Prediction of Co nanoparticle morphologies stabilized by ligands: towards a kinetic model

Van Bac Nguyen, Magali Benoit,* Nicolas Combe and Hao Tang

Cobalt nanoparticles (NPs) synthesized in liquid environments present anisotropic shaped nanocrystals such as disks, plates, rods, wires or cubes. Though the synthesis parameters (precursor, reducing agent, stabilizing ligands, concentration, temperature or rate of precursor injection) controlling the final morphologies are experimentally well controlled, little is known concerning the growth mechanisms at the atomic scale. In this work, we intend to predict the morphology variation of hcp cobalt NPs as a function of the ligand concentration. To this aim, we consider two well-established thermodynamic models and develop a new kinetic one. These models require the knowledge of the adsorption behaviors of stabilizing molecules as a function of surface coverage on preferential facets of NPs. To this end, density functional theory (DFT) calculations were performed on the adsorption of a model carboxylate ligand CH₃COO on different Co crystalline surfaces. The shapes of the Co NPs obtained by these models are compared to experimental morphologies and other theoretical results from the literature. While thermodynamic models are in poor agreement with experimental observations, the variety of shapes predicted by the kinetic model is much more promising. Our study confirms that the morphological control of NPs is mostly driven by kinetic effects.

1 Introduction

Nanoparticles or nanocrystals are some of the most important families of functional materials. Their nanometric size, associated with their composition, surface orientations, morphology and environment, has contributed to many important properties such as electronic, magnetic, catalytic, optical, etc. and to their applications in information storage and medical imaging, among others. To this end, morphological control is critical. Hence, many efforts have been devoted to understanding their formation mechanism and the origin of their stability.

Among metallic nanoparticles, cobalt with its hexagonal closed-packed (hcp) structure is particularly interesting because its growth can yield anisotropic shapes. Applications such as information storage or permanent magnets (due to their high magnetization and magneto-crystalline anisotropy energy) or catalysis can especially benefit from these anisotropic shapes.

Various morphologies of hcp Co NPs such as disks, platelets, rods and wires have been synthesized in liquid environments. The precursor, reducing agents, stabilizing ligands as well as concentration, temperature or the rate of precursor injection are all parameters on which the final Co NP morphology depends. If the final Co NP morphology dependence on the synthesis conditions is experimentally rather well controlled, little is known concerning the growth mechanisms at the atomic scale.

Our work precisely aims at uncovering the growth mechanism of Co NPs in liquid environments in order to be able to predict the NP morphologies. Compared to experimental investigations that remain very difficult, theoretical and numerical studies can provide some clues on the growth mechanism at the atomic scale. In this manuscript, we perform a theoretical and numerical study of the growth mechanism in order to predict the NP morphologies.

In the literature, two main classes of models have been used to tentatively explain the NP morphologies: thermodynamic models and kinetic models. Recently, Atmane et al. used thermodynamic arguments to qualitatively explain the various observed NP morphology (from a rod to a platelet) dependencies as a function of ligand concentration: using density functional theory (DFT), they calculated the Co-liquid interface energies as a function of ligand concentration and suggested that NPs should show larger facets corresponding to the lowest NP-liquid interface energies explaining the observation of NPs with a high aspect ratio. While Atmane et al. have fixed the ligand surface coverage by minimizing the interface energies, Bealing et al., working on PbSe nanocrystals (NCs), proposed to fix this ligand surface coverage as an adsorption isotherm similar to that of Langmuir. By applying the Wulff construction method, the equilibrium shapes of these PbSe NCs were then predicted to
change from a cube to an octahedron as a function of ligand concentration similar to observations performed on cobalt NPs. On the other hand, A. Barnard et al. proposed a kinetic surface area limited (SAL) model applied to the case of fcc gold NPs. Though the growth of these NPs does not involve any ligand, an interesting description of NP growth is proposed using this model based on a limited set of parameters which can be computed via first-principles calculations.

In this work, we intend to predict the morphology variation of hcp cobalt NPs as a function of the ligand concentration (or chemical potential variation). To this aim, we consider and compare several thermodynamic and kinetic models.

We first consider the predictions of the two cited thermodynamic models for Co NPs (the lowest interface energy model and an adsorption isotherm model) by determining the NP shape using the Wulff construction. These predictions will emphasize the fact that the rod-like morphology does not correspond to a thermodynamic equilibrium state as suggested by different experimental groups.

We then propose a kinetic model that describes explicitly the competition between the incorporation rate of Co atoms and the adsorption rate of ligands. Even if this model is relatively simple and relies on strong assumptions, it intends to go beyond the kinetic models of the literature by explicitly describing the evolution of the Co NP and of the Co and ligand concentration in the liquid. We show that this simple model is able to capture the main features of the morphological changes as a function of the ligand concentration and especially, to reproduce the various observed NP morphologies (from a rod to a platelet) in experiment.

In this manuscript, we reduce our study by focusing on a single model carboxylate ligand (CH$_3$COO) adsorbed on the three most stable surfaces of Co, i.e. (0001), (10–10) and (01–11). All the numerical calculations are based on DFT the technical details of which will be presented in the first section of this manuscript. The calculations of the pure Co surfaces, pure Co NP morphologies and ligand adsorption properties on the different Co facets will then be given. The following part of the paper are then devoted to the NP morphology predictions by the thermodynamic models and by the kinetic model.

Finally a discussion on the successes and failures of these different models is given together with suggestions for future improvements of the kinetic model.

## 2 Computational details

The calculations were performed using the VASP code version 5.3.3. PAW pseudopotentials for Co, C, O and H atoms were used with a cutoff energy for the plane wave basis set of 800 eV. For the exchange and correlation energy functional, since dispersion interactions are not properly accounted for with GGA functionals, we decided to consider three functionals: two modified functionals, the PBE functional with the Grimme correction (referred to as DFT-D in the following) and the Lundqvist functional with the modified optb86B, and we compared the results for bulk properties with those obtained with the PBE functional. Technically, a special k-point mesh of $21 \times 21 \times 21$ using the Monkhorst–Pack scheme was necessary to achieve a good convergence of Co bulk calculations (Table 1).

The PBE functional gives lattice parameters and the bulk modulus in very good agreement with experiments though the cohesive energy is not very well reproduced.

The dispersion corrected functionals for the bulk properties of Co are worse. However, since the dispersion interactions are known to be important for the simulations of adsorbed molecules on a metal surface, we tried to benefit from the good agreements given by the PBE functional for the Co bulk properties and the dispersion corrected functional for the interaction between adsorbed molecules and Co atoms: we used the PBE functional but a Grimme correction will be added to describe the interaction between atoms of adsorbed molecules and of the metal surface. This method appears as a good compromise to include dispersion interactions for adsorption properties and avoid the degradation of the bulk properties inside the Co slab by the dispersion interactions. Our choice results from the comparison of different functionals on the adsorption energy and on the Co–O distances of a carboxylate radical CH$_3$COO$^-$ on the Co surface.

