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AN INTRODUCTION TO CORROSION MECHANISMS AND MODELS

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1.1 INTRODUCTION

The history of mankind is distinguished by the pronounced effort to understand the processes of nature and to manipulate these processes for the improvement of the human condition and survivability. One remarkable instance of this effort can be found in the realm of materials engineering; here, advances have been so significant that historical eras are frequently named by the materials that characterized them: the Stone Age, Bronze Age, and Iron Age [1]. Materials engineers in our present age have a significant number of alloy components and fabrication techniques at their disposal. Consequently, there is a vast range of properties for which materials can be tailor-made, based on considerations such as materials lifetime, strength, ductility, and temperature range. In the world of metals, corrosion is an ever-present concern, and there are an often bewildering number of modes via which materials failure by corrosion may occur, such as localized corrosion (pitting), stress corrosion

cracking, galvanic corrosion, crevice corrosion, uniform corrosion, or hydrogen embrittlement [2]. As in past ages, corrosion scientists and engineers of today must confront such problems by conceptualizing the modes *via* which these effects may occur, leading to direct testing of these hypotheses through a combination of modeling and experiment. Ultimately, the objective is to provide solutions, such as ever more durable materials and/or processes for current and future applications.

In the precomputation era, materials modeling was restricted to mechanical (i.e., physical, tangible) models, hypothetical *Gedanken* experiments, or analytic calculations based on the continuous phenomena known to materials physics. However, it is known that physicochemical processes such as corrosion ultimately occur as discrete, atomistic events that involve the making, breaking, or rearrangement of bonds between atoms, such as dissolution, substitution, and diffusion. To date, kinetic models for these processes have been fitted to experimental data in an effort to understand their relative importance and hence develop predictive models for corrosion rates. However, the ability to extrapolate such models to as yet unstudied conditions, in which case the mechanisms of corrosion may be subtly (or drastically) changed, is hindered by the lack of a first-principles justification for the values obtained from such fitting experiments. Empirical *rules of thumb* may be useful in, for example, identifying the relative importance of such alloying ingredients as chromium, molybdenum, or nitrogen to the corrosion resistance of a series of iron-based alloys under a given set of conditions [3]. However, such rules do not provide the fundamental insights as to the mechanism *via* which these effects occur, as would be necessary to significantly advance materials development. In an age where the ability to control materials design at the nanoscale is beginning to appear feasible, it is important to develop the theoretical tools to guide such low-level design effects and to reach levels of corrosion resistance optimization previously considered unthinkable.

Molecular modeling provides the ability to simulate and analyze hypothetical processes at the atomic level [4]. Such models have been used extensively in the realm of chemistry [4, 5], as well as in solid-state physics and materials science [6, 7]. Now, we have progressed to the point where the conjunction between chemistry and solid-state physics, namely, interfacial science, is also being tackled by such methods [8]. While heterogeneous catalysis initially dominated this particular application of molecular modeling to interfacial systems, the field of corrosion has recently been attracting more and more attention. This increase in interest can be seen from the analysis in Figure 1.1, which shows that the current interest in applying molecular modeling techniques (highlighted here as *molecular dynamics* and *density functional theory (DFT)*) to problems in corrosion science is roughly equivalent to the surge of interest that spurred the application of these techniques to problems in catalysis at the beginning of the twenty-first century.

Molecular modeling of corrosion, by definition, requires the construction of a model system, which consists of atoms and molecules, that is as faithful as possible a representation of the corroding system of interest. Since corroding systems contain an extraordinary degree of complexity—encompassing features such as: the microstructure of the material; the elemental composition; multiple phases including metals, alloys, and oxides; surface–solute–solvent interactions; and electrochemical interfaces—the construction of an appropriate model therefore requires an advanced understanding of corrosion mechanisms. As shown in Figure 1.2, interfacial processes such as corrosion lie at the intersection of chemistry and materials science. A particular challenge for molecular modeling is that, at least for present computers, only a finite number of atoms and molecules (somewhere between dozens and, at best, billions) can be simulated [9–11]. Thus, one must be especially judicious in choosing the

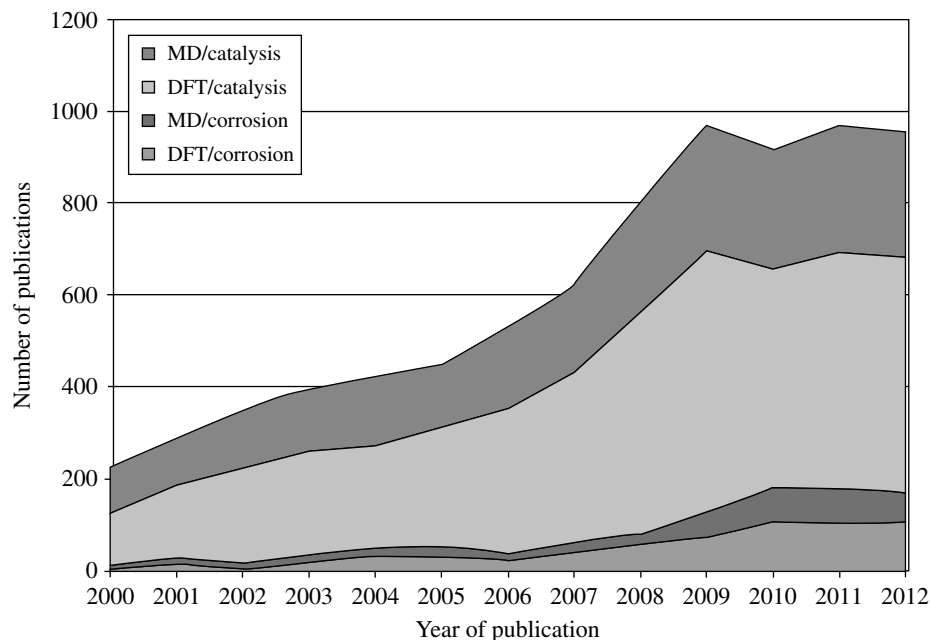


FIGURE 1.1 Number of peer-reviewed publications with topics *molecular dynamics* or *density functional theory* combined with either *catalysis* or *corrosion*. Data obtained from the Web of Knowledge database by Thomson Reuters, 2013. <https://access.webofknowledge.com/>.

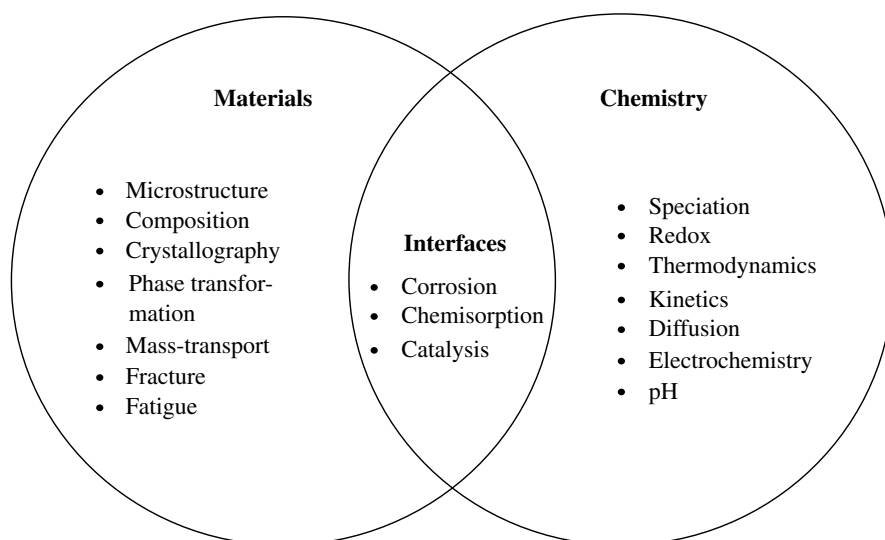


FIGURE 1.2 Interfacial problems, such as corrosion, occur at the intersection between materials science and chemistry.

representation of the corroding system (recall that even a billion atoms of Fe weigh $<1 \times 10^{-10}$ mg). The challenge is, therefore, significant; how does one model a macroscopic and inherently multiscale process such as corrosion using molecular modeling techniques? Approaches to tackle this challenge form the scope of this book. We begin in this chapter by introducing a series of corrosion mechanisms and then discuss the principal modeling techniques used to represent and simulate these systems from the molecular perspective.

