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Nanocrystallites, adsorption, surface tension, and Wulff rule

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Chemisorption on the surface of metal nanocrystallites (NCs) sometimes induces their reshaping. This interesting phenomenon was observed experimentally in various systems. Related theoretical studies imply that it can be described using the Wulff rule with the surface tension dependent on the coverage of the NC facets by adsorbate. There is, however, no agreement as to how the surface tension should be calculated in this case. Relying on the laws of statistical physics, I clarify the situation in this area in general and also in the framework of the mean-field approximation in three situations: (i) with adsorption-desorption equilibrium, (ii) with a fixed amount of adsorbate at a NC, and (iii) with a fixed amount of adsorbate at facets of a NC. Under these conditions, the surface tension is shown to be described by the same expressions.

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I. INTRODUCTION

Under ordinary conditions, the shape of macroscopic crystallites is determined by the specifics of their growth or, in other words, by kinetics and thermodynamics. The shape of nanocrystallites (NCs) can depend on the conditions of their fabrication as well, but it is often close to that predicted by thermodynamics at equilibrium or, more specifically, by the Wulff rule [1], as has long been shown experimentally in numerous studies of metal NCs (reviewed in [2–5]). At first, such studies were related primarily to heterogeneous catalysis, where metal NCs have been used for many decades. In this area, the NC size and shape are of central importance in the context of reactivity on and sintering of NCs (see, e.g., Refs. [6,7] and [8,9], respectively). With the recent rapid developments in nanoscience, the understanding of the factors determining the shape of NCs has become central from many other basic and applied perspectives, including, e.g., the optical properties (localized surface plasmon resonance) of NCs [10,11], template-mediated solution-based chemistry [12,13], hydrogen storage [14,15], and various sensors [16,17]. For these reasons, the specifics of the use of the Wulff rule merit attention.

The conventional derivation of the Wulff rule (see, e.g., Sec. 155 in [18]) implies that a NC is formed out of one material, there is no adsorption on its surface, and there is no contact with the support. In this case, for a given T and NC volume, a NC can be described as a closed system, and its equilibrium shape corresponds to a minimum of its free energy, F. This energy is represented as a sum of the volume and surface parts, F_{v} and F_{s}. F_{v} is considered to be constant, and accordingly the NC equilibrium shape is assumed to correspond to a minimum of F_{s}. Mathematically, F_{s} is calculated by integrating the surface tension, α, over the whole NC surface,

$$F_{\mathrm{s}} = \oint \alpha\, dS. \tag{1}$$

The surface tension is defined as the coefficient in the expression for the work $dR = \alpha\, dS$ needed for a reversible change of S by an infinitesimal amount dS. NCs are facetted, and accordingly Eq. (1) can be rewritten as

$$F_{\mathrm{s}} = \sum_i \alpha_i S_i, \tag{2}$$

where α_i and S_i are the surface tension and the area of the facets of type i. The differential form of (2) is

$$dF_{\mathrm{s}} = \sum_i \alpha_i\, dS_i. \tag{3}$$

The minimization of (2), performed taking (3) into account, yields the Wulff rule (or, in other words, Wulff construction) saying that a NC possesses the geometrical origin, and the distance from this origin to the facets of type i is proportional to α_i. With properly defined α_i, this rule can be generalized to the case of NCs located on a flat support [19] or more complex cases including, e.g., NCs sandwiched between parallel substrates [20]. In all these versions of the derivation of the Wulff rule, the facets of NCs are considered to be well defined. This approximation is valid in many practically important situations. In general, with appreciably increasing temperature, there is, however, a transition from the Wulff shape of NCs to the spherical shape described by the Kelvin model [21]. This aspect is beyond the scope of the present study.

In heterogeneous catalysis and numerous more recent applications, the use of NCs includes adsorption on their surface, and the presence of adsorbates can influence the NC shape. This important phenomenon was experimentally observed in many systems (e.g., [22–26]). Kinetic models of adsorption and catalytic reactions are numerous (reviewed

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in [27–32]), and this interdisciplinary area customarily attracts the attention of the statistical physics community (see, e.g., recent publications in Phys. Rev. E [33–39] and references therein). In such models, the structure of the support is usually considered to be fixed, and restructuring of NCs is not analyzed. With the appearance of reliable experiments [22–26], however, the situation has changed, and adsorbate-induced restructuring of NCs has attracted the attention of theoreticians (see, e.g., original studies [40–58] and reviews [59–61]). The corresponding kinetic models imply the applicability of the Wulff rule, and they are based on (i) the introduction of the specific expressions for the dependence of α_i on the adsorbate coverages, θ_i, or reactant pressures (because the coverages can be expressed via pressures), and (ii) subsequent Wulff construction performed with the obtained values of α_i. The general shortcoming of these studies is that the dependence of α_i on θ_i is introduced axiomatically, and there is no agreement in the proposed prescriptions for the calculation of the adsorbate-related part of α_i. One of the reasons for this state of the art appears to be that during the changes of the facet areas, the amount of adsorbate is changed and it depends on the conditions of adsorption. Under such circumstances, it is not immediately obvious what should be minimized and how that should be done in order to validate the Wulff rule.