### 3 Pure Co: surface energies and NP morphologies

In this section, we calculate the surface energies of pure Cobalt for various surface orientations and deduce the equilibrium shape of a Co NP in vacuum.

Technically, surface energy calculations are carried out using simulation cells made of a slab of 15 atomic layers, periodic in the $x$ and $y$ directions, and with the surface of interest perpendicular to the $z$ direction. For the determination of the surface energies, a vacuum of at least 12 Å was necessary to avoid interactions between the slab images. In that case, a $k$-point mesh of $21 \times 21 \times 1$ was needed.

Table 2 presents the surface energies for pure cobalt for various orientations.

The (0001), (10–10) and (01–11) surface orientations present the lowest surface energies. From Table 2, the equilibrium morphology of a Co nanoparticle in vacuum was calculated using the Wulff construction: Fig. 1 displays this equilibrium shape.

The equilibrium morphology presents a very weak anisotropy.
Table 2  Surface energies of Co in vacuum

<table>
<thead>
<tr>
<th>Facet</th>
<th>$\gamma$ [eV Å$^{-2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0001)</td>
<td>0.132</td>
</tr>
<tr>
<td>(10–10)</td>
<td>0.140</td>
</tr>
<tr>
<td>(01–11)</td>
<td>0.149</td>
</tr>
<tr>
<td>(2110)</td>
<td>0.156</td>
</tr>
<tr>
<td>(1–102)</td>
<td>0.157</td>
</tr>
<tr>
<td>(10–12)</td>
<td>0.158</td>
</tr>
<tr>
<td>(1–100)</td>
<td>0.175</td>
</tr>
</tbody>
</table>

Fig. 1  Wulff equilibrium shape of a Co nanoparticle in vacuum.

Table 3  Adsorption energies of CH$_3$COO on the different surfaces of Co at different normalized coverages

<table>
<thead>
<tr>
<th>Surface</th>
<th>Supercell size</th>
<th>Number of ligands</th>
<th>Normalized coverage</th>
<th>$\theta$ [Å$^{-2}$]</th>
<th>$E_{\text{ads}}$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0001)</td>
<td>4 x 2</td>
<td>4</td>
<td>1</td>
<td>0.093</td>
<td>-2.036</td>
</tr>
<tr>
<td></td>
<td>2 x 3</td>
<td>2</td>
<td>2/3</td>
<td>0.062</td>
<td>-3.431</td>
</tr>
<tr>
<td></td>
<td>2 x 2</td>
<td>1</td>
<td>1/2</td>
<td>0.046</td>
<td>-3.363</td>
</tr>
<tr>
<td></td>
<td>2 x 3</td>
<td>1</td>
<td>1/3</td>
<td>0.031</td>
<td>-3.328</td>
</tr>
<tr>
<td>(10–10)</td>
<td>2 x 2</td>
<td>4</td>
<td>1</td>
<td>0.099</td>
<td>-1.993$^a$</td>
</tr>
<tr>
<td></td>
<td>2 x 2</td>
<td>3</td>
<td>2/3</td>
<td>0.066</td>
<td>-3.233$^a$</td>
</tr>
<tr>
<td></td>
<td>4 x 2</td>
<td>4</td>
<td>1/2</td>
<td>0.050</td>
<td>-3.644</td>
</tr>
<tr>
<td></td>
<td>2 x 3</td>
<td>1</td>
<td>1/3</td>
<td>0.033</td>
<td>-3.692</td>
</tr>
<tr>
<td></td>
<td>2 x 2</td>
<td>1</td>
<td>1/4</td>
<td>0.025</td>
<td>-3.651</td>
</tr>
<tr>
<td>(01–11)</td>
<td>2 x 2</td>
<td>4</td>
<td>1</td>
<td>0.087</td>
<td>-1.396$^a$</td>
</tr>
<tr>
<td></td>
<td>2 x 3</td>
<td>4</td>
<td>2/3</td>
<td>0.058</td>
<td>-2.901$^a$</td>
</tr>
<tr>
<td></td>
<td>2 x 2</td>
<td>2</td>
<td>1/2</td>
<td>0.043</td>
<td>-3.567</td>
</tr>
<tr>
<td></td>
<td>2 x 3</td>
<td>1</td>
<td>1/3</td>
<td>0.029</td>
<td>-3.574</td>
</tr>
<tr>
<td></td>
<td>2 x 4</td>
<td>1</td>
<td>1/4</td>
<td>0.023</td>
<td>-3.717</td>
</tr>
</tbody>
</table>

The adsorption energies are computed using the following equation:

$$E_{\text{ads}} = \frac{1}{n_{hkl}} \times (E_{\text{Co}^\text{L}}^{\text{Co}^\text{L}} - E_{\text{Co}^\text{L}}^\text{ads} - E^L)$$  \hspace{1cm} (2)$$

where $n_{hkl}$ is the number of adsorbed ligands on the Co (hkl) facet, $E_{\text{Co}^\text{L}}^{\text{Co}^\text{L}}$ is the total energy of the system made of the Co slab and the adsorbed ligands, $E_{\text{Co}^\text{L}}^\text{ads}$ is the total energy of the Co relaxed slab and $E^L$ is the energy of a ligand molecule in vacuum.

CH$_3$COO adsorbs preferentially on the top positions, forming two Co-O bonds of $\approx$1.95 Å. For the (0001) surface, this adsorption configuration is preserved for all investigated coverages. For the (10–10) and (01–11) surfaces, the highest possible coverages for this adsorption configuration are $\theta = 0.050$ Å$^{-2}$ for (10–10) and $\theta = 0.043$ Å$^{-2}$ for (01–11). It is possible to increase the coverage of these surfaces by considering alternative adsorption sites. For instance, for $\theta = 0.066$ Å$^{-2}$ on the (10–10) surface, 2 ligand molecules can be adsorbed on the top sites while 2 other ligand molecules are adsorbed with one O atom in the top position and the other on the hollow site.

The calculated adsorption energies are reported in Table 3 for the different coverages $\theta$. For each calculation, the size of the super-cell, the number of ligands per super-cell, and the coverage are mentioned. The presence of adsorption configurations different from the top positions is explicitly mentioned in Table 3.

The adsorption energy of CH$_3$COO strongly varies with the coverage: the minimum adsorption energy is obtained for the normalized coverage of 2/3 for the (0001) facet, 1/3 for the (10–10) facet and 1/4 in the case of the (01–11) facet.

Fig. 2 shows the variation of $E_{\text{ads}}$ as a function of the coverage $\theta$ per surface unit, for each studied facet. The adsorption energies on the (10–10) and (01–11) facets show a strong increase for $\theta \geq 0.05$ Å$^{-2}$. This increase comes from the fact that, for these two facets, it is not possible to maintain the (the aspect ratio is roughly 0.94). The predominant facets of the equilibrium morphology are (0001), (10–10) and (01–11) justifying our choice (mentioned in the introduction) to focus only on these facets in the following.