1.2 MECHANISMS IN CORROSION SCIENCE

The conversion of metals back into their native oxide forms, or some similarly preferred thermodynamic state, can take many forms and can be exacerbated by various chemical or environmental conditions. Thus, corrosion itself has no single mechanism of action [12]. Various mechanisms have been proposed to account for effects such as atmospheric corrosion [13–15], chloride-induced pitting [16–25], sulfidation [26–40], acidic dissolution, crevice corrosion [13, 41–44], stress corrosion cracking [45–49], ammoniacal attack [18, 19, 23–25, 29–31, 33, 50], and so on. In order to make the following discussion as general as possible and to avoid going into detail regarding some of the more specific corrosion instances that will be addressed in later chapters, we here take the liberty of dividing corrosion processes into a number of sequential (although they often occur in parallel) steps, each of which may be subject to chemical and/or environmental modification. By categorizing the leading causes and mechanistic pathways of corrosion in this way, we will then show how, in each case, molecular modeling could feasibly be applied to provide greater insights into the fundamental processes and hence guide next-generation corrosion mitigation strategies and the design of corrosion-resistant materials.

The Collins English Dictionary [51] defines corrosion as:

a process in which a solid, especially a metal, is eaten away and changed by a chemical action, as in the oxidation of iron in the presence of water by an electrolytic process.

Corrosion is a chemical process that occurs at the solid/environment interface, that is, at the external or internal surface of a material where it meets a fluid (gaseous or solvent) phase. The sciences appropriate to the study of this process include: surface science; electrochemistry; physical, inorganic, and analytical chemistry; physics; materials science; metallurgy; and, finally, theory, which encompasses both modeling and simulation. The chief reactions that contribute to aqueous corrosion are electrochemical in nature and, for this reason, can be broken down into anodic metal dissolution and the corresponding cathodic reactions of hydrogen evolution and oxygen reduction [3]. Factors that may affect these reactions, and thus the overall process of corrosion, include the structure and composition of the bulk solid phase, as well as the composition of the electrolyte and the changes that these subsystems undergo during the process of corrosion.

This breakdown is given further elaboration in the list of topics that accompanies the Venn diagram in Figure 1.2. Small changes in materials microstructure, alloy composition, and mass-transport pathways (such as the *short-circuit* diffusion routes in passive oxide films) [52–57] can be particularly significant for the overall corrosion properties of the material. Similarly, phase transformations that occur as a function of temperature, or the impurity content at either grain boundaries or in the bulk, may again affect the resilience of a material to corrosion, especially when the material is also placed under mechanical strain (such as in instances of stress corrosion cracking). Even factors such as the materials texture [58],

grain-boundary engineering [55, 59, 60], and the crystallographic orientations that are exposed at the surface can affect its reaction with the environment.

From the chemistry side, the environmental conditions can be highly important. The pH may affect speciation of organic or mineral acid moieties, thus changing their propensity for surface reaction. Variations in the electrode potential (that can be induced galvanically, from the materials side, or chemically, via ionic concentration gradients in the electrolyte) can play a large role in biasing a system toward or away from passivation. The myriad of physical and chemical interactions that go into surface adsorption, bond breaking and bond formation, and solvation by the solution play a continuous role in mediating the overall thermodynamics and kinetics of corrosion reactions [61, 62]. Chemical species, such as inhibitors, can be introduced to bias the surface chemistry such that corrosion kinetics are subdued, whereas other chemical species (such as halides) can accelerate them [25b, c, 32, 38, 63, 64].

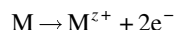
These two features of corrosion—materials control and environmental control—meet in the very processes that occur at the interface, which is the critical region where corrosion reactions take place, but is also the least understood [65–68]. Hence, there is a strong motivation for developing the theoretical framework via which these reactions can be simulated, predicted, and, ultimately, controlled.

1.2.1 Thermodynamics and Pourbaix Diagrams

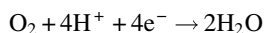
The starting point for the scientific understanding of chemical processes is thermodynamics. For a metal subject to aqueous, that is, electrochemical, corrosion, the scheme introduced by Marcel Pourbaix provides the framework for a first assessment of materials stability [69]. Pourbaix considered that the Gibbs free energy associated with an electrochemical reaction is a function of two key variables: the electrode potential and the pH. These two variables can be used to define the Gibbs free energy of the dissolution, oxidation, hydroxylation, and hydride reactions. Since these are the primary products of corrosion under aqueous conditions, a broad range of corrosion phenomena can be surveyed visually with Pourbaix's approach. This visual aspect is conveyed via the *Pourbaix potential–pH diagram*—a phase diagram that outlines the most stable phase (as defined by the phase with the lowest Gibbs free energy) in the two-dimensional space limited by reasonable values that can be expected for the pH and potential (typically between –2 and +2 V vs. normal hydrogen electrode (NHE) and pH 0–14). As an example, the Pourbaix diagram for iron is provided in Figure 1.3.

The electrochemical model for corrosion breaks the process down into anodic and cathodic *half-cell* reactions, each having their own equations, which may include:

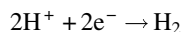
For dissolution:



For oxygen reduction:



For hydrogen reduction:



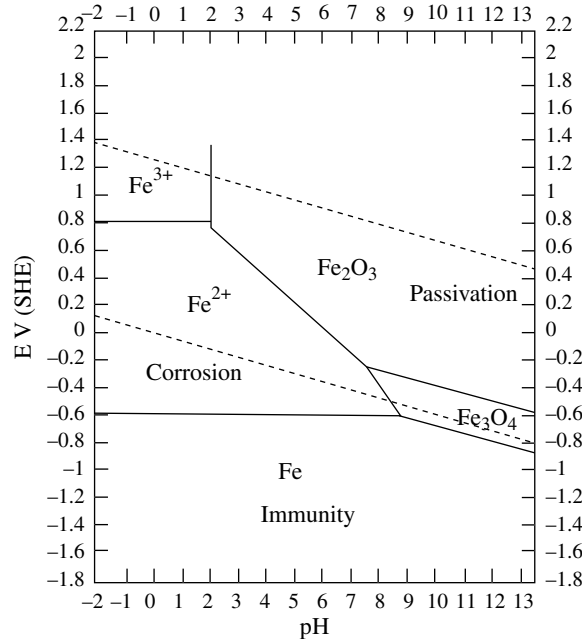


FIGURE 1.3 The Pourbaix diagram for iron. Adapted from Strehblow and Marcus [70].

Reactions that involve a number of protons or hydroxide ions being exchanged are dependent upon pH, via the equation [71]

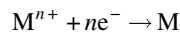
$$\Delta G \approx \Delta G^0 \pm 2.303mRT \text{pH}$$

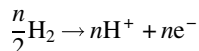
where m is the number of protons exchanged in the reaction and the $\pm$ depends on whether protons are produced or consumed, respectively. T is the temperature, R is the ideal gas constant, and ΔG^0 is the standard Gibbs free energy (activity $a = 1$, pressures of gases $p = 1 \text{ atm} = 1.013 \text{ bar}$).