Herein, the application of the Wulff rule to the description of adsorbate-induced restructuring of NCs is scrutinized and clarified from the perspective of statistical physics in three situations: with adsorption-desorption equilibrium (Sec. II), with a fixed amount of adsorbate at a NC (Sec. III), and with a fixed amount of adsorbate at the facets of a NC (Sec. IV). The results obtained are employed as a basis for discussion of the earlier proposed prescriptions (Sec. V).

II. AT ADSORPTION-DESORPTION EQUILIBRIUM

In the analysis below, a NC is considered to adsorb molecules of two types, A and B. First (Sec. IIA), adsorption is assumed to be competitive, i.e., each NC facet contains one type of adsorption site, and each site is vacant or occupied by A or B. The case of cooperative adsorption of A and B is treated as well (Sec. IIB). The corresponding general thermodynamic expressions derived for α_i are illustrated by the equations obtained in the mean-field (MF) approximation. As a rule, adsorption is assumed to be molecular, $A_g \rightleftharpoons A_s$ and $B_g \rightleftharpoons B_s$ (the subscripts "g" and "s" correspond to the gas phase and the surface, respectively). The situations with dissociation are discussed briefly. Multicomponent adsorption is not treated explicitly because the related analysis can easily be done by analogy with that presented.

A. Competitive adsorption

Under adsorption-desorption equilibrium, a NC together with adsorbate represents an open system, and it should be described by using the grand canonical distribution (Sec. 35 in [18]). Practically, this means that one should operate with the thermodynamic potential Ω or, more specifically, with its surface part, defined for molecular coadsorption as

$$\Omega_s = F_s(\bar{N}_A, \bar{N}_B) - \mu_A \bar{N}_A - \mu_B \bar{N}_B, \tag{4}$$

where $F_s(\bar{N}_A, \bar{N}_B)$ is the free energy, $\bar{N}_A$ and $\bar{N}_B$ are the average numbers of adsorbed species, and μ_A and μ_B are the corresponding chemical potentials. As usual for NCs [Eq. (2)], potential (4) can be represented as a sum of those corresponding to different facets,

$$\Omega_s = \sum_i \Omega_i, \quad \text{with} \tag{5}$$

$$\Omega_i = F_i^\circ + F_i^\star(\bar{N}_{Ai}, \bar{N}_{Bi}) - \mu_A \bar{N}_{Ai} - \mu_B \bar{N}_{Bi}, \tag{6}$$

where F_i° is the facet free energy in the absence of adsorbate [this energy is the same as in (2)], $F_i^\star(\bar{N}_{Ai}, \bar{N}_{Bi})$ is the adsorbate free energy, and $\bar{N}_{Ai}$ and $\bar{N}_{Bi}$ are the corresponding average numbers of adsorbed species.

In terms of the surface tension, the facet-related thermodynamic potential is represented as

$$\Omega_i = \alpha_i S_i \quad \text{with} \quad \alpha_i = \alpha_i^\circ + \alpha_i^\star, \quad \text{or} \tag{7}$$

$$\Omega_i = (\alpha_i^\circ + \alpha_i^\star) S_i, \tag{8}$$

where α_i° is the tension in the absence of adsorbate, and $\alpha_i^\star$ is the adsorbate-related term. Comparing (8) with (6) yields

$$\alpha_i^\circ = F_i^\circ / S_i, \tag{9}$$

$$\alpha_i^\star = [F_i^\star(\bar{N}_{Ai}, \bar{N}_{Bi}) - \mu_A \bar{N}_{Ai} - \mu_B \bar{N}_{Bi}]/S_i. \tag{10}$$

Basically, Eqs. (4)–(10) are phenomenological and applicable irrespective of whether adsorption is competitive or cooperative. In the case of competitive adsorption under consideration, each NC facet contains one type of adsorption site. In particular, the number of adsorption sites at facets of type i is given by $N_{si} = S_i/s_i$, where s_i is the surface area per site, and accordingly (10) can be rewritten as

$$\alpha_i^\star = \left[\frac{F_i^\star(\bar{N}_{Ai}, \bar{N}_{Bi})}{N_{si}} - \mu_A \frac{\bar{N}_{Ai}}{N_{si}} - \mu_B \frac{\bar{N}_{Bi}}{N_{si}} \right] \Big/ s_i. \tag{11}$$