4 Adsorption properties

In this section, we calculate the adsorption energies of the carboxylate radical CH$_3$COO$^-$ ligand on the Co surface for different Co surface orientations and different coverages. The coverage is here defined as the number of adsorbed ligands per surface unit: $\theta_{hkl} = \frac{n_{hkl}}{S_{hkl}}$, with $n_{hkl}$ being the number of adsorbed ligands on the area $S_{hkl}$. In the following, for convenience, we will also use the normalized coverage $\Theta$, defined as:

$$\Theta_{hkl} = \frac{\theta_{hkl}}{\theta_{hkl}^{\text{max}}}$$  \hspace{1cm} (1)$$

where $\theta_{hkl}^{\text{max}}$ is the maximum possible coverage on the (hkl) facet. $\Theta_{hkl}$ simply refers to the number of adsorbed ligands divided by the number of adsorption sites and thus presents the advantage of ranging between 0 and 1. Of course, $\theta_{hkl}$ and $\Theta_{hkl}$ are proportional and one or the other can be freely used according to the context.

Technically, the calculation of the adsorption energies is performed on slabs of 4 layers (the size of the slabs was reduced in order to reduce the computational cost) with the 2 bottom layers fixed at the bulk positions. Super-cells made of multiples of the unit cell in the x and y directions were then constructed in order to describe the different coverages and the number of $k$-points decreased accordingly.

$$E_{\text{ads}} = \frac{1}{n_{hkl}} \times (E_{\text{Co}^\text{L}}^{\text{Co}^\text{L}} - E_{\text{Co}^\text{L}}^\text{ads} - E^L)$$  \hspace{1cm} (2)$$

$^a$These numbers correspond to the average adsorption energies of molecules in two different adsorption configurations.
adsorption of the carboxylate on the “top” positions while increasing the coverage. The adsorption is therefore less favorable and the adsorption energy increases. For the (0001) facet, one can notice a small decrease of the adsorption energy for intermediate values of $\theta$ ($\approx 0.06 \text{ Å}^{-2}$) which might correspond to a stabilization of the ligands on the basal surface due to long range interactions.

The variation of $E_{\text{ads}}$ as a function of $\theta$ is the key factor to understand the ligand adsorption on the surfaces. Therefore, in order to build a growth model at the end of this manuscript, the adsorption energies as a function of the coverage must be fitted by a continuous function. The choice of the function form was based on the fact that interactions between the molecules are of the van der Waals type and can be approximated by a Lennard-Jones type potential $V(r) = A/r^6 - B/r^{12}$, where $A$ and $B$ are parameters and $r$ is the distance between the adsorbed molecules. Since the coverage $\theta$ is proportional to $1/r^2$, the following polynomial function has been adopted for the fit: $E_{\text{ads}} = a + b \times \theta^3 + c \times \theta^6$, where $a$, $b$, and $c$ are adjustable parameters. The resulting fits for the three facets are displayed in Fig. 2 as continuous lines. For the (0001) facet, the fit by the polynomial function is very good whereas for the two other facets, deviations from the points can be observed.

5 Thermodynamic models

In this section, we present two thermodynamic models allowing the prediction of the NP morphologies: the “lowest interface energy” model and the “adsorption isotherm” model. These models are applied to the particular case of the Co NP stabilized by the CH$_3$COO molecules. Both models use the DFT calculations of the interface energy given in the previous section and the Wulff construction. The main difference between these models resides in the assumptions made to find the ligand coverage at equilibrium.

Below, we first present the definition and calculations of the interface energies before giving the results for both thermodynamic models.

5.1 Interface energy

The interface energy $\gamma_{hkl}^{\text{int}}$ between the cobalt (hkl) facet with the adsorbed ligand molecules and the liquid is given by:

$$\gamma_{hkl}^{\text{int}} = \gamma_{hkl} + \theta_{hkl} \times E_{hkl}^{\text{ads}}(\theta_{hkl}) - \theta_{hkl} \times \Delta \mu$$

where $\gamma_{hkl}$ is the surface energy of the pure Co(hkl) facet in vacuum before the adsorption of the ligands, $E_{hkl}^{\text{ads}}(\theta_{hkl})$ is defined as the adsorption energy of a ligand molecule on the Co(hkl) facet (depending on the $\theta_{hkl}$ coverage), and $\Delta \mu = \mu(c,T) - \mu^{\text{vac}}$ is the chemical potential energy difference of the ligand in the solution at concentration $c$ and temperature $T$, and in vacuum.

This definition of the interface energy implies several important assumptions. First, the solvent effects on the adsorption energy of the molecule on the metallic surface are neglected. Second, the adsorption energies are not modified by the temperature effects. Indeed, in principle, the adsorption of the ligand molecule takes place at a finite temperature whereas DFT calculations compute the adsorption energies at 0 K. In their work on Fe nanoparticles stabilized by ligands, Fischer et al. have shown that it is possible to take into account the temperature effects on adsorption energies, and that the main contribution comes from the vibrational entropy of the molecules adsorbed on the surfaces. This entropy contribution can be approximated by considering the vibrational frequencies of the molecules. In the present case, the vibrational frequencies of the CH$_3$COO molecules adsorbed on the different facets of interest have been evaluated using finite difference calculations. The vibrational density of states does not strongly depend on the facet orientation. We therefore considered that this entropy term could be omitted when comparing the different facet interface energies at a constant temperature.

In eqn (3), the difference of chemical potential $\Delta \mu$ is unknown. $\Delta \mu$ is related to the concentration of ligands in solution by

$$\Delta \mu = \Delta \mu_0 + k_B T \ln \left( \frac{c}{c_{\text{ref}}} \right)$$

where $\Delta \mu_0 = \mu(T,c_{\text{ref}}) - \mu^{\text{vac}}$ is the difference between the chemical potential of the ligand in vacuum and in the solution at the reference concentration $c_{\text{ref}}$. Changing the concentration of ligands in solution is thus physically equivalent to change $\Delta \mu$. In the following, we have chosen to use $\Delta \mu$ as a varying parameter and we will thus never refer to the concentration of ligands in solution.

The evolution of the interface energies as a function of $\Delta \mu$ is reported in Fig. 3 for each facet and each normalized coverage.

From Fig. 3, the bare (0001), half-covered (10–10) and 2/3 covered (0001) facets have the lowest interface energies, respectively, for $\Delta \mu < -3.45 \text{ eV}$, $-3.45 \text{ eV} < \Delta \mu < -3.31 \text{ eV}$ and $\Delta \mu > -3.31 \text{ eV}$. Our results are similar to those of the study of Atmane et al., except that $\Delta \mu$ boundaries slightly differ. These discrepancies come from the difference in the functional used.
in the DFT calculations and especially from the treatment of dispersion interactions.

### 5.2 Lowest interface energy model

For a given \( \Delta \mu \), the lowest interface energy model considers that the ligand normalized coverage \( \Theta_{hkl} \) of a \( (hkl) \) facet is determined by minimizing the interface energy. From these minimum interface energies, the NP morphologies are constructed using the Wulff construction.

