic systems are independent of ambient conditions, nanoscale systems are not. Consequently, differences in environment will lead to differences in system properties. Moreover, properties such as the surface free energy, edge effects and particle rotation are important in nanoscale systems, and must be accounted for in the total energy. This is reflected by a modification of the Gibbs–Duhem equation at the nanoscale and constitutes a fundamental modification of classical thermodynamics.
2. In nanosystems, the number of particles is countable, and the thermodynamic limit does not apply. This results in, a.o., a depression of the melting point due to the Gibbs–Thomson effect and a size-dependence of the chemisorption energy. The description of such effects is still possible within the framework of classical thermodynamics, albeit including a size-dependence.
3. Fluctuations significantly affect nanoscale systems, which is not the case at macroscales. Taking these effects into account also requires a modification of the thermodynamic description of the system.

These effects also play a significant role in plasma-assisted catalysis where a number of plasma and catalytic effects can be gainfully used in a number of applications such as air pollution [15], catalytic reforming of natural gas into value-added chemical products [14,16] or catalyzed growth of a variety of nanostructures of various

dimensionality, morphology, structure, and chemical composition [17,18,41,63–68].

#### 4. Conclusion

Thus far, we have examined a number of fundamental approaches and phenomena in the thermodynamics of nanoscale systems, which are of particular importance for plasma catalysis. Specifically, the nanoscale size of catalysts typically used in plasma catalysis adds an additional term to the expression for the internal energy of the system, the subdivision energy. Second, nanoscale systems are affected by fluctuations, which can be accounted by using the fluctuation theorems. Another important aspect of nanocatalysis and plasma nanocatalysis is the depression of the melting point, as described by the Gibbs–Thomson effect. This effect demonstrates that for temperatures typically used in catalytic processes, the catalyst may be either solid, semi-liquid or liquid, depending on the catalyst size. Finally, we have also described the size dependence of the chemisorption energy, implying the (in principle) size dependence of volcano plots, often reported in the catalysis literature.

#### Acknowledgments

K. O. acknowledges partial support by the Australian Research Council and the Science Leader Program of CSIRO's Office of Chief Executive.