In fact, the latter expression contains the free energy per site, $f_i^\star = F_i^\star / N_{si}$, and adsorbate coverages, $\theta_{Ai} = \bar{N}_{Ai}/N_{si}$ and $\theta_{Bi} = \bar{N}_{Bi}/N_{si}$, i.e., it can be rewritten as

$$\alpha_i^\star = (f_i^\star - \mu_A \theta_{Ai} - \mu_B \theta_{Bi})/s_i. \tag{12}$$

In the one-component case (e.g., for A species), it is reduced to

$$\alpha_i^\star = (f_i^\star - \mu_A \theta_{Ai})/s_i. \tag{13}$$

Thus, under adsorption-desorption equilibrium, the shape of a NC can be obtained by minimization of the thermodynamic potential, defined by (5) and (8), with the surface tensions defined by (9) and (12) [or (13)]. The tensions α_i° defined by (9) correspond to the adsorbate-free case and are the same as those used in the conventional derivation of the Wulff rule (Sec. I). During the conventional derivation (minimization of the free energy), α_i° are considered to be independent of the NC shape, or, in other words, of S_i. The tensions $\alpha_i^\star$ defined by (12) contain the values, $f_i^\star$, θ_{Ai}, and θ_{Bi}, calculated per adsorption site. By analogy with α_i°, these values and accordingly α_i° and α_i can be considered to be independent of the NC shape, i.e., of S_i. Under these conditions, the differential form of (5) is given by

$$d\Omega_s = \sum_i \alpha_i dS_i. \tag{14}$$

This means that the situation here is mathematically similar to that in the adsorbate-free case (Sec. I) except that F_{s} is replaced by Ω_{s}. In particular, the Wulff rule remains valid provided the contribution of adsorbate to the surface tension is given by (12) [or (13)].

Concerning the analysis above, I can add that the assumption that α_i° and $\alpha_i^{\star}$ are independent of the NC shape, or, in other words, of S_i, is physically reasonable provided the NC size is not too small. The corresponding corrections are expected to be comparable to or smaller than those related to variation of the NC size. The latter corrections are small although not fully negligible for the sizes down to 2–3 nm. According to the DFT calculations (Fig. 5 in [62]), for example, the size-dependent contribution to the CO binding energy on the (111) facets of Pd NCs is negative (the binding is slightly less favorable) and inversely proportional to the size and, for the 3-nm size, is about -7 kJ/mol while the energy itself is close to 180 kJ/mol. In this size limit, the scale of the dependence of $\alpha_i^{\star}$ on the Pd NC shape or size is expected to be smaller than 7 kJ/mol because $\alpha_i^{\star}$ is in fact dependent on the lateral adsorbate-adsorbate interactions [see Eq. (17) below], which are appreciably smaller than the binding energy, and their variation is smaller as well.

To scrutinize the adsorbate-related contribution to the surface tension [Eq. (12)], we need explicit expressions for $f_i^{\star}$ and relations between the coverages and chemical potentials. It can be done in the framework of the lattice-gas model by using various approximations well developed in statistical physics. The corresponding equations are usually cumbersome except those obtained in the conventional MF approximation [32]. In the present context this approximation is sufficient, and we have

$$\begin{aligned} f_i^{\star} = {} & -E_{\mathrm{A}i}\theta_{\mathrm{A}i} - E_{\mathrm{B}i}\theta_{\mathrm{B}i} + \epsilon_{\mathrm{AA}}\theta_{\mathrm{A}i}^2/2 + \epsilon_{\mathrm{BB}}\theta_{\mathrm{B}i}^2/2 + \epsilon_{\mathrm{AB}}\theta_{\mathrm{A}i}\theta_{\mathrm{B}i} \\ & + k_{\mathrm{B}}T[\theta_{\mathrm{A}i}\ln(\theta_{\mathrm{A}i}) + \theta_{\mathrm{B}i}\ln(\theta_{\mathrm{B}i}) \\ & + (1-\theta_{\mathrm{A}i}-\theta_{\mathrm{B}i})\ln(1-\theta_{\mathrm{A}i}-\theta_{\mathrm{B}i})], \end{aligned} \tag{15}$$