Reactions that involve the loss or gain of electrons (oxidation or reduction, respectively) are dependent upon the potential. The reaction free energy varies with potential according to the equation [70]

$$\Delta G = -nFE$$

where n is the number of electrons consumed for the cathodic direction of the reaction, that is, the reduction process, and ΔG the related change of the Gibbs free energy. The counter reaction for the production of the electrons is by convention the oxidation of hydrogen gas to hydrogen ions for the standard hydrogen electrode with a hydrogen pressure of $p(\text{H}_2) = 1 \text{ atm} = 1.013 \text{ bar}$ and a hydrogen ion activity of $a(\text{H}^+) = 1$. The following two equations give an example for the reduction of metal ions Me^{n+} and the compensating hydrogen oxidation:





For a reactive metal like iron, the discussed electrodeposition associated to hydrogen oxidation is not possible with a strongly positive ΔG . The reverse process, that is, iron dissolution associated to hydrogen evolution, is the spontaneous reaction with a very negative ΔG . E is the electrode potential measured against the standard hydrogen electrode. With $a = 1$ for all activities and $p = 1$ atm for gas pressures, the electrode potential equals its standard value $E = E^0$ for the electrochemical reaction of interest. For these conditions the relation $\Delta G^0 = -nFE^0$ holds with the standard Gibbs free energy change ΔG^0 holds. The standard electrode potentials E^0 are listed for all metal–metal-ion and redox electrodes [71b] similar to the standard Gibbs free energy ΔG^0 of electrochemical reactions. For Fe dissolution to Fe^{2+} , the electrode potential equals $E^0 = -0.44$ V, a relatively negative value for a reactive metal.

Reactions that are only dependent upon pH are represented in the Pourbaix diagrams by vertical lines. Reactions that are only dependent upon potential are marked as horizontal lines. Reactions that involve both will have some slope that depends jointly upon the ratio between proton/hydroxide activities and electron transfer coefficients, in which case both of the above equations have to be applied.

As seen in Figure 1.3, the typical Pourbaix diagram consists of three regions, corresponding to immunity (the metallic phase has the lowest free energy), passivation (the oxide phase has the lowest free energy), and corrosion (either the metal cation phase is most stable or the soluble hydroxides/oxyanions). The electrochemical boundaries associated with the oxidation and reduction of water are also typically shown as boundary points within these diagrams via the use of dotted or dashed lines.

As described in more detail in subsequent chapters of this book, the Pourbaix principle has been extended to include adsorbed surface phases and other variables, including the presence of sulfides or chlorides [62, 73–76]. The analog for high-temperature corrosion by gaseous agents is the Ellingham diagram, in which the free energy associated with oxidation reactions is plotted against temperature [77]. However, as with any thermodynamic analysis, one should keep in mind that the kinetics often play a crucial role in the observed behavior. For instance, Anderko and Shuler's study of iron sulfide phases indicated that many metastable phases are significant and should be displayed in the practical Pourbaix diagram due to the slow kinetics associated with the formation of the most stable thermodynamic phase [78].

1.2.2 Electrode Kinetics

While thermodynamics provides a starting point, kinetics is essential for providing any corrosion model of practical utility. The term *electrode kinetics* is often used as, in the electrochemical paradigm, the oxidation and reduction occur at independent sites, which can be considered as separate electrodes marking a solid/electrolyte interface at which the half-cell reactions take place. In the case of chemical corrosion, these half-cell reactions can take place at the same location, in which case there is no external current flow between the half-reaction centers, but instead, direct charge transfer between the reactants via electronic contact at the same metal site.

The electrode potential exerts a powerful control over corrosion kinetics, just as the chemical potential or the electrochemical potential does in thermodynamics. The deviation of the electrode potential E from its equilibrium value E_{eq} given by the Nernst equation,

the so-called overvoltage $\eta = E - E_{\text{eq}}$, is the driving force for the kinetics of the electrode process. This kinetic control can be broken down into the following categories:

1. Transport of reactants and products, controlled by the diffusion overvoltage
2. Chemical reaction rates, controlled by the reaction overvoltage
3. Adsorption and desorption on the electrode surface with charge transfer, controlled by the charge transfer overvoltage

The charge transfer overvoltage is fairly well understood in terms of the Butler–Volmer equation: [71a]

$$i = i_0 \left(e^{\alpha z F \eta / RT} - e^{-(1-\alpha) z F \eta / RT} \right)$$

where z is the number of elementary charges of the species passing the electrode–electrolyte interface ($z = -1$ for an electron, $z \geq +1$ for a metal cation), α is the transfer coefficient, and η is the overpotential, which marks the deviation of the electrode potential from the equilibrium potential for the reaction being considered. F is Faraday’s constant. Inspection of this equation shows that, for large positive overpotentials, the first exponential dominates, whereas, for large negative overpotentials, the second exponential is more critical. In these two cases, one can show that the overpotential should be linear with respect to the log of the current density. This relation is known as the Tafel equation.

In the limit of small overpotentials ($\eta \sim 0$), the Butler–Volmer equation can be linearized to yield the charge transfer resistance (R_{CT}):

$$i = \frac{i_0 z F \eta_{\text{CT}}}{RT}$$

$$\eta_{\text{CT}} = i R_{\text{CT}}$$

$$R_{\text{CT}} = \frac{RT}{i_0 z F}$$

Observed deviations from this behavior can be attributed to the interference of diffusion control.

Mass-transport (i.e., diffusion or electromigration) effects are particularly acute in the cases of cracking, pitting, and crevice corrosion, whereby occlusion effects can create highly concentrated solutions that move an otherwise stable system into regions of thermodynamic instability at the local level [13, 14, 41–43, 79–82]. When porous films or particular solution flow conditions exist, mass-transport effects should also be taken into account [83, 84]. Molecular dynamics and Monte Carlo simulations of interfaces over the past few decades have provided some insight into the concentration gradients that occur close to the electrochemical interface [85–91], and these, coupled with computational fluid dynamics simulations, can indicate the extent to which mass-transport effects can dominate an overall corrosion scenario [92].

At the same time, surface effects can be strongly dependent upon local species that adsorb on the exposed surface and thereby modify in a direct way the rates of those chemical reactions that contribute to a given corrosion pathway. When comparing mass-transport

effects to surface phenomena, therefore, such scenarios should also be taken into account. Researchers in the field of heterogeneous catalysis, for example, have applied molecular modeling to understand the effects by which environmental species and/or reaction by-products can poison certain reaction pathways and favor others [93]. In the world of corrosion, certain species are suspected to promote hydrogen uptake by metals [45, 94–98] and, in other cases, to inhibit surface passivation [99–102]. The tools that have been successfully applied to assess such surface processes in the field of catalysis can and have been applied to similar problems in corrosion science [65, 93, 103–108].

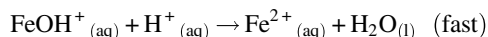
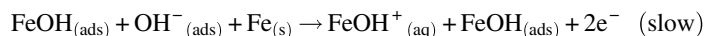
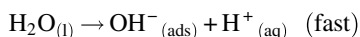
1.2.3 Metal Dissolution

The most quintessential element of corrosion is the loss of mass from a structural component, which may be embodied by the generic metal dissolution reaction:



The metal may be directly passing from a bare metal surface into an aqueous solution [109–111] or passing through an oxide (alternatively, sulfide, chloride, etc.) film via point defect-mediated mass transport [112], among other mechanisms. This reaction may be accelerated (or, potentially, retarded) by the complexation of the surface metal atoms by species in the environment. For instance, sulfur, hydroxide, or chloride could form bonds with the surface adatoms on a bare metal surface, thereby weakening the metal/surface bonds and facilitating the corrosion reaction [25b, c, 113]. Some atomistically resolved investigations of this process suggest that the surface structure provides a high degree of control, leading to such features as surface faceting and crystallographic pitting [25b, c, 113b, 114].

In the case of iron dissolution, the following reactions are believed to play a role according to K.E. Heusler:



Thus, surface adsorption of water and subsequent dissociation and reaction with surface iron adatoms form a complete mechanism for dissolution [114b]. In addition to experimental investigations of reaction kinetics and surface characterization, molecular modeling can play a key role in assessing the various aspects associated with these mechanisms. The Butler–Volmer framework also provides a means for assessing the role of overpotential in affecting the overall rate of reaction [71a].