Fig. 4 reports these Wulff polyhedra for \( \Delta \mu = -4.0 \) eV, \( \Delta \mu = -3.43 \) eV, \( \Delta \mu = -3.0 \) eV and \( \Delta \mu = -2.0 \) eV.

For \(-4 \) eV < \( \Delta \mu < -3 \) eV, these polyhedra are very similar to the one reported at \( \Delta \mu = -4.0 \) eV and are analogous to the polyhedra of the pure Co NP reported in Fig. 1 (excepted that only three facets are considered here compared to the seven ones used in Fig. 1). When increasing the difference of chemical potential \( \Delta \mu \), the NP morphology slightly evolves to reach an almost prismatic shape with an aspect ratio of 0.92 at \( \Delta \mu = -2 \) eV.

Experimentally, the morphology of Co NPs stabilized by carboxylate molecules has been found to evolve from nanorods to nanodisks as a function of the concentration of the ligands in solution. Aspect ratios vary from values as high as \( \approx 10 \) to \( \approx 0.3 \) for the disks while the concentration of ligands is varied by a factor 2. Since a variation of the concentration of ligands by a factor 2 corresponds to a variation in \( \Delta \mu \) of approximately 0.027 eV at 450 K, we conclude that the lowest interface energy model is not able to explain the different experimental shapes.

### 5.3 Adsorption isotherm

In the previous model, the interface energies used in the Wulff construction were the minimum ones with respect to the coverage, \( \Theta \). Instead, C. Bealing et al. have proposed to use an “equilibrium” coverage for each facet which is controlled by the concentration of the ligands in the solvent and the temperature.\(^{11}\) Physically, such an assumption implies that the ligand coverage on each facet is provided by an equilibrium between absorbed ligands and ligands in the liquid phase. This equilibrium normalized coverage \( \Theta_{hkl}^{eq} \) for the \( (hkl) \) facet can be derived from the Langmuir isotherm which is based on the probability of adsorbing and desorbing a ligand on the \( (hkl) \) surface.

In the following, we will apply the model proposed by C. Bealing et al. to the present case of the Co NP stabilized by CH\(_3\)COO ligands. Let us consider the free enthalpy difference between the ligand in the solution and once adsorbed, for each \((hkl)\) facet:

\[
\Delta G_{hkl} = \mu_{ads}(T, \Theta_{hkl}) - \mu(T,c)\text{.}
\]

where \( \mu_{ads}(T, \Theta_{hkl}) \) and \( \mu(T,c) \) are, respectively, the chemical potential of the adsorbed ligand (at temperature \( T \) and normalized coverage \( \Theta(hkl) \)) and the chemical potential of the ligand in solution (at temperature \( T \) and concentration \( c \)). Eqn (6) is deduced from the relation between the adsorption energy of the ligand on \( (hkl) \) facet and in vacuum assuming again that solvent effects are negligible:

\[
E_{ads}(\Theta_{hkl}) = \mu_{ads}(T, \Theta_{hkl}) - \mu_{vac}\text{.}
\]

The equilibrium coverage \( \Theta_{eq}^{hkl} \) for the \((hkl)\) facet is then given by:\(^{11}\)

\[
\Theta_{hkl}^{eq} = \frac{e^{-\Delta G_{hkl} / k_{B}T}}{1 + e^{-\Delta G_{hkl} / k_{B}T}}\text{.}
\]

Eqn (9) is related to Langmuir’s isotherm when \( E_{ads}^{hkl}(\Theta_{hkl}) \) does not depend on \( \Theta_{hkl} \).

Using the polynomial fits of the \( E_{ads,vac}(\theta_{hkl}) \) curves, it is possible to solve eqn (9) numerically to find the equilibrium coverage for each facet and for each value of \( \Delta \mu \). Fig. 5 presents the resulting equilibrium normalized coverages for the three investigated facets. For all facets, the equilibrium normalized coverage is zero for small values of \( \Delta \mu \) and then increases until it reaches the maximum value of \( \Theta_{eq}^{hkl} = 1 \). The two \((10–10)\) and \((01–11)\) facets (red and green lines) behave similarly and are monotonous functions of \( \Delta \mu \) but the \((10–10)\) facet reaches the maximum coverage for a smaller \( \Delta \mu \) than the \((01–11)\) facet.

The \((0001)\) facet presents a peculiarity which is due to the non-monotonous \( E_{ads}^{hkl}(\Theta_{hkl}) \) function (see Fig. 2 for this facet). Between \(-3.42 \) eV and \(-3.33 \) eV, there are 3 values of \( \Theta_{eq}^{(0001)} \) satisfying eqn (9) for a given value of \( \Delta \mu \) (dotted blue line in Fig. 5).
Assuming that, during the first growth steps, there are no ligands on the surface and that the ligand coverage increases progressively, we chose to replace this ill-defined region by the solid blue line in Fig. 5. Note that this assumption should hardly affect the final results due to the very limited range of $D_m$ values involved.

From the knowledge of the equilibrium coverage $Y_{eq}^{hkl}$, one can compute the interface energies for each considered facet at equilibrium from eqn (3) as a function of $D_m$. Fig. 6 reports the interface energies for the three considered facets as a function of $D_m$. Fig. 6 also reports the corresponding NP equilibrium shapes calculated using the Wulff construction for $D_m = 4.0$ eV, $3.0$ eV, $2.0$ eV and $1.0$ eV. From Fig. 6, one can clearly see that the differences between the interface energies of the three facets roughly remain constant for $\Delta \mu < -2.0$ eV, giving basically the same Wulff polyhedron. For $\Delta \mu > -2.0$ eV, the differences between the interface energies increase.

For $\Delta \mu < -2.0$ eV, the NP morphology is very close to those calculated using the lowest interface energy model, i.e. an ovoid-like polyhedron (aspect ratios of 0.94 for $\Delta \mu = -4.0$ eV, 0.92 for $\Delta \mu = -3.0$ eV and 0.93 for $\Delta \mu = -2.0$ eV). For $\Delta \mu > -2.0$ eV, the differences between the interface energies become larger and the morphology changes to a prism again similar to the results of the lowest interface energy model (an aspect ratio of 0.81 for $\Delta \mu = -1.0$ eV for instance). For the reasons cited above for the lowest interface energy model, the adsorption isotherm model is thus not able to explain the various experimental shapes of Co NPs stabilized by ligands, i.e. the rod-like and disk-like shapes presenting aspect ratios ranging from 10 to 0.3.

5.4 Summary

These two thermodynamic models are commonly used in the literature to predict or explain the morphologies of the chemically synthesized NPs. These models are very simple and based on important assumptions, among which the neglected solvent effects and the fact that the morphologies are driven by equilibrium properties. In the case of Co NPs, these models clearly fail in predicting the experimental morphologies as a function of the difference in chemical potential $\Delta \mu$ and thus of the ligand concentration.

In the following, in order to go beyond the thermodynamic model and to better describe experimental observations, we propose and study a simple model which takes into account the growth kinetics of these NPs.