where $E_{\mathrm{A}i} > 0$ and $E_{\mathrm{B}i} > 0$ are the adsorbate binding energies in the low-coverage limit, and ϵ_{AA}, ϵ_{BB}, and ϵ_{AB} are the parameters related to the lateral adsorbate-adsorbate interaction (these parameters are positive for repulsion). The latter parameters take in a lumped way all the lateral interactions [nearest-neighbor (nn), next-nn, etc.] into account. In the MF approximation, this lumped description is possible because the adsorbed particles are considered to be located at random. In terms of the nn interactions $\epsilon_{\mathrm{AA}}^{\star}$, $\epsilon_{\mathrm{BB}}^{\star}$, and $\epsilon_{\mathrm{AB}}^{\star}$, we have, e.g., $\epsilon_{\mathrm{AA}} = z\epsilon_{\mathrm{AA}}^{\star}$, $\epsilon_{\mathrm{BB}} = z\epsilon_{\mathrm{BB}}^{\star}$, and $\epsilon_{\mathrm{AB}} = z\epsilon_{\mathrm{AB}}^{\star}$, where z is the number of nn sites.

In general, the chemical potentials are defined via the coverages as

$$\mu_{\mathrm{A}} = \frac{\partial F_i^{\star}}{\partial N_{\mathrm{A}i}} = \frac{\partial f_i^{\star}}{\partial \theta_{\mathrm{A}i}} \quad \text{and} \quad \mu_{\mathrm{B}} = \frac{\partial F_i^{\star}}{\partial N_{\mathrm{B}i}} = \frac{\partial f_i^{\star}}{\partial \theta_{\mathrm{B}i}}.$$

Using these relations and (15) for $f_i^{\star}$, we obtain

$$\begin{aligned} \mu_{\mathrm{A}} = {} & -E_{\mathrm{A}i} + \epsilon_{\mathrm{AA}}\theta_{\mathrm{A}i} + \epsilon_{\mathrm{AB}}\theta_{\mathrm{B}i} \\ & + k_{\mathrm{B}}T\ln[\theta_{\mathrm{A}i}/(1-\theta_{\mathrm{A}i}-\theta_{\mathrm{B}i})], \\ \mu_{\mathrm{B}} = {} & -E_{\mathrm{B}i} + \epsilon_{\mathrm{BB}}\theta_{\mathrm{B}i} + \epsilon_{\mathrm{AB}}\theta_{\mathrm{A}i} \\ & + k_{\mathrm{B}}T\ln[\theta_{\mathrm{B}i}/(1-\theta_{\mathrm{A}i}-\theta_{\mathrm{B}i})]. \end{aligned} \tag{16}$$

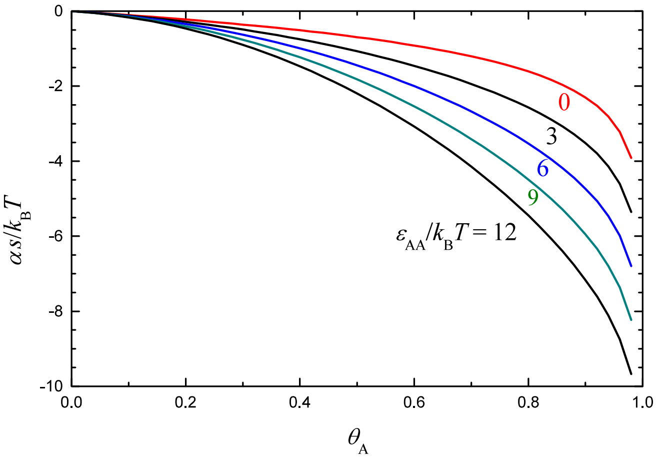

FIG. 1. Adsorbate-related part of the surface tension [Eq. (18)], normalized to $k_{\mathrm{B}}T/s$, is shown as a function of coverage for one-component adsorption with $\epsilon_{\mathrm{AA}}/k_{\mathrm{B}}T = 0$, 3, 6, 9, and 12. Physically, ϵ_{AA} represents the change of the adsorbate-adsorbate interaction with increasing coverage from zero to saturation. In terms of the nn lateral interactions ($\epsilon_{\mathrm{AA}}^{\star}$), this parameter is expressed as $\epsilon_{\mathrm{AA}} = z\epsilon_{\mathrm{AA}}^{\star}$, where z is the number of nn sites. For chemisorbed species, the adsorbate-adsorbate interaction is typically repulsive, $\epsilon_{\mathrm{AA}} > 0$, and its scale is usually in the range from 20 to 80 kJ/mol. For $T = 500$ K, the corresponding ratio $\epsilon_{\mathrm{AA}}/k_{\mathrm{B}}T$ is from 5 to 20. For comparison, the surface tensions of the (111) and (100) faces of Pt are 1.44 and 1.64 J/m^2 (Table 3 in [65]). The corresponding energies per adsorption site with $s = 10$ Å^2 are 1.44×10^{-19} and 1.64×10^{-19} J or 86 and 98 kJ/mol.