Thermodynamically, dissolution should occur whenever the free energy of the solvated metal ion at a given concentration is lower than the free energy of the atom in the metal, plus the thermodynamic potential of the electrons exchanged during the reaction via the standard hydrogen electrode. Such thermodynamic conditions are summarized in the series of potential–pH phase diagrams that have been extensively collated by Pourbaix [69]. Even in cases where a metal is covered by a thin protective oxide, deleterious corrosion effects can

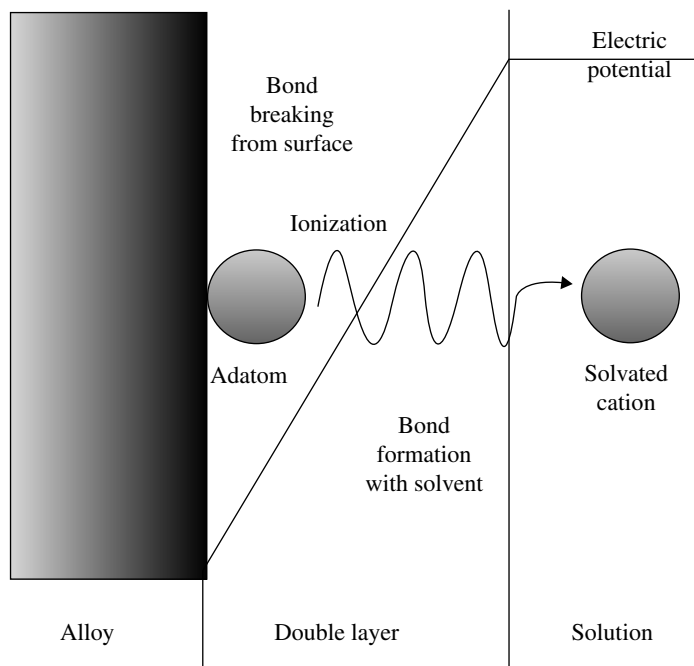
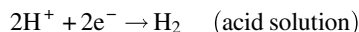


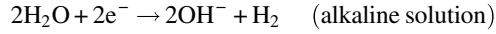
FIGURE 1.4 Schematic of the transport of a metal atom across the electrochemical double layer (from left to right).

arise from the dissolution of metal atoms directly exposed by virtue of cracks or pores in the protective film. The dissolution of metal atoms at the bare metal/solution interface, and also at the oxide/solution interface, requires the metal atoms to traverse the so-called electrochemical double layer [71a]. This concept, arising from electrochemistry, is based on a potential difference between the metal and the solution, due to aligned water dipoles, the ionic strength of the solution, and any bias existing on the metal [89, 115–121]. Dissolution of metal atoms, therefore, involves the breaking of cohesive forces between the metal atom and its neighbors in the solid state, electron transfer resulting in an ion formation (it is presently unclear exactly when this step occurs) [109–111], the formation of a solvation sphere around the nascent metal ion, and the movement of the ion through the potential gradient existing at this *double layer* (Fig. 1.4) [110]. Clearly, such a process involves a number of atomistic events that are sensitive to several highly localized environmental parameters that are amenable to a molecular modeling analysis.

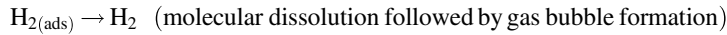
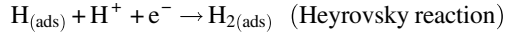
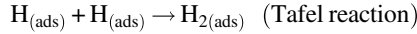
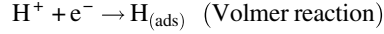
1.2.4 Hydrogen Evolution and Oxygen Reduction

Since aqueous corrosion is often electrochemical in nature, the reactions that lead to loss of metal via dissolution require a cathodic counterpart, which is often either hydrogen evolution or oxygen reduction [3]. Hydrogen evolution involves the reduction of a proton (or a hydronium ion, i.e., a proton within a water molecule) to form molecular H_2 :

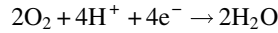




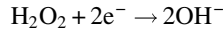
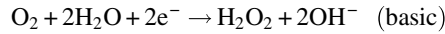
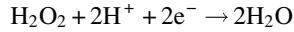
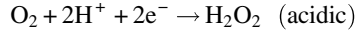
The hydrogen evolution reaction in acid solution has been broken down into the following steps:



In experimental reality, the presence of oxygen is found to greatly accelerate the rate of corrosion, which is due to the action of oxygen as an oxidant via the oxygen reduction reaction. The overall reaction is expressed as



The reaction steps differ in acidic and basic reactions, namely,



The oxygen reduction reaction has received a large amount of attention recently, from both modeling and experimental investigations, due to its importance in the development of fuel cell systems [74, 103, 122–125]. The rate of corrosion reactions may be controlled by either the anodic or cathodic process, depending upon which of the two half-cell reactions is rate limiting. This combination is elaborated further in the following text.

1.2.5 The Mixed Potential Model for Corrosion

In the electrochemical mechanism of corrosion, the metal dissolution—which involves the loss of electrons vis-à-vis oxidation—must be accompanied by a cathodic reaction that consumes electrons, which is typically oxygen or proton or water reduction. According to the Butler–Volmer equation, the current density for the anodic reaction varies according to

$$i_a = i_{a,0} e^{zF(E-E_{0,a})/RT}$$

A similar expression exists for the cathodic reaction:

$$i_c = i_{c,0} e^{-zF(E-E_{0,c})/RT}$$

Here, $E_{0,a}$ and $E_{0,c}$ are the equilibrium potentials for the anodic and cathodic process, respectively, and $i_{a,0}$ and $i_{c,0}$ are the respective current densities at these potentials. In a corroding system, where both reactions are occurring simultaneously, the total current is the difference of these terms:

$$i = i_a - i_c = i_{a,0} e^{zF(E-E_{0,a})/RT} - i_{c,0} e^{-zF(E-E_{0,c})/RT}$$

Under open-circuit conditions (i.e., when the metal surface is not connected to an external potentiostat), the net current $i_a - i_c$ will be zero, and the electrode potential E will adjust according to the corrosion potential, E_{corr} . In this case, the corrosion current density (i.e., the current density associated with the loss of metal) is $i_a = i_c = i_{\text{corr}}$.

In the limit of large anodic polarization, π , relative to the open-circuit potential E_{corr} , the variation of current with potential will be log-linear and vice versa for large cathodic potentials (relative to open-circuit potential). This behavior can be modeled by the semilogarithmic Tafel equations:

$$\log i = \log i_{\text{corr}} + \frac{\pi}{b_a} \quad (\text{large anodic potential, } \pi)$$

$$\log |i| = \log i_{\text{corr}} - \frac{\pi}{b_c} \quad (\text{large cathodic potential, } \pi)$$

The corrosion potential can then be found by extrapolating the linear portions of these two equations in the plot of log current density versus potential.

The variation in current with potential implies that there exists an electrochemical resistance that results from the coupling of anodic and cathodic reactions. Following from the expressions for the corrosion current density, as given earlier, this *polarization resistance* R_p can be obtained from the equations:

$$i = i_{\text{corr}} \left(\exp \frac{\pi \ln 10}{b_a} - \exp \frac{-\pi \ln 10}{b_c} \right)$$

$$\frac{1}{R_p} = \left(\frac{di}{d\pi} \right)_{\pi \rightarrow 0} = i_{\text{corr}} \left(\frac{\ln 10}{b_a} + \frac{\ln 10}{b_c} \right)$$

$$R_p = \frac{b_a b_c}{\ln 10 (b_a + b_c) i_{\text{corr}}}$$

These equations, therefore, allow the experimentalist to extract fundamental quantities from a mixed potential system in order to understand aspects of the decoupled anodic and cathodic reactions.