6 Kinetic model

In this model, we describe the NP growth by taking explicitly into account the Co atom adsorption rate and the ligand adsorption rate on the different NP facets. As for the thermodynamic models, we reduce our study to three facets, (0001), (10–10) and (01–11), and the ligand molecule is CH₃COO. We describe the NP shape using $L_{hkl}$, the distances from the NP center to the ($hkl$) facets, and $S_{hkl}$ which denote the surfaces of the ($hkl$) facets. Fig. 7 schematically displays a NP and reports the quantities $L_{hkl}$ and $S_{hkl}$.

Our kinetic model relies on three ingredients and provides a complete set of three coupled differential equations describing the kinetic of the Co NP growth. The ingredients are the following:
• the normal growth speed of a Co facet which depends on the incorporation rate of Co atoms in the NP
• the conservation of the number of Co atoms in the system
• the adsorption rate of ligands on the NP facets

6.1 Normal growth speed of a Co facet

Each facet is considered as a set of independent Co sites that can or cannot be covered by ligands. We assume that a Co can only be absorbed on Co sites non-covered by ligands and that a Co covered by a ligand cannot desorb. The number \( N_{\text{hkl}} \) of adsorbed Co atoms on the \((hkl)\) facet depends on the rate of adsorption and desorption of a Co atom and on the number of available sites:

\[
\frac{dN_{\text{hkl}}}{dt} = \frac{p_{\text{hkl}}^{\text{Co,ads}}}{p_{\text{hkl}}} \left(N_{\text{tot}}^{\text{hkl}} - 2 \times n_{\text{hkl}}^L\right) - \frac{p_{\text{hkl}}^{\text{Co,des}}}{p_{\text{hkl}}} \left(N_{\text{tot}}^{\text{hkl}} - 2 \times n_{\text{hkl}}^L\right)
\]  

(10)

where \( p_{\text{hkl}}^{\text{Co,ads}} \) and \( p_{\text{hkl}}^{\text{Co,des}} \) are the adsorption and desorption rates of a single Co on the \((hkl)\) facet, \( N_{\text{tot}}^{\text{hkl}} \) is the total number of Co adsorption sites of the \(S_{\text{hkl}}\) surface, and \( n_{\text{hkl}}^L(t) \) is the number of ligands adsorbed on the \((hkl)\) facet. Note that, in the case of CH₃COO molecules absorbed on the Co surface, one ligand adsorbs on two Co adsorption sites so that the number of available Co sites on facet \((hkl)\) is simply \( N_{\text{tot}}^{\text{hkl}} - 2 \times n_{\text{hkl}}^L \).

The detailed balance of the adsorption/desorption rates of the Co atoms relates the adsorption and desorption rates to thermodynamic quantities:

\[
\frac{p_{\text{hkl}}^{\text{Co,des}}}{p_{\text{hkl}}^{\text{Co,ads}}} = \exp\left[\left(\mu_{\text{Co}}^{\text{NP}}(T) - \mu_{\text{Co}}^{\text{sol}}(T, c_{\text{Co}}(t))\right)/k_B T\right]
\]  

(11)

where \( \mu_{\text{Co}}^{\text{NP}}(T) \) and \( \mu_{\text{Co}}^{\text{sol}}(T, c_{\text{Co}}(t)) \) are the chemical potentials of Co at temperature \( T \), respectively, in the NP and in the solution at concentration \( c_{\text{Co}}(t) \) at time \( t \). The chemical potential of Co in the solution reads:

\[
\mu_{\text{Co}}^{\text{sol}}(T, c_{\text{Co}}(t)) = \mu_{\text{Co}}^{\text{sol}}(T, c_1) + k_B T \ln \frac{c_{\text{Co}}(t)}{c_1}
\]  

(12)

where \( c_1 \) is a reference concentration. Choosing \( c_1 \) as the concentration at which the Co in the solution is in equilibrium with the Co in the solid phase of the NP (at temperature \( T \)) i.e. \( \mu_{\text{Co}}^{\text{sol}}(T, c_1) = \mu_{\text{Co}}^{\text{NP}}(T) \), we simply get:

\[
\mu_{\text{Co}}^{\text{NP}}(T) - \mu_{\text{Co}}^{\text{sol}}(T, c_{\text{Co}}(t)) = -k_B T \ln \frac{c_{\text{Co}}(t)}{c_1}
\]  

(13)

So that, eqn (10) reads:

\[
\frac{dN_{\text{hkl}}}{dt} = p_{\text{hkl}}^{\text{Co,ads}} \left(1 - \frac{c_1}{c_{\text{Co}}(t)}\right) N_{\text{tot}}^{\text{hkl}} (1 - \Theta_{\text{hkl}}(t))
\]  

(14)

where we have used the definition of the normalized coverage \( \Theta_{\text{hkl}}(t) = 2n_{\text{hkl}}^L(t)/N_{\text{hkl}}^{\text{tot}} \). Finally by introducing the normal growth speed \( \frac{dL_{\text{hkl}}}{dt} \) of the \((hkl)\) facet, we get:

\[
\frac{dL_{\text{hkl}}}{dt} = \frac{dN_{\text{hkl}}}{dt} \frac{d\text{hkl}}{dL_{\text{hkl}}}
\]  

(15)

with \( d_{\text{hkl}} \) being the thickness of a Co monolayer perpendicular to the \([hkl]\) direction in the Co bulk. So, it is finally:

\[
\frac{dL_{\text{hkl}}}{dt} = p_{\text{hkl}}^{\text{Co,ads}} \left(1 - \frac{c_1}{c_{\text{Co}}(t)}\right) (1 - \Theta_{\text{hkl}}(t)) d_{\text{hkl}}
\]  

(16)

The growth of a given \((hkl)\) facet thus depends on the concentration \( c_{\text{Co}}(t) \) of Co in the solution and on the number of available sites on the facet (depending on \( \Theta_{\text{hkl}}(t) \)). We easily check that eqn (16) describes the following simple limited cases: (i) at equilibrium between the Co atoms in the liquid and in the NP, \( c_1 = c_{\text{Co}}(t) \), the growth stops in agreement with eqn (16), (ii) in the absence of available adsorption sites (\( \Theta_{\text{hkl}}(t) = 1 \)), the growth stops as well, and (iii) the normal growth speed of a facet is an increasing function of the Co concentration \( c_{\text{Co}}(t) \) in the solution.

6.2 Conservation of Co atoms

The total number \( N_{\text{Co}}^{\text{tot}} \) of Co atoms present in the system (NP + solution) must be conserved during the NP growth:

\[
\sum_{\text{hkl}} \frac{dN_{\text{hkl}}}{dt} + N_{\text{Co}}^{\text{tot}} \frac{d}{dt}\left(\frac{c_{\text{Co}}(t)}{c_1}\right) = 0
\]  

(17)

where \( c_0 = c_{\text{Co}}(0) \) is the initial Co concentration in the solution at the beginning of the growth process characterized by the absence of any NP in the solution.