Substituting (15) and (16) into (12) yields

$$\begin{aligned} \alpha_i^{\star} = {} & \big[-\epsilon_{\mathrm{AA}}\theta_{\mathrm{A}i}^2/2 - \epsilon_{\mathrm{BB}}\theta_{\mathrm{B}i}^2/2 - \epsilon_{\mathrm{AB}}\theta_{\mathrm{A}i}\theta_{\mathrm{B}i} \\ & + k_{\mathrm{B}}T\ln(1-\theta_{\mathrm{A}i}-\theta_{\mathrm{B}i})\big]/s_i. \end{aligned} \tag{17}$$

For species of one type (e.g., A), this expression is reduced to

$$\alpha_i^{\star} = \big[-\epsilon_{\mathrm{AA}}\theta_{\mathrm{A}i}^2/2 + k_{\mathrm{B}}T\ln(1-\theta_{\mathrm{A}i})\big]/s_i. \tag{18}$$

Equations (17) and (18) show how the adsorbate-related contribution to the surface tension depends on the coverages (see, e.g., Fig. 1). Under adsorption-desorption equilibrium, the coverages depend on pressure. To get this dependence, one can take into account that according to the grand-canonical distribution or, more specifically, according, e.g., to (16), the coverages can be expressed via the chemical potentials. For molecules of one type and in the absence of the lateral interaction, for example, (16) yields

$$\theta_{\mathrm{A}i} = \frac{\exp[(\mu_{\mathrm{A}} + E_{\mathrm{A}i})/k_{\mathrm{B}}T]}{1 + \exp[(\mu_{\mathrm{A}} + E_{\mathrm{A}i})/k_{\mathrm{B}}T]}. \tag{19}$$

In this case, (18) can be rewritten in terms of the chemical potential as

$$\alpha_i^{\star} = -k_{\mathrm{B}}T\ln\{1 + \exp[(\mu_{\mathrm{A}} + E_{\mathrm{A}i})/k_{\mathrm{B}}T]\}/s_i. \tag{20}$$

In turn, the chemical potential is related to pressure as

$$\mu_{\mathrm{A}} = \mathrm{const} + k_{\mathrm{B}}T\ln(P_{\mathrm{A}}). \tag{21}$$

Substituting (21) into (18) allows one to identify the dependence of $\alpha_i^{\star}$ on pressure.

In the analysis above, adsorption is considered to be molecular, $A_g \rightleftharpoons A_s$ and $B_g \rightleftharpoons B_s$. In the situations with dissociation, $A_2^g \rightleftharpoons 2A_s$ and/or $B_2^g \rightleftharpoons 2B_s$, the equations presented [except (21)] remain applicable provided μ_A and μ_B are identified with the chemical potential of adsorbed species. To apply them, one need only redefine the expressions describing the dependence of μ_A and/or μ_B on the gas-phase pressures. In the $A_2^g \rightleftharpoons 2A_s$ case, for example, Eq. (21) should be replaced by

$$\mu_A = \text{const} + \frac{k_B T}{2} \ln\left(P_{A_2}\right), \tag{22}$$

where P_{A_2} is the A_2 pressure.

B. Cooperative adsorption

In real systems, adsorbed atoms and molecules often occupy different sites. For example, we consider here the situation when on each facet, A and B are located in sites of types 1 and 2, respectively. In this case, coverages θ_{Ai} and θ_{Bi} can be associated with these respective sites as well. With this modification, the general equations (4)–(14) obtained above remain valid. The entropic term in the MF expression (15) should, however, be replaced by

$$\begin{aligned} &k_B T[\theta_{Ai}\ln(\theta_{Ai}) + (1-\theta_{Ai})\ln(1-\theta_{Ai})] \\ &\quad + k_B T[\theta_{Bi}\ln(\theta_{Bi}) + (1-\theta_{Bi})\ln(1-\theta_{Bi})]. \end{aligned}$$