1.2.6 Selective Dissolution of Alloys

Since most structural metals are, in fact, alloys, it is necessary to consider how metals corrode when found in combination. A classic system here, amenable to detailed investigation due to the nobility of the components, is the AuCu alloy system [126]. These alloys are

characterized by a very low dissolution current at potentials that are positive with respect to the Cu/Cu^{2+} equilibrium potential, but negative with respect to the Au/Au^{3+} electrode. There exists a critical potential E_{cr} , however, above which the dissolution current increases sharply. This critical potential increases with the Au content of the alloy [127]. The general mechanism proposed for this phenomenon is that above the Cu/Cu^{2+} potential surface, copper atoms may dissolve, but as they do, they leave Au enriched at the metal surface. Therefore, continued Cu dissolution is blocked by Au atoms that cap the surface. When the critical potential is reached, the steep increase in current is due to the fast Cu corrosion current density corresponding to the high overpotential for Cu dissolution. The stress corrosion cracking of brass in ammonia-rich environments presents another example of this failure mode, caused by the loss of Zn from the alloy as a result of selective dealloying [128, 129].

1.2.7 Passivity of Metals and Alloys

In addition to dissolution, reaction of solution or atmospheric constituents with the metal very often results in the formation of a surface film, most commonly a metal oxide, that can be as thin as a nanometer (i.e., a few atomic layers) [112, 129b, c, 130–136]. The rate of formation of this passive film and the rate at which it dissolves into solution ultimately determine the stability of the material in its environment. In this way, iron, which is thermodynamically stable only in a small region of the Pourbaix diagram (see Fig. 1.3), can be usefully employed over a significantly wider range of conditions due to the extremely slow dissolution kinetics of the passivating oxide film. Passive film stability has been described mechanistically via several models, including the *high-field* and *point defect* models, which attribute the overall stability to kinetic factors such as the migration of vacancies or other oxide defects through the thickness of the film, as a function of the electric potential across the film [112, 129b, c, 137, 138]. Other important mechanistic details include the transfer of metal ions from the underlying metal substrate to the oxide film and the interfacial chemistry occurring between the oxide film and the solution itself. Localized corrosion may also occur when particular defects in the oxide are subject to a preferential attack from species such as chloride in the environment [25b, c, 137, 138]. Such pathways and their associated kinetic parameters could be directly assessed from first-principles and molecular modeling techniques, although a complete analysis of the many pathways and interfacial transitions remains a significant challenge. Metal surfaces exposed to aqueous solution or water vapor may have a compound passive film, which consists of an outermost hydroxide or oxyhydroxide and an inner layer oxide. Further complexities arise due to composition gradients in the material and the relative oxidation strengths of different alloy components [129b, c].

The electrochemical behavior of passivation is such that as the potential increases from the cathodic direction, one first encounters the *active region* in which typical current densities may be up to $100 \text{ mA}/\text{cm}^2$ and more. This corresponds to free corrosion of the metal, before a protective oxide or oxyhydroxide film forms. As the potential becomes increasingly anodic, the current density diminishes, down to $1 \mu\text{A}/\text{cm}^2$, as the corrosion product film lowers the rate at which corrosion can occur. This is the region of passivity. It can extend over several hundred mV. Beyond this region lies the transpassive film: oxygen evolution and transpassive dissolution can occur on semiconducting passive films. For more inert materials (Al and the valve metals, Zr, Hf, etc.), the passive region can extend to a larger range of anodic potentials due to the insulating nature of the oxide films that severely retard ion mass transport and electron transfer across the passive layer.

Localized corrosion can occur in the otherwise passive region of potentials. In the case of localized corrosion, the passive film is locally breached, due to mechanical or chemical compromise of the oxide film or structural defects, such as grain boundaries, triple points, surfacing dislocations, or intermetallic phases such as carbide and/or sulfides. Localized corrosion manifests itself in the plot of corrosion current versus electrode potential (the polarization curve) as *noisy* peaks in the passivation region, due to the stochastic nature of this mode of corrosion.

1.2.8 Inhibition of Corrosion

The corrosion rate of metals may be reduced by the addition of inorganic or organic compounds, called inhibitors, to their environment [139]. The inhibitor efficiency is defined as the relative reduction of the corrosion current density, where $i_{c,0}$ and i_c are the corrosion current densities without and with addition of the inhibitor, respectively:

$$n_i = \frac{(i_{c,0} - i_c)}{i_{c,0}}$$

The mode of inhibition depends upon the material, the environment, and the mechanism of corrosion that is being inhibited. For instance, the inhibitor may adsorb at the metal surface and thus reduce its anodic dissolution [140]. Alternatively, the inhibitor may act to repress the cathodic reactions such as hydrogen evolution or oxygen reduction. In keeping with this concept of adsorption-based inhibitors, inhibitors typically are molecular species with alkyl chains and an active head group such as CN^- (cyanides), SH (thiols), NH_2 (amines), COO^- (carboxylates), and OPO_3^{3-} (phosphates). Numerous approaches to optimize the design and synthesis of inhibitors have been developed based on quantitative structure–property relationship analysis, a type of molecular modeling that is coupled with statistical analysis and correlations with empirical data for inhibition efficiency [141, 142]. Such approaches correlate molecular properties, for example, the electron density at the binding head group, with the inhibitor efficiency. Only recently have molecular approaches been employed to study the mechanisms of inhibition [143].

Since inhibitors can influence either the cathodic or anodic reaction, their effect on the open-circuit (i.e., corrosion) potential will differ according to this mode of action. This relationship can be understood by comparing the Tafel diagrams in Figure 1.5. Suppression of the reduction current lowers the Tafel semilog line, thus moving the point of intersection of the anodic and cathodic regions to a lower open-circuit potential (more cathodic). On the other hand, suppressing the anodic reaction will increase the open-circuit potential into more anodic regions. Finally, the inhibitor may be mixed mode, in which case there may be little or no change in the open-circuit potential of the system. In all cases, the corrosion current is lowered by the presence of the inhibitor on the surface.

1.2.9 Environmentally Assisted Cracking and Embrittlement

Corrosion failure can also occur when environmental species absorb into the metallic lattice itself, modifying the materials properties to the point that it can no longer maintain its specified loading [46]. Most commonly, this is attributed to the absorption of hydrogen, yet embrittlement and stress corrosion cracking can also occur via other species, including sulfide, iodide, and chloride [58, 144–148]. In such cases, the chemically aggressive species