The first term of eqn (17) takes into account the incorporation of Co into the NPs, while the second describes the variation of Co atoms in the solution.

6.3 Ligand adsorption rate

During the NP growth, the ligands adsorb and desorb from the Co surface. The number \( n_{\text{hkl}}^L \) of absorbed ligands varies as a function of time following:

\[
\frac{dN_{\text{hkl}}^L}{dt} = \frac{1}{2} \frac{d}{dt}(\Theta_{\text{hkl}}(t)L_{\text{hkl}}^{\text{tot}})
\]  

(18)

\[
= \frac{N_{\text{tot}}^{\text{hkl}}}{2} \left[p_{\text{hkl}}^{\text{L,ads}} (1 - \Theta_{\text{hkl}}(t)) - p_{\text{hkl}}^{\text{L,des}} \Theta_{\text{hkl}}(t)\right]
\]

where \( p_{\text{hkl}}^{\text{L,ads}} \) and \( p_{\text{hkl}}^{\text{L,des}} \) are the adsorption and desorption rates of ligands on the \((hkl)\) facet, and \( N_{\text{tot}}^{\text{hkl}} \) is the total number of Co adsorption sites on the \((hkl)\) surface. \( \Theta_{\text{hkl}}(t) \) is the ligand coverage at time \( t \). Note again that one ligand adsorbs on 2 Co adsorption sites. We assume that ligands can only adsorb on available Co sites.

The detailed balance of the adsorption and desorption processes of ligands reads:

\[
\frac{p_{\text{hkl}}^{\text{L,ads}}}{p_{\text{hkl}}^{\text{L,des}}} = \exp\left[-\left(\mu_{\text{ads}}^{\text{NP}}(T, \Theta_{\text{hkl}}) - \mu(T, c)\right)/k_B T\right]
\]  

(19)

where \( \mu_{\text{ads}}^{\text{NP}}(T, \Theta_{\text{hkl}}) \) and \( \mu(T, c) \) are the chemical potentials of the adsorbed ligands and of the ligands in solution at concentration \( c \) and temperature \( T \). As already mentioned, the chemical potential difference \( \mu_{\text{ads}}^{\text{NP}}(T, \Theta_{\text{hkl}}) - \mu(T, c) \) can be related to the adsorption energies computed in DFT via:

\[
\mu_{\text{ads}}^{\text{NP}}(T, \Theta_{\text{hkl}}) - \mu(T, c) = E_{\text{ads}}(\Theta_{\text{hkl}}) - \Delta \mu
\]  

(20)
Therefore:
\[
\frac{P_{L_{hkl}}^{\text{Lads}}}{P_{L_{hkl}}^{\text{Co ads}}} = \exp\left(\frac{-E_{hkl}^{\text{Lads}}(\theta_{hkl}) + \Delta \mu}{k_B T}\right)
\] (21)

In the following, we assume that the concentration of ligands in the solution does not change during the NP growth. This is justified by the fact that only a small fraction of ligands in the solution are expected to be captured by the NP surfaces, so that the ligand concentration hardly varies during the growth. Using eqn (21) and (18) reads:
\[
\frac{d}{dt}(\theta_{hkl}(t)N_{hkl}^{\text{tot}}) = N_{hkl}^{\text{tot}}P_{L_{hkl}}^{\text{Lads}}\left[1 - \theta_{hkl}(t) - \exp\left((E_{hkl}^{\text{Lads}}(\theta_{hkl}) - \Delta \mu)/k_B T\right)\right]
\] (22)

Note that eqn (22) allows us to recover the adsorption isotherm: at equilibrium, the number of ligands on the facets should not vary, \(d(\theta_{hkl}(t)N_{hkl}^{\text{tot}})/dt = 0\), so that:
\[
1 - \theta_{hkl}^\text{eq} - \exp\left((E_{hkl}^{\text{Lads}}(\theta_{hkl}^\text{eq}) - \Delta \mu)/k_B T\right) = 0
\] (23)
and
\[
\theta_{hkl}^\text{eq} = \frac{\exp\left(-E_{hkl}^{\text{Lads}}(\theta_{hkl}^\text{eq}) + \Delta \mu\right)/k_B T}{1 + \exp\left(-E_{hkl}^{\text{Lads}}(\theta_{hkl}^\text{eq}) + \Delta \mu\right)/k_B T}
\] (24)

Eqn (24) actually corresponds to the adsorption isotherm eqn (9).

During the growth, the total number of sites \(N_{hkl}^{\text{tot}}\) on a facet increases with time. However, its derivative with respect to time is expected to be small compared to \(d(\theta_{hkl}(t)/dt\) so that we neglect the variation of \(N_{hkl}^{\text{tot}}\) with time in eqn (22). Finally, the ligand adsorption rate equation reads:
\[
\frac{d(\theta_{hkl}(t))}{dt} = P_{L_{hkl}}^{\text{Lads}}\left[1 - \theta_{hkl}(t) - \exp\left((E_{hkl}^{\text{Lads}}(\theta_{hkl}) - \Delta \mu)/k_B T\right)\right]
\] (25)

Eqn (16), (17) and (25) provide a complete set of equations enabling us to calculate the NP morphology evolution.

6.4 Modelling details

In order to solve eqn (17), (16) and (25), we need to first set the different parameters involved in these equations: \(P_{L_{hkl}}^{\text{Lads}}, P_{L_{hkl}}^{\text{Co ads}}, E_{hkl}^{\text{Lads}}, E_{hkl}^{\text{Co ads}}, \Delta \mu, c_0\) and \(N_{hkl}^{\text{tot}}\). The \(d_{hkl}\) parameters are deduced from the crystal structure of Co.

The DFT calculations of \(P_{L_{hkl}}^{\text{Lads}}\) and \(P_{L_{hkl}}^{\text{Co ads}}\) require the use of simulation techniques such as the nudged elastic band method\(^{18}\) able to capture the transition states. The rates \(P_{L_{hkl}}^{\text{Lads}}\) and \(P_{L_{hkl}}^{\text{Co ads}}\) presumably depend on the coverage \(\theta_{hkl}(t)\), on the ligands and Co concentrations in the solution and on the temperature. In addition, the solvent effects are presumably not negligible. Therefore, the calculations of \(P_{L_{hkl}}^{\text{Lads}}\) and \(P_{L_{hkl}}^{\text{Co ads}}\) are difficult and in any case would be computationally very demanding: such calculations are clearly out of the scope of this manuscript.

Since our goal here is to investigate the role of the kinetics in the NP morphologies, as a first approximation, we have assumed that the ratio \(P_{L_{hkl}}^{\text{Lads}}/P_{L_{hkl}}^{\text{Co ads}}\) does not depend on the coverage \(\theta_{hkl}(t)\) nor on Co or ligand concentrations in the solvent and nor on the facet orientation. This ratio \(P_{L_{hkl}}^{\text{Lads}}/P_{L_{hkl}}^{\text{Co ads}}\) physically corresponds to a parameter controlling the competition between ligands and cobalt incorporation.