With the latter modification, one can easily obtain that Eqs. (16) and (17) should be rewritten as

$$\begin{aligned} \mu_A &= -E_{Ai} + \epsilon_{AA}\theta_{Ai} + \epsilon_{AB}\theta_{Bi} \\ &\quad + k_B T \ln[\theta_{Ai}/(1-\theta_{Ai})], \\ \mu_B &= -E_{Bi} + \epsilon_{BB}\theta_{Bi} + \epsilon_{AB}\theta_{Ai} \\ &\quad + k_B T \ln[\theta_{Bi}/(1-\theta_{Bi})], \\ \alpha_i^\star &= \big\{-\epsilon_{AA}\theta_{Ai}^2/2 - \epsilon_{BB}\theta_{Bi}^2/2 - \epsilon_{AB}\theta_{Ai}\theta_{Bi} \\ &\quad + k_B T \ln[(1-\theta_{Ai})(1-\theta_{Bi})]\big\}\big/ s_i. \end{aligned}$$

III. FIXED AMOUNT OF ADSORBATE AT A NC

Let us now consider the situation when a NC has fixed numbers of adsorbed A and B species on its surface and there is no communication with the gas phase. This situation can easily be realized in experiments because the timescale of desorption can be large. The observation of adsorbate-induced restructuring of NCs in this case is of course usually hardly possible, because the corresponding timescale is as a rule expected to be larger than that of desorption. With this reservation, the analysis of the case under consideration is instructive from the point of view of statistical physics (this remark is applicable also to Sec. IV).

In the absence of communication with the gas phase, a NC can be described as a closed system, and its equilibrium shape corresponds to a minimum of its surface free energy,

$$F_s = \sum_i [F_i^\circ + F_i^\star(N_{Ai}, N_{Bi})], \tag{23}$$

where F_i° and $F_i^\star(N_{Ai}, N_{Bi})$ are its adsorbate-free and adsorbate-related parts, and N_{Ai} and N_{Bi} are the adsorbate numbers at facets of type i. Mathematically, this situation is slightly different compared to those discussed in Secs. I and II because the total numbers of adsorbed A and B species are fixed and the change of the NC shape is accompanied by redistribution of adsorbed species over different facets. The key steps of the analysis here are, however, similar to those in Sec. II. In particular, Eq. (23) can be rewritten as

$$F_s = \sum_i (\alpha_i^\circ + f_i^\star/a_i) S_i, \tag{24}$$

where all the designations are as in Sec. II. On the other hand, the differential of F_s represented in terms of surface tension can phenomenologically be represented as

$$dF_s = \sum_i \alpha_i\, dS_i = \sum_i (\alpha_i^\circ + \alpha_i^\star)\, dS_i. \tag{25}$$

To relate (24) and (25), the adsorbate-related term in (23) or (24) can be rewritten in another general form as

$$F_i^\star = f_i^\star\Big(\frac{N_{Ai}}{N_{si}}, \frac{N_{Bi}}{N_{si}}\Big) N_{si}, \tag{26}$$

where $N_{Ai}/N_{si} \equiv \theta_{Ai}$ and $N_{Bi}/N_{si} \equiv \theta_{Bi}$ represent coverages. If N_{Ai}, N_{Bi}, and N_{si} are independent variables, the differential form of (26) is

$$\begin{aligned} dF_i^\star &= f_i^\star\, dN_{si} + \mu_A(dN_{Ai} - \theta_{Ai}\, dN_{si}) \\ &\quad + \mu_B(dN_{Bi} - \theta_{Bi}\, dN_{si}). \end{aligned} \tag{27}$$

If the total numbers of A and B are fixed, we have $\sum_i dN_{Ai} = 0$ and $\sum_i dN_{Bi} = 0$. With these conditions, the differential of $dF_s^\star$ obtained by summation of $dF_i^\star$ given by (27) is

$$dF_s^\star = \sum_i (f_i^\star - \mu_A\theta_{Ai} - \mu_B\theta_{Bi})\, dN_{si}, \quad \text{or} \tag{28}$$

$$dF_s^\star = \sum_i [(f_i^\star - \mu_A\theta_{Ai} - \mu_B\theta_{Bi})/s_i]\, dS_i. \tag{29}$$

Comparing this expression with the adsorbate-related term in (25), we have

$$\alpha_i^\star = (f_i^\star - \mu_A\theta_{Ai} - \mu_B\theta_{Bi})/s_i. \tag{30}$$

This expression for $\alpha_i^\star$ is identical to that [Eq. (12)] derived in Sec. II, i.e., as one could expect, the adsorbate-related surface tension is the same in both cases.