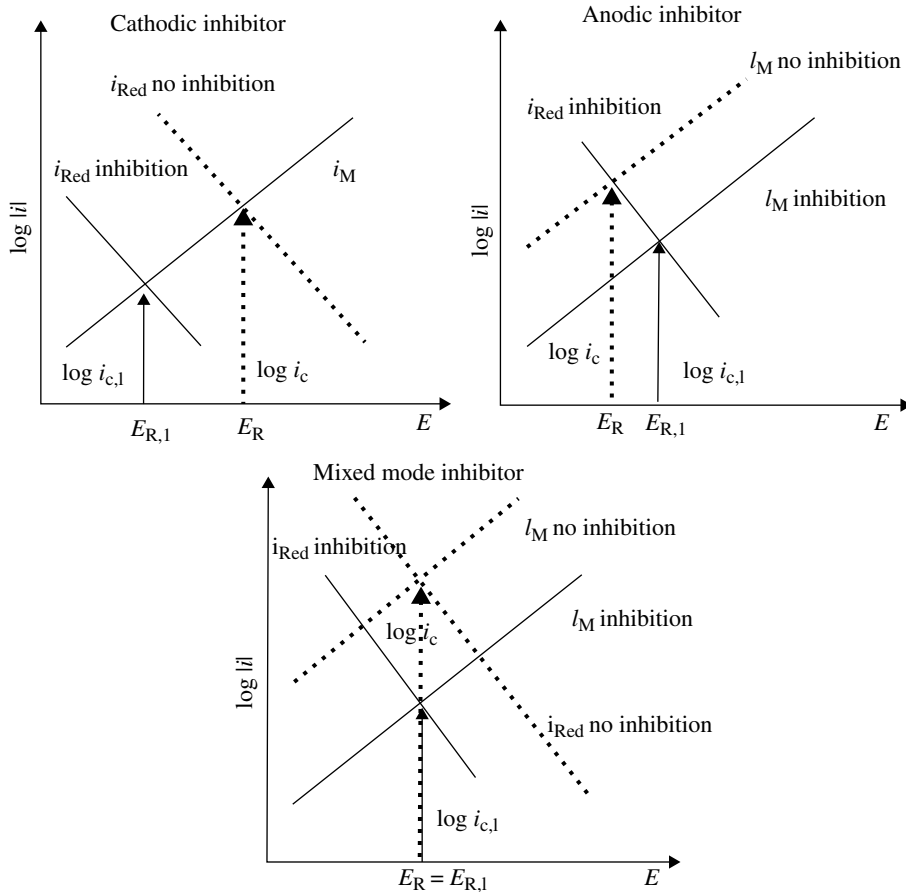


FIGURE 1.5 Mixed potential diagram demonstrating the possible modes of behavior for corrosion inhibitors. Adapted from Strehblow and Marcus [70].

clearly plays a role in altering the nature of the metal–metal bonding and the response of the metal’s deformation modes, such as dislocations, elastic response, or grain-boundary motion. Therefore, the ability to interrogate how interposed environmental species modify these properties from a first-principles approach, and to simulate various hypothetical scenarios, could lead to new materials design approaches, such as alloying, surface modification, or nanostructuring to improve the longevity of materials under combined stress corrosion conditions.

1.2.10 Crystallographic Pitting

Postmortem inspection of corroded specimens often indicates a predilection for corrosion and/or stress corrosion cracking to proceed along grain boundaries in the metallic structure [149–156]. Somewhat related to this observation is the fact that under certain conditions, corrosion pits may adopt a *crystallographic* appearance, conforming to the

underlying symmetry elements of the metal [25b, c, 113b, 157–159]. These observations suggest that certain features of the metal, and in particular the directionality and local sensitivity of the cohesive forces binding the metal atoms to one another, can play a significant role in directing the overall corrosion response of the metal. Therefore, powerful modeling techniques that directly incorporate the best physical models for describing interatomic interactions could be used to help interpret such observations and, through the modeling of various hypothetical scenarios, suggest physically justifiable approaches for their mitigation.

1.2.11 Summary of Corrosion Mechanisms

This extremely cursory overview suffices to show that there are several molecular and atomistic level interactions that are involved in any single corrosion event and that there is a large number of possible mechanisms that still require a rigorous theoretical treatment. In the following section, we introduce a number of molecular-level modeling techniques that have been, or could be, applied to the further detailed study of these mechanisms for materials presently used in industry and materials yet to be discovered and/or applied.

1.3 MOLECULAR MODELING

The chief aim of atomistic and molecular modeling techniques is to compute the thermodynamic, mechanical, and/or kinetic properties of a system composed of isolated or periodic, static or dynamic, arrangements of atoms and molecules [4, 7, 160–162]. Common to all these modeling techniques are physics-based representations of the interactions between the atomic and molecular constituents. These interactions may be computed based on a broad spectrum of techniques ranging from approximate pair potentials at one extreme through to accurate determination of the electronic structure based on quantum mechanics [6, 7]. Forces and charges on atoms, as well as system and subsystem energies, are the primary quantities obtainable from these methods, though quantum mechanical methods may also yield further properties that depend on the behavior of the electrons. By exploring the dependence of these quantities on the atomistic, molecular, and materials structure and composition, one can build an elaborate picture of the overall thermodynamic, mechanical, and kinetic properties of the system one is trying to represent.

At its root, molecular modeling consists of the solution of physics-based equations for the interactions between the basic constituents of matter—atoms and molecules—and any externally applied forces, such as electric forces due to potential [163]. One may use minimization techniques to find low-energy (and therefore physically reasonable) configurations of atoms and molecules [164], in order to rank different configurations, or understand bonding arrangements, or integrate the equations through time to simulate dynamical trajectories for these systems [165]. The underlying physical equations are often based upon the fundamental Coulombic interactions between nuclei and electrons that, in conjunction with the kinetic energy, ultimately determine bonding in solids and molecules and thereby all other properties. While a deeper understanding of molecular modeling techniques can be gained only through a more extensive study of the literature [4, 5, 7], we take some time here to introduce some of key concepts for the more pertinent approaches.

1.3.1 Electronic Structure Methods

Electronic structure methods comprise the most exact techniques for interrogating the internal structure and properties of molecules and materials [5, 7]. At best, they require no arbitrary parameters and can be systematically improved to obtain very nearly exact solutions [166]. At the same time, these methods are the most computationally expensive, requiring one to determine the fine structure of the electronic orbitals that define bonding in materials, some of which information may not be required to explore all problems. Schrödinger's time-independent wave equation usually forms the starting point for these methods, in that the internal energy E of a configuration of atoms and electrons is determined as the eigenvalue of the Hamiltonian operator, acting on the electronic wave function Ψ :

$$H\Psi = E\Psi$$

Here, it is usual to make the Born–Oppenheimer approximation that allows a classical treatment of the nuclei to be separated from a quantum mechanical description of the electrons. In this case, the wave function becomes just that of the electrons, and the nuclear–nuclear interaction is added to the energy as a sum over point particles. Consequently, the Hamiltonian operator H includes the kinetic energy of the electrons, the electron–electron interactions, and the electron–nuclei interactions. The wave function determined by solving this eigenproblem consists of a Slater determinant of the molecular orbitals for a molecule or, alternatively, the band structure of a solid. Unfortunately, direct solution of this equation is complicated by the electron–electron interactions. Often, it is necessary to introduce a mean-field approximation that neglects the individual dynamical electron–electron correlations but instead treats the electrons as moving in the average field created by the other electrons. Various corrections have been developed to improve upon this approximation [160, 167, 168].

In the world of molecular modeling, quantum mechanical approximations typically start from one of two approaches. The first of these is Hartree–Fock theory, which has the advantage of being systematically improvable through methods such as perturbation theory (e.g., Møller–Plesset theory, starting from second order, MP2) and configuration interaction (CI) [166]. In the world of materials, and rather commonly now in the molecular sciences, a second approach known as density functional theory (DFT) has become more widespread. As the name suggests, here, the focus is more on the electron density rather than the wave function, and Schrödinger's wave equation is replaced in most practical applications with the analogous Kohn–Sham equations [169, 170]. While DFT suffers from the disadvantage of not being able to arbitrarily converge on the exact solution, it is typically able to yield superior results to Hartree–Fock theory for a reduced computational cost relative to MP2, CI, or other such so-called post-Hartree–Fock methods.

The solution to both Hartree–Fock and DFT approaches requires a self-consistent approach, in which trial solutions are iteratively refined until convergence to within a given precision is achieved. Solutions are typically expressed as a matrix of coefficients describing the contribution of various basis functions to the electronic structure of the system. These basis sets are a numerically convenient way of representing the wave functions and can be localized atomic-like orbitals, or plane waves in the 3D space of the simulation cell, or many other forms [164]. The improvement of these techniques is an ongoing endeavor, and yet, despite this enormous challenge, the approximate functionals to date remain among the most accurate tools for evaluating structure and energy relationships in materials and molecules [161, 162, 171–175]. Functionals and semiempirical approaches have been recently developed to better describe the weak electron correlations associated with dispersion forces,

for example, whereas hybrid functionals and the *Hubbard U* method have been developed to take into account strong electron correlations [7, 167, 176–179]. Because of the fundamental nature of modeling techniques based on electronic structure, they are often called first principles or *ab initio*. As in all models, much care must be taken in setting up such a calculation to ensure that the results produced are both valid and relevant to the materials system of interest [180].