#### References

- [1] A.J. Gellman, N. Shukla, *Nat. Mater.* 8 (2009) 87–88.
- [2] B.R. Cuenya, *Thin Solid Films* 518 (2010) 3127–3150.
- [3] A.Z. Moshfegh, *J. Phys. D: Appl. Phys.* 42 (2009) 233001.
- [4] A.T. Bell, *Science* 299 (2003) 1688–1691.
- [5] R.M. Mohamed, D.L. McKinney, W.M. Sigmund, *Mater. Sci. Eng. R* 73 (2012) 1–13.
- [6] K. Philippot, P. Serp, in: P. Serp, K. Philippot (Eds.), *Nanomaterials in Catalysis*, Wiley-VCH Verlag GmbH, 2013.
- [7] G. Ertl, *Angew. Chem. Int. Ed.* 47 (2008) 3524–3535.
- [8] H. Bönnemann, K.S. Nagabhushana, in: B. Corain, G. Schmid, N. Toshima (Eds.), *Metal Nanoclusters in Catalysis – The Issue of Size Control*, Elsevier, 2008.
- [9] J.H. Oh, J.S. Lee, *J. Nanosci. Nanotechnol.* 14 (2014) 3753–3757.
- [10] M. Bizarro, M.A. Tapia-Rodriguez, M.L. Ojeda, J.C. Alonso, A. Ortiz, *Appl. Surf. Sci.* 255 (2009) 6274–6278.
- [11] N.R. Shiju, V.V. Guliants, *Appl. Catal. A: Gen.* 356 (2009) 1–17.
- [12] J.M. Campelo, D. Luna, R. Luque, J.M. Marinas, A.A. Romero, *ChemSusChem* 2 (2009) 18–45.
- [13] O. Deutschmann, H. Knözinger, K. Kochloef, T. Turek, *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co., 2009.
- [14] E.C. Neyts, A. Bogaerts, *J. Phys. D: Appl. Phys.* 47 (2010) 224010.
- [15] H.H. Kim, *Plasma Process. Polym.* 1 (2004) 91–110.
- [16] H.L. Chen, H.M. Lee, S.H. Chen, Y. Chao, M.B. Chang, *Appl. Catal. B: Environ.* 85 (2008) 1–9.
- [17] E.C. Neyts, *J. Vac. Sci. Technol. B* 30 (2012) 030803.
- [18] M. Meyyappan, *J. Phys. D: Appl. Phys.* 44 (2011) 174002.
- [19] S.H. Lim, Z. Luo, Z. Shen, J. Lin, *Nanoscale Res. Lett.* 5 (2010) 1377–1386.
- [20] T.L. Hill, *Nano Lett.* 1 (2001) 273–275.
- [21] C. Tsallis, *J. Stat. Phys.* 52 (1988) 479.
- [22] C.X. Wang, G.W. Yang, *Mater. Sci. Eng. R* 49 (2005) 157–202.
- [23] D.J. Evans, D.J. Searles, *Adv. Phys.* 51 (2002) 1529–1585.
- [24] F. Delogu, *J. Phys. Chem. B* 109 (2005) 21938–21941.
- [25] T.L. Hill, *Nano Lett.* 1 (2001) 111–112.
- [26] G.M. Wang, E.M. Sevick, E. Mittag, D.J. Searles, D.J. Evans, *Phys. Rev. Lett.* 89 (2002) 050601.
- [27] C. Bustamante, J. Liphardt, F. Ritort, *Phys. Today* 58 (2005) 43–48.
- [28] G.R. Vakili-Nezhaad, G.A. Mansoori, *J. Comput. Theor. Nanosci.* 1 (2004) 227–229.
- [29] H. Touchette, *Physica A* 305 (2002) 84–88.
- [30] P. Mohazzabi, G.A. Mansoori, *J. Comput. Theor. Nanosci.* 2 (2005) 138–147.
- [31] V. Garcia-Morales, J. Cervera, J. Pellicer, *Phys. Lett.* 336 (2005) 82–88.
- [32] S.C. Parker, C.T. Campbell, *Phys. Rev. B* 75 (2007) 035430.
- [33] A.W. Searcy, J.W. Bullard, *J. Am. Ceram. Soc.* 77 (1994) 2314–2318.
- [34] Ph. Buffat, J.-P. Borel, *Phys. Rev. A* 13 (1976) 2287–2298.
- [35] T. Bachels, H.-J. Güntherodt, R. Schäfer, *Phys. Rev. Lett.* 85 (2000) 1250–1253.
- [36] H. Haberland, T. Hippler, J. Donges, O. Kostko, M. Schmidt, B. von Issendorff, *Phys. Rev. Lett.* 94 (2005) 035701.