IV. FIXED AMOUNT OF ADSORBATE AT FACETS

In addition, it is instructive to consider the hypothetical situation when a NC has fixed numbers of adsorbed A and B species on its facets and there is no adsorbate diffusion between facets and communication with the gas phase. In this case, Eqs. (23)–(26) remain valid. In Eq. (27), the terms containing dN_{Ai} and dN_{Bi} should, however, be dropped because the amount of adsorbate at facets is fixed. With this modification, Eqs. (28)–(30) remain valid as well. The only difference is that the chemical potentials μ_A and μ_B for the whole NC should be replaced by those, μ_{Ai} and μ_{Bi}, for facets, because there is no adsorbate diffusion between them, i.e., the surface tension can be defined as

$$\alpha_i^\star = (f_i^\star - \mu_{Ai}\theta_{Ai} - \mu_{Bi}\theta_{Bi})/s_i. \tag{31}$$

V. DISCUSSION

Taken together, the results obtained in Secs. II–IV show that the adsorbate-related contribution to the surface tension can be described by using the same general equations [(12), (30), and (31)] under different conditions including (i) adsorption-desorption equilibrium, (ii) a fixed amount of adsorbate at a NC, and (iii) a fixed amount of adsorbate at facets of a NC. For this reason, these expressions are expected to be applicable also under reactive conditions.

The important point is that the surface tension expressed in terms of surface coverages depends on the lateral interaction between adsorbed particles and contains an entropic contribution but is independent of the adsorbate binding energies calculated in the low-coverage limit. The repulsive adsorbate-adsorbate interaction decreases the surface tension. These conclusions are evident from Eqs. (17) and (18), derived in the conventional MF approximation with the lateral interactions proportional to the square of coverages, and they hold in general for arbitrary interactions as it follows from Eqs. (12), (30), and (31).

With the results we have at hand here, it is now instructive to discuss briefly the earlier theoretical studies [40–58] implying the applicability of the Wulff rule for the analysis of the NC shape under various conditions with participation of adsorbed species and proposing axiomatically the specific expressions for the dependence of the adsorbate-related part of the surface tension on the adsorbate coverages. Along these lines, I outline the available results in historical order. To prevent confusion, I reproduce the equations proposed earlier by using the original designations, and recalling the corresponding original terminology.

In our generic kinetic model illustrating the specifics of the change of the NC shape with variation of the reactant composition in catalytic reactions under steady-state conditions [40] (see also Ref. [59]), the surface tensions of the facets of two types, 0 and 1, were assumed to depend on the coverage of one of the reactants as

$$\gamma_0(\theta_B) = \gamma_0^0 + A_0\theta_B \quad \text{and} \quad \gamma_1(\theta_B) = \gamma_1^0 + A_1\theta_B, \tag{32}$$

where γ_0^0 and γ_1^0 are the tensions corresponding to the adsorbate-free case, and A_0 and A_1 are the phenomenological adsorbate-related parameters. The way to calculate A_0 and A_0 was not discussed. In fact, the introduced linear dependence of the surface tension on adsorbate coverage [Eq. (32)] can be viewed as a rough approximation of what might be in reality [cf. (32) with (18) and Fig. 1].

Lin *et al.* [41] (see also [42–45]) discussed the surface tension in the context of an adsorption isotherm of species of one type. The surface tension was introduced by referring to "the Gibbs adsorption equation." In particular, its adsorbate-related part is defined as [Eq. (9) in [41] or Eq. (7) in [44]]

$$\gamma - \gamma_0 = \Gamma_\infty RT[\ln(1-x) - knx^2/(n+1)], \tag{33}$$

where Γ_∞ is "the maximum surface concentration," x is the coverage, k and n are the parameters related to the adsorbate-adsorbate interaction, and R is the molar gas constant. Equation (33) can be obtained from (13) in the MF approximation provided the contribution of the adsorbate-adsorbate interaction to $f_i^\star$ is represented as $\epsilon_{AA}\theta_{Ai}^{n+1}/(n+1)$ (in my designations). In the conventional MF approximation with $n = 1$, Eq. (33) is reduced to [see Eq. (7) in [42] or [43]]

$$\gamma - \gamma_0 = \Gamma_\infty RT[\ln(1-x) - kx^2/2]. \tag{34}$$

Except for the designations, the latter expression is identical to (18).

Parmon and Bukhtiyarov [47] discussed the surface restructuring induced by ideal multicomponent adsorption. Using "the Gibbs energy," they expressed the surface tension as [see the left- and right-hand parts of Eq. (3) in [47]; note also that a similar equation was used in [46]]

$$\sigma = \sigma_0 + \frac{kT}{s}\ln(1-\theta), \tag{35}$$

where σ_0 is the adsorbate-free surface tension, θ is "the total equilibrium coverage of the surface," s is "the surface area per adsorption site," and k is the Boltzmann constant. Ideal adsorption implies that the adsorbate-adsorbate interaction is negligible. Under this condition, Eq. (35) is identical to (17) [or (18) and (34) in the one-component case]. Physically, Eq. (35) describes the entropic contribution to the surface tension. In the case of chemisorbed species, this contribution is usually smaller than that related to the adsorbate-adsorbate interaction (Fig. 1).