More approximate solutions to the electronic structure problem come from tight-binding and semiempirical molecular orbital theory [181, 182]. These methods simplify and efficiently approximate the expressions within the quantum mechanical problem in order to reduce the computational cost. To compensate for this, empirical parameters are often introduced that are obtained from fitting to experimental or high-level quantum mechanical data. However, because of this fitting process, the parameter sets so developed can rarely be confidently extended beyond the range of systems for which they were originally designed. Since corrosion systems typically bridge length scales that incorporate bulk materials, the interfacial region and an environmental (such as aqueous) solution phase, obtaining a parameter set suitable for spanning all these behaviors presents a formidable challenge [183, 184].

1.3.2 Interatomic Potentials (Force Fields)

Whereas *ab initio* techniques can be applied to the various modeling scenarios described in this and the following subsections, typically a more efficient approach is required in order for systems of a more realistic size or timescale to be simulated. Based on potential energy surfaces constructed from *ab initio* techniques or implied from various experimental quantities, such as the bulk modulus, one can derive approximate relationships for the interactions between atoms, including the electronic effects only in an implicit way. Such relationships, called interatomic potentials [185], can be rigorously derived by expanding the energy as a series of terms that depend on increasing numbers of different atoms: [186]

$$U = \sum_i U_i + \frac{1}{2} \sum_{i,j} U_{ij} + \frac{1}{6} \sum_{ijk} U_{ijk} + \cdots$$

Despite the exact relationship expressed in this equation, the accurate forms for the interaction terms and how they depend on relative positions are not exactly known [187]. Thus, using reasonable physical arguments, a number of approximations have been derived. Furthermore, if the expansion is continued to the point where it includes all atoms, and therefore is exact, this becomes exponentially expensive to solve as the size of the system increases. Fortunately, it turns out that the magnitude of the contribution also rapidly diminishes as the number of atoms involved in the interaction term increases. Hence, the series can be truncated quite rapidly while still giving reasonable results. For ionic materials, it is often sufficient to stop at the second term, which corresponds to pairwise potentials. In the case of covalent organic materials, it is usually necessary to include three- and four-body terms too. There now exists a variety of different expressions for approximate energy calculations, each of which have their own appellation as a family of interatomic potentials (for instance, embedded atom [188–194], Stillinger–Weber [195], Buckingham potentials [177], etc.).

Through experience, it is now generally well understood which potential model is appropriate for a given type of material. For purely ionic systems, for example, the one-body term, $E_a(i)$, may be neglected, and the potential determined simply by the sum of Coulombic

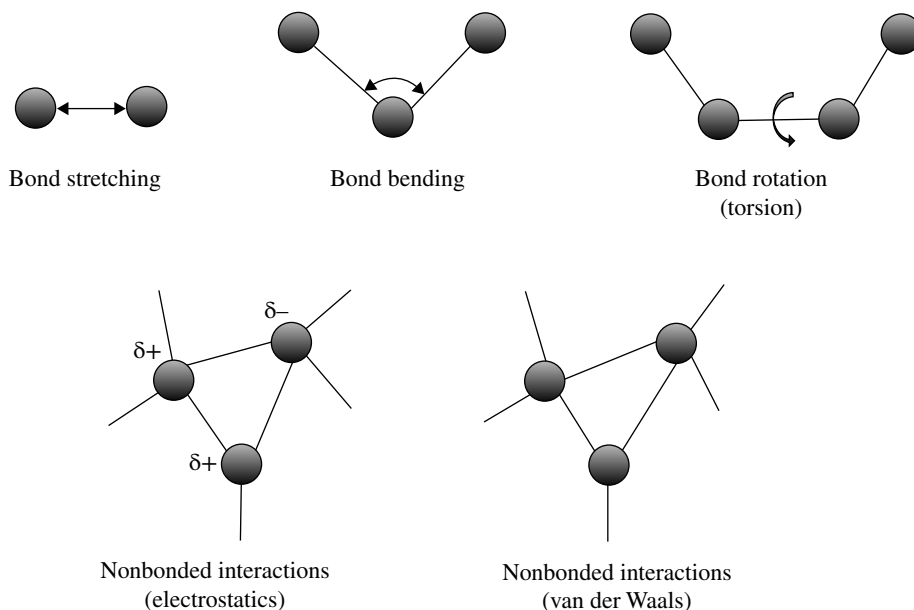


FIGURE 1.6 Schematic representation of the interactions that form the basis for molecular mechanics simulations of bonded and nonbonded systems.

interactions between the ion and its neighbors, plus a short-range repulsive term. This description may be augmented by a *shell* model for the ion polarizability [196, 197] or self-charging terms that allow the charge on an ion to fluctuate based on the relative electronegativity and hardness of its neighbors (thus introducing a one-body term, $E_a(i)$, corresponding to the energy associated with local charging) [198, 199].

In molecular systems, three-body (angular) and four-body (torsional or out-of-plane) terms can also be added to the energy function, thus providing greater flexibility and therefore accuracy in the overall potential scheme [4]. Such a breakdown is illustrated in the schematic of Figure 1.6. This technique, known generally as molecular mechanics, is widely used in the simulation of biological molecules and polymer systems, due to its relatively rapid computation for systems of many atoms; its intuitive appeal, in terms of a ball-and-stick concept; and its ability to incorporate additional interactions, such as nonbonded dispersion forces. Here, Coulombic and other nonbonded interactions are typically excluded between nearest and next-nearest neighbors to avoid confusing the physical interpretation of the potential functions. Similarly, so-called 1–4 nonbonded interactions between atoms that are separated by three bonds are often reduced by a scale factor, so that the torsional potential dominates the energy.

Embedded atom interatomic potentials can be formally derived from DFT [188–194]. This class of interatomic potentials generally works well for bulk metallic systems (i.e., accurately reproduces mechanical and structural properties), due to its relationship to the band model of electronic structure, which is related to the overlap of local electron densities to form the *free electron* gas of the metallic system. By parameterizing the form of the electron density about an atomic center, one can build a model for the electron overlap in these systems and, hence, the *many-body* features of alloy systems. The resultant expression for

the energy is the sum over the local atomic embedding energy, which is in turn a function of the local electron density—the sum of the overlaps from neighboring atoms—as well as pairwise, short-range repulsions. The functional forms utilized in the embedded atom (and modified embedded atom) approaches are derived from fundamental forms for equations of state (such as the Rose equation) [200].

A limitation of many classes of interatomic potential is that the *identity* of an atom is typically fixed, such that if it moves from a metallic to an ionic environment—as happens in corrosion, for example—the potential is unable to capture the local change in either oxidation state or bonding that occurs. New classes of potentials have been developed to overcome this restriction. Reactive force fields, in particular, are attracting increasing interest for interfacial problems, due to their inbuilt ability to accommodate changes in coordination and oxidation state [11, 201–203].

The criteria for assessing the usability of a particular interatomic potential include:

1. **Transferability:** A potential derived from the properties of one particular material should remain accurate when applied to the same atom type in a different environment. The extent to which transferability is desired may depend upon the range of applications the *potential engineer* wishes to explore: potentials derived for transition metals as complexes dissolved in aqueous solutions are unlikely to be useful for exploring the properties of those same metals in the solid state.
2. **Computational efficiency:** The amount of computational effort required to evaluate the energy of an atom in a given context should be small relative to the effort required to do so from first principles and sufficiently fast to simulate the time and length scales desired for a given application. General rules of thumb (which will likely change in the near future due to the development of new algorithms and computational architectures) are:
 - Quantum mechanics: <1000 atoms; <100 ps for molecular dynamics
 - Interatomic potentials: <1,000,000 atoms; <1 μ s for molecular dynamics
3. **Extensibility:** This last requisite is often overlooked in the fashioning of a given potential scheme but refers to the ability for *potential engineers* to extend the accuracy or transferability of the interatomic potential in rigorous and systematic ways. This may include the addition of further terms in a Taylor expansion or the inclusion of higher manybody terms to the potential.