- [37] Y. Shibuta, T. Suzuki, *J. Chem. Phys.* 129 (2008) 144102.
- [38] E.C. Neyts, A. Bogaerts, *J. Phys. Chem. C* 113 (2009) 2771–2776.
- [39] A. Jiang, N. Awasthi, A.N. Kolmogorov, W. Setyawan, A. Börjesson, K. Bolton, A.R. Harutyunyan, S. Curtarolo, *Phys. Rev. B* 75 (2007) 205426.
- [40] C.Q. Sun, Y. Wang, B.K. Tay, S. Li, H. Huang, Y.B. Zhang, *J. Phys. Chem. B* 106 (2002) 10701–10705.
- [41] K. Ostrikov, E.C. Neyts, M. Meyyappan, *Adv. Phys.* 62 (2013) 113–224.
- [42] K. Ostrikov, H. Mehdipour, *ACS Nano* 5 (2011) 8372–8382.
- [43] N. Saadatjou, A. Jafari, S. Sahebdehfar, *Chem. Eng. Commun.* 202 (2015) 420–448.
- [44] R.A. van Santen, A.J. Markvoort, *Faraday Discuss.* 162 (2013) 267–279.
- [45] W. Somers, A. Bogaerts, A.C.T. van Duin, E.C. Neyts, *J. Phys. Chem. C* 116 (2012) 20958–20965.
- [46] W. Somers, A. Bogaerts, A.C.T. van Duin, S. Huygh, K.M. Bal, E.C. Neyts, *Catal. Today* 211 (2013) 131–136.
- [47] K. Esfarjani, G.A. Mansoori, in: M. Rieth, W. Schommers (Eds.), *Handbook of Theoretical and Computational Nanotechnology*, vol. X, 2005, pp. 1–45.
- [48] Y. Engelmann, A. Bogaerts, E.C. Neyts, *Nanoscale* 6 (2014) 11981–11987.
- [49] J.A. Elliott, Y. Shibuta, H. Amara, C. Bichara, E.C. Neyts, *Nanoscale* 5 (2013) 6662–6676.
- [50] E.C. Neyts, A.C.T. van Duin, A. Bogaerts, *Nanoscale* 5 (2013) 7250–7255.
- [51] L. Meng, Q. Sun, J. Wang, F. Ding, *J. Phys. Chem. C* 116 (2012) 6097–6102.
- [52] J. Guo, H. Lou, H. Zhao, D. Chai, X. Zheng, *Appl. Catal. A: Gen.* 273 (2004) 75–82.
- [53] C. Fukuhara, R. Hyodo, K. Yamamoto, K. Masuda, R. Watanabe, *Appl. Catal. A: Gen.* 468 (2013) 18–25.
- [54] B.C. Enger, A. Holmen, *Catal. Rev. Sci. Eng.* 54 (2012) 437–488.
- [55] E. Neyts, Y. Shibuta, A. Bogaerts, *Chem. Phys. Lett.* 488 (2010) 202–205.
- [56] M. Diarra, H. Amara, F. Ducastelle, C. Bichara, *Phys. Status Solidi B* 249 (2012) 2629–2634.
- [57] A.R. Harutyunyan, N. Awasthi, A. Jiang, W. Setyawan, E. Mora, T. Tokune, K. Bolton, S. Curtarolo, *Phys. Rev. Lett.* 100 (2008) 195502.
- [58] I.V. Yudanov, A. Genest, S. Schauerer, H.-J. Freund, N. Rösch, *Nano Lett.* 12 (2012) 2134–2139.
- [59] D.J. Evans, D.J. Searles, *Phys. Rev. E* 50 (1994) 1645.
- [60] G.E. Crooks, *Phys. Rev. E* 60 (1999) 2721.
- [61] C. Jarzynski, *Phys. Rev. Lett.* 78 (1997) 2690.
- [62] E.M. Sevick, R. Prabhakar, S.R. Williams, D.J. Searles, *Annu. Rev. Phys. Chem.* 59 (2008) 603–633.
- [63] U. Cvelbar, K. Ostrikov, *M. Mozetic, Nanotechnology* 19 (2008) 405605.
- [64] U. Cvelbar, *J. Phys. D: Appl. Phys.* 44 (2011) 174014.
- [65] F.G. Petzold, J. Jasinski, E.L. Clark, J.H. Kim, J. Absher, H. Toufar, M.K. Sunkara, *Catal. Today* 198 (2012) 219–227.
- [66] S. Sharma, M.K. Sunkara, *J. Am. Chem. Soc.* 124 (2002) 12288–12293.
- [67] I. Levchenko, M. Keidar, S.Y. Xu, H. Kersten, K. Ostrikov, *J. Vac. Sci. Technol. B* 31 (2013) 050801.
- [68] R.M. Sankaran, *J. Phys. D: Appl. Phys.* 44 (2011) 174005.