The use of the Wulff rule in combination with DFT calculations was discussed by Barmparis and Remediakis [48] (see also Ref. [60]). They introduced the adsorbate-dependent surface tension for Au NCs as follows:

"The equilibrium shape of nanoparticles that interact with their environment can be found by means of a Wulff construction based on interface tensions, $\gamma_{hkl}^{\text{int}}$, between Au and its environment instead of surface tensions, γ_{hkl}. It turns out that the two are related by the simple formula

$$\gamma_{hkl}^{\text{int}} = \gamma_{hkl} + \theta\frac{E_{\text{ads}}}{A_{\text{at}}}, \tag{36}$$

where $\theta = N_{\text{ads}}/N_{\text{surface}}$ is the coverage (number of adsorbates, N_{ads}, over number of surface atoms, N_{surface}), $A_{\text{at}} = A/N_{\text{surface}}$ is the total surface area, A, over the total number of surface atoms, N_{surface}, and E_{ads} is the adsorption energy. Equation (36) includes implicitly the effects of adsorbate-adsorbate interactions, as both the adsorption energy and the equilibrium coverage depend on such interactions."

In (36), γ_{hkl} and $\gamma_{hkl}^{\text{int}}$ are, by definition, the surface tensions without and with adsorbate. The adsorbate-related contribution to the surface tension is represented in terms of adsorbate coverage as $\theta E_{\text{ads}}/A_{\text{at}}$. This contribution contains the full adsorbate binding energy, E_{ads}, including implicitly its main part, calculated in the low-coverage limit, and lateral adsorbate-adsorbate interaction. The contribution of this binding energy to the total energy is defined to be $N_{\text{ads}}E_{\text{ads}}$ [see Eq. (4) in [48]], i.e., its main part is negative [e.g., $E_{\text{ads}} = -0.36$ eV for CO adsorption on Au(110) at low coverages [48]], and in the case of repulsive adsorbate-adsorbate interaction (>0) this energy increases (its absolute value becomes smaller) with increasing coverage. Thus, the surface tension is predicted to contain the main part of the adsorbate binding energy and the part related to adsorbate-adsorbate interaction. The latter part increases with increasing coverage provided the adsorbate-adsorbate interaction is repulsive. Both of these predictions do not seem to be correct, because according to thermodynamics the surface tension is independent of the main part of the binding energy and decreases with increasing coverage in the case of repulsive adsorbate-adsorbate interaction (Sec. II).

Concerning (36), I can add that its structure is similar to that in (32). In particular, the adsorbate-related term is proportional to coverage in both expressions. In (32), the coefficients of proportionality (A_0 and A_1) are, however, not identified with the ratio of the adsorbate binding energy and the area per surface metal atom ($E_{\mathrm{ads}}/A_{\mathrm{at}}$) as in (36). Another more important remark is that (36) was widely used (sometimes without references) in theoretical studies (e.g., [49–58]) and presented in reviews (e.g., [60,61]). My commentaries in the paragraph above are directly applicable to these studies.

VI. CONCLUSION

As explained in Secs. I and V, the available theoretical studies scrutinizing the adsorbate-related part of surface tension in the context of its use in the Wulff rule for describing the shape on NCs are controversial. In Secs. II–IV, I have clarified the situation in this area in general and by employing the MF approximation. The key outcome of my analysis has already been summarized in the beginning of Sec. V. Its broad relevance to different areas of nanoscience is clear from the Introduction (Sec. I). Concerning the earlier results (Sec. V), my analysis confirms the equations proposed earlier for the one-component MF case by Lin *et al.* [41–44]. The corresponding entropic term is the same as that in Refs. [46,47].

Finally, I can add that besides the adsorbate-related factor, the Wulff rule has in the 10–100 nm scale many other interesting aspects. One of them is that the surface tension induces compressive strain in NCs, and this strain slightly influences the energetics of rate processes occurring at NCs (this effect has been mentioned in Sec. II with Ref. [62]). Another one already mentioned in the Introduction is that, with increasing temperature, there is a transition from the Wulff shape of NCs to the spherical shape described by the Kelvin model [21]. Another related area in which it is not obvious how the Wulff rule can be applied is the one that encompasses alloyed NCs (for the Ostwald ripening of such NCs, see, e.g., [63,64]).

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