We introduce the dimensionless parameter \(\lambda\) controlling this ratio:
\[
\lambda = \frac{P_{L_{hkl}}^{\text{Lads}}}{P_{L_{hkl}}^{\text{Co ads}}}\left(1 - \frac{c_1}{c_0}\right)
\] (26)

\[
\tau = \frac{1}{P_{L_{hkl}}^{\text{Co ads}}}\frac{C_{0\text{ads}}}{C_{0\text{tot}}}\left(1 - \frac{c_1}{c_0}\right)
\] (28)

\[
\tau\text{ can be used to introduce a dimensionless time } \tilde{t} = t/\tau.
\]

Similarly, we introduce dimensionless lengths:
\[
\tilde{L}_{hkl} = \frac{L_{hkl}}{d_{0001}}
\] (29)

Eqn (16), (17) and (25) now become:
\[
\frac{d(\theta_{hkl}(t))}{dt} = \lambda\left[1 - \exp\left((E_{hkl}^{\text{Lads}}(\theta_{hkl}) - \Delta \mu)/k_B T\right)\right]
\] (30)
\[
\sum_{hkl} \frac{dN_{hkl}}{dt} + N_{hkl}^{\text{tot}}\frac{c_0}{c_1} + c_0\frac{d(C_0(t))}{dt} = 0
\] (31)
\[
\frac{d\tilde{L}_{hkl}}{dt} = \frac{1 - c_1/c_0}{1 - c_1/c_0}(1 - \theta_{hkl}(t))\tau
\] (32)

The resolution of eqn (30)–(32) requires the setting of the following parameters:
- The initial size of the nanoparticle: \(L_{0001}, L_{10-10}\) and \(L_{01-11}\).
- The temperature \(T\).
- The total number of Co atoms \(N_{hkl}^{\text{Co}}\).
- The ratio \(c_0/c_1\) of the initial Co concentration \(c_0\) to the equilibrium concentration \(c_1\).
- \(\lambda\) which controls the Co and ligand adsorption rates.
- The chemical potential difference \(\Delta \mu\).

Initial seed size.

The chemical potential difference \(\Delta \mu\)

Temperature.

The temperature is fixed to 450 K corresponding to experimental growth conditions.
6.5 Results

Total number \( N_{\text{Co}}^{\text{tot}} \) of Co atoms and \( \frac{c_0}{c_1} \) ratio. We first investigate the role of the total number \( N_{\text{Co}}^{\text{tot}} \) of Co atoms and of the \( \frac{c_0}{c_1} \) ratio.

Since our model considers only the growth of one single NP, it does not describe the concentration of NPs in the solution. \( N_{\text{Co}}^{\text{tot}} \) is thus the number of available Co atoms per created NP. Since \( c_1 \) corresponds to the concentration of Cobalt in the liquid in equilibrium with the NP, the two parameters \( N_{\text{Co}}^{\text{tot}} \) and \( \frac{c_0}{c_1} \) determine the final volume \( V_{\text{NP}}^f \) of the nanoparticle at the end of the growth.

\[
V_{\text{NP}}^f = N_{\text{Co}}^{\text{tot}} \left(1 - \frac{c_1}{c_0}\right) \times \frac{V_b}{\mathcal{R}} \quad (33)
\]

where \( V_b \) is the molar volume in the Co bulk phase and \( \mathcal{R} \) the Avogadro number.

Fig. 8 shows the evolution of the NP size with different values of \( c_1/c_0 \) and \( N_{\text{Co}}^{\text{tot}} \). These simulations are done with \( \lambda = 1 \) and \( \Delta \mu = -3.0 \) eV. All these simulations are carried out until the concentration of Co in the solution is \( c_{\text{Co}}(t) = 1.000001 \times c_1 \). Under these conditions, the ligands reach the equilibrium coverage after less than a few \( \tau \).

In Fig. 8(a), the ratio \( c_1/c_0 = 0.01 \) is fixed, and dashed lines correspond to \( N_{\text{Co}}^{\text{tot}} = N_0 = 15.24 \times 10^6 \) and solid lines to \( N_{\text{Co}}^{\text{tot}} = N_0/8 \). As expected, the maximum size of the nanoparticle (size at the end of the growth) increases with the total number \( N_{\text{Co}}^{\text{tot}} \) of Co atoms in the system while the normal growth speeds of facets do not depend on \( N_{\text{Co}}^{\text{tot}} \).

In Fig. 8(b), the total number \( N_{\text{Co}}^{\text{tot}} \) of Co atoms is fixed and two \( c_1/c_0 \) ratios are investigated \( c_1/c_0 = 0.01 \) and \( c_1/c_0 = 0.5 \). The final NP size increases with the initial concentration \( c_0 \) of Co in the liquid.

In the following, in order to compare our results with experiments, we have fixed \( N_{\text{Co}}^{\text{tot}} \) and the ratio \( c_1/c_0 \) so that the NP size at the end of the growth is roughly 20 nm, corresponding to experimental observations. In addition, we have chosen the ratio \( c_1/c_0 \ll 1 \) i.e. a large supersaturation of Co in the liquid at the beginning of the growth. According to these two arguments, we have chosen \( N_{\text{Co}}^{\text{tot}} = 15.24 \times 10^6 \) and \( c_1/c_0 = 0.01 \) in the following.

\( \lambda \) and \( \Delta \mu \) parameters. The \( \lambda \) parameter controls the adsorption rate of ligands compared to the Co one while \( \Delta \mu \) controls the equilibrium ligand coverage.

We numerically solve eqn (30)–(32), and report the ratios between the characteristic lengths of the NP at the end of the growth in Fig. 9 as a function of \( \Delta \mu \) and for different values of \( \lambda = 1, 0.1, 0.01 \) and 0.001. In the following, we will call “aspect ratio”, the ratio between \( L_{(0001)} \) and \( L_{(10-10)} \), the characteristic distances defining the (0001) and (10–10) surfaces (see Fig. 7).

For the three values of \( \lambda = 1, 0.1 \) and 0.01, the graphs in Fig. 9 show strong similarities. Three different regions can be distinguished:

(1) for \( \Delta \mu < -3.45 \) eV, the two length ratios increase from 1 to values around 2 as a function of the difference in chemical potential \( \Delta \mu \). The morphology of the Co NP changes from a spherical shape to an elongated shape with a maximum aspect ratio of 2.39 which is reached for \( \Delta \mu = -3.45 \) eV.

(2) for \(-3.45 \) eV < \( \Delta \mu \) < \(-3.3 \) eV, the length ratios rapidly decrease from values around 2.4 and 1.9 for the (10–10) and (01–11) facets to values around 0.7 and 0.5, respectively. The NP adopts a disk-like shape with an aspect ratio of 0.68 for \( \Delta \mu = -3.3 \) eV.

(3) From \( \Delta \mu > -3.3 \) eV, the length ratios decrease smoothly and the shape of the NP remains disk-like with an aspect ratio of 0.49 for \( \Delta \mu = -2.0 \) eV.

One can understand these features by considering the extreme case where \( \lambda \) is high: in such a case, the ligand coverage would reach its equilibrium value much faster than the characteristic time of the Co growth. The ligand coverage tends very quickly to its equilibrium value shown in Fig. 5 and retains it all along the growth. Hence, for \( \Delta \mu < -3.45 \) eV, the ligand coverage on the (10–10) and (01–11) facets increases with \( \Delta \mu \) while the coverage on the (0001) facet still remains very small. This situation significantly reduces the normal growth speed of the (10–10) and (01–11) facets (because there are few available Co sites) whereas the (0001) facet is still growing at a speed roughly corresponding to its initial speed. As a result, the morphology of the Co NP changes from a spherical shape to a more elongated shape while increasing \( \Delta \mu \). These arguments agree with the NP morphologies reported in Fig. 9. The maximum aspect ratio corresponds to a situation where the (0001) surface is
not covered by ligands but the other surfaces are partially covered. For \(-3.45 \text{ eV} < \Delta \mu < -3.3 \text{ eV}\), the \(\Theta^\text{eq}\) coverage on the (0001) surface quickly increases with \(\Delta \mu\), thus reducing the normal growth speed with the consequence of decreasing the aspect ratio of the final NP morphologies. The change in \(\Delta \mu\) in this region is about \(2k_B T\) which is equivalent to an increase of \(\approx 7.3\) times the ligand concentration in the solution at 450 K. For \(\Delta \mu > -3.3 \text{ eV}\), the coverage on the (0001) surface becomes higher than the ones on the (10–10) and (01–11) facets, so that the aspect ratio of the final NP morphologies decreases.

If we can understand Fig. 9 for values of \(\lambda = 1, 0.1\) and 0.01 from the analysis of the expected growth at high \(\lambda\), the decrease of \(\lambda\) reduces the difference between the characteristic time needed by the ligand to reach the equilibrium coverage on a facet and the characteristic time of the Co growth. For small values of \(\lambda\), for instance \(\lambda = 10^{-3}\), the aspect ratio almost does not change with the difference of chemical potential: the ligands do not have enough time to reach their equilibrium coverage before the NP growth ends. The Co growth proceeds in the quasi-absence of ligands \((\Theta_\text{hkl}(t) \approx 0\) for all facet orientations) during the growth, so that the normal growth speeds for all the facets are equal, regardless of the orientation.

6.6 Discussion

Even relatively simple, the application of this model has shown several important kinetic aspects that are not present in the thermodynamic models:

1. The anisotropic shape evolution (from spherical, to elongated and to disk-like shape) as a function of the concentration of ligands.
2. The growth kinetic (time for a NP to reach its maximum size) as a function of \(\lambda\).
3. The evolution of the size as a function of the initial concentration of cobalt \(c_0\).

Obviously, the predicted morphologies are not in perfect agreement with the experimental ones: our kinetic model fails to predict NP morphologies with very high aspect ratios, such as the ones observed experimentally. But the kinetic model succeeds to predict rod-like (and disk-like) NPs with an aspect ratio significantly higher (lower) than the one predicted by the thermodynamic models. For these reasons, on the one hand, we believe that the interpretations or descriptions of experimental observations do require a kinetic model while thermodynamic models can only give simple clues on the growth process. On the other hand, the...
kinetic model proposed in this manuscript relies on several assumptions or approximations that presumably affect our results and would need some significant improvements.

- One of the key parameters of the kinetic model is the \( \lambda \) parameter which controls the ratio between the incorporation of Co and of the ligands on the Co surface. Clearly, \( \lambda \) as well as the adsorption rate of the ligands, \( \lambda_{\text{ads}} \), and of the Co atoms, \( \lambda_{\text{Co,ads}} \), presumably depends on the coverage \( \Theta_{\text{ads}}(t) \), on the concentration of ligands and Co in the liquid and on the surface orientations. By eluding these dependencies, a lot of physics of the NP growth is eluded. However, as already mentioned, these dependencies are very difficult to evaluate and are clearly out of the scope of this manuscript. We are currently working to try to address at least partly some of these issues.

- The dependence of \( \lambda, \lambda_{\text{ads}} \) and \( \lambda_{\text{Co,ads}} \) on the coverage \( \Theta_{\text{ads}}(t) \) is also related to the absence of correlation in the proposed kinetic model. Every Co site is independent, so that the rate of adsorption of the ligands or of the Co atoms on an available Co site does not depend on the presence of ligands on a neighboring Co site. Again, clearly, one can expect that such correlations might affect the growth. For instance, it seems to be reasonable to expect that the rate of adsorption of Co on an available Co site is decreased by the presence of a ligand on a neighboring Co site. Such an effect could, in principle, be taken into account in a mean field theory by introducing a non-linear dependence of the available Co site as a function of the coverage \( \Theta_{\text{ads}}(t) \) in eqn (32).

- The diffusion of the ligands and cobalt atoms on the Co surfaces has not been taken into account. As a consequence, our kinetic model does not predict that at an infinite long time, the NP morphologies tend to the Wulff equilibrium shapes. The main assumption here comes from the fact that we consider all the adsorption sites as independent. In this respect, our model differs from the SAL model\(^{13,39}\) in which the main driving forces of growth are dominated by the diffusion of the atoms from the bulk to the NP and on the surfaces. However, in the SAL model intended to describe the NP growth without ligands, the ligand adsorption and desorption rates are naturally not taken into account. The introduction of the surface diffusion of Co atoms or ligands in our kinetic model similar to the work done for the SAL model is one of the perspectives of our work.

- Finally, all the quantitative values (especially the adsorption energies) used in our model rely on DFT calculations eluding solvent effects and temperature effects. As mentioned, if temperature effects did not significantly impact the final NP morphology, realistic calculations including solvent effects are required. Unfortunately, state of the art DFT simulations hardly succeed in modeling these solvent effects or at a computational price not compatible with our system (involving a lot of configurations: different surfaces and coverage).

## 7 Conclusions

In this work, we have presented different models for the morphology prediction of Co NPs stabilized by the CH\(_3\)COO ligand. In the first part, two thermodynamic models were investigated: the lowest interface energy model and the adsorption isotherm model. The application of these two models has shown the evolution of the NP morphology as a function of the difference in the chemical potential of ligands (and thus of the ligand concentration). However, these thermodynamic equilibrium shapes failed to predict the rod-like form of the NPs observed in experiments. In order to take into account the kinetic effects on the morphology of the Co NPs, we propose a new model based on the competition between the adsorption rate of ligands and the incorporation rate of cobalt atoms. This model has shown its ability to predict elongated morphologies, quasi-spherical and disk-like shapes depending on the concentration of ligands in solution. This anisotropy of shape is thus clearly related to kinetics effects. Our kinetic model, even still relatively simple and relying on several arguable assumptions, is a promising method to explain the variety of forms of metallic NPs synthesized in solution.

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## References