Once confidence has been established in the fidelity of a given interatomic potential, that potential may then be used to simulate collective properties of an ensemble of configurations representing the corrosion scenario of interest by techniques such as energy minimization, thermodynamic analysis (lattice dynamics and free energy calculation), transition state theory, molecular dynamics, or Monte Carlo simulation. For studying diffusion properties in liquids, interatomic potentials are generally preferred to *ab initio* methods, due to the large timescales that must be simulated. For solid-state diffusion, either quantum mechanical or interatomic potentials have been used, since the typically larger barriers are suited to the use of transition state theory, rather than molecular dynamics [56, 204–206]. Corrosion problems, due to their complexity and the fundamental transformations that take place in a material, have chiefly been studied with quantum mechanics or reactive force fields [16, 143, 207, 208], although there exist many phenomena relevant to corrosion that can be studied with pair-potential techniques, such as mass transport in fluids or the accumulation of defects in a material.

1.3.3 Energy Minimization

Statistical mechanics teaches us that the most probabilistic states of a system are those that possess the lowest Gibbs free energy [209]. At low temperatures, these states are among those with the lowest potential energy—although kinetic barriers can lead one to be *trapped* in a local minimum state, rather than the true global minimum. This is demonstrated by the coexistence of both diamond and graphite at ambient conditions [210]. At higher temperatures, entropic effects begin to dominate and so must also be accounted for.

The technique of energy minimization is used to vary the atomic coordinates of the system (i.e., relative positions in Cartesian coordinates or, alternatively, the bond lengths and bond angles of a molecular system) until a local minimum in energy is reached [211]. In the case of a solid, this can also be supplemented by varying the lattice parameters until the material is no longer under stress. For a reactive system, several local minima will exist, corresponding to reactant and product states, as well as many alternative configurations that may not significantly contribute to the reaction of interest, but may nevertheless be important to understand as potential side reactions or intermediates that link the reactant and product states. For very *soft* systems, such as in solution, the number of local minima may be exceedingly large, as water molecules can arrange into multiple configurations of similar thermodynamic stability. Furthermore, in such systems, temperature imparts a high degree of thermal motion to the solvent molecules, thus making transit across the barriers separating these minima facile. In solid systems, this is less often the case: barriers between local minima tend to be higher relative to the thermal energy, kT . The kinds of interfaces found in a corroding system, therefore, will require a mix of approaches to the determination of the most stable states of the system.

Energy minimization techniques include, most commonly, the methods of steepest descents and conjugate gradients [4]. Here, steepest descents follow the lowest energy pathway, as determined by the gradient (i.e., first derivative of the energy) at each point, while conjugate gradient methods begin similarly but include a *history* component, which accelerates the optimization process. While these two methods are widely used, due to the need to only compute the gradients, there are many more sophisticated optimization algorithms that also employ the Hessian (i.e., the matrix of second derivatives of the energy). Such Hessian-based methods offer convergence in fewer steps, at the expense of increasing the computational cost per step. There are also many intermediate methods that use an approximate initial Hessian (e.g., a unit matrix) and then apply an updating formula that improves this guess as the optimization progresses.

The molecular modeler typically begins with an educated guess for the atomic configuration of the system, based on crystallographic and/or molecular symmetry constraints, as well as the typically bond lengths and angles for such systems, and then refines possible structures based on these computational techniques. Frequently, multiple hypothetical structures can be fine-tuned in this way, and their energies compared to see which states are more stable than others.

Energy minimization produces a structure that is thermodynamically stable at 0 K (not necessarily the lowest energy one, however). In order to produce results that are meaningful at higher temperatures, one must consider the ways in which the system will vary as the temperature is increased. The first approximation utilized in this context (from the solid-state perspective) is lattice dynamics [6]. Equivalently, for molecular approaches, one considers the entropic and enthalpic contributions arising from the rotational, translational, and vibrational degrees of freedom [5]. In solid-state systems, the effect of temperature

manifests itself through the excitation of phonons, and so the key quantity of interest is the phonon density of states. The quasiharmonic approximation makes the assumption that the main effect of phonons is through the thermal expansion of the unit cell. Here, the lattice parameters are varied so as to minimize the sum of the potential energy and the vibrational free energy at a given temperature, while the atomic positions within the unit cell relax according to the internal energy. Utilization of this approximation is usually valid to half the melting point. Above this temperature, anharmonic effects become significant, and so molecular dynamics becomes the preferred means to simulate thermal expansion.

Sometimes, the actual structure of a system is hard to anticipate simply based on chemical intuition. In this case, techniques such as simulated annealing or machine-learning approaches can be used to randomly search the configuration space spanned by the suspected reactants and/or products and identify a series of local minima. Such techniques are known as *global search algorithms*, although, in reality, a global search can rarely be guaranteed unless the configuration space is narrow enough that a systematic search can be made [4, 5].

The outputs of an energy minimization can be highly instructive. Starting with a minimized structure, one can use the arrangement of atoms in the system (such as bond lengths and angles) to compare with diffraction or NMR techniques, for example. One can also compute the vibrational spectrum to compare with optical spectroscopy techniques. The relative energy of different states can be an indicator of their contribution to a given reaction scheme. Once energy minimization has been performed for several hypothetical states that are assumed to be pertinent for a given reaction mechanism or pathway, statistical mechanics interpretations can then be applied to make some specific thermodynamic assertions. For instance, the enthalpy of reaction can be estimated, or the probabilistic distribution of particles among two distinct states that differ in energy can be determined via the Boltzmann distribution [209]:

$$\frac{n_1}{n_2} = e^{-\Delta E/kT}$$

Other postprocessing techniques allow the computation of the density of states/molecular orbital structure, local charges on atoms or fragments of the system, dipole and multipoles, magnetic properties, and the electrostatic potential. Energy minimization can also be performed in the presence of perturbations, such as external fields or imposed electrode potentials [212].

1.3.4 Transition State Theory

While thermodynamic analysis provides guidelines as to the equilibrium state of a system, for truly predictive modeling—especially at relatively low temperatures where activation barriers may exceed the average thermal energy and level of excitation—kinetics can be equally as important. Whereas estimates of rates can be made from thermodynamic reaction energies, using paradigms such as the Evans–Polanyi relationship through proper configurational sampling activation energies for reactions can be directly determined via molecular modeling [104, 213]. The Arrhenius equation can then be applied to provide predictions of rates, provided a suitable prefactor can be assumed [214]:

$$k = Ae^{-\Delta G^*/RT}$$

In the case of diffusion, this expression takes the form of the Eyring equation:

$$k = \kappa \left(\frac{kT}{h} \right) e^{-\Delta G^\ddagger / RT}$$

where κ is the transmission coefficient. These rates can then be used to directly assist in the interpretation of experimental data, or to compare alternative reaction pathways with one another, or combined to run stochastic or integrodifferential simulations of overall reaction sequences. For instance, if an experimentally determined Arrhenius barrier is available, it could be compared to the Arrhenius barriers obtained computationally for several different hypothetical pathways, and the correct pathway distinguished if one is found to be in agreement. A chief difficulty with Arrhenius-based modeling is in the selection of the proper pre-factor, though methods do exist to compute the transmission coefficient, such as the reactive flux technique.

The activation energy can be determined once an atomic configuration, corresponding to the transition state, has been located. Transition states are local maxima along a reaction coordinate that connect two local minima on the potential energy (the reactants and products). Additionally, they are also saddle points in the local potential energy space, as they should be local minima for all directions other than that connecting the reactants and products. Thus, transition state searches rely upon computing the derivatives of the potential energy with respect to the atomic coordinates. Most search methods for transition states involve the first derivatives only, such as the synchronous transit or nudged elastic band methods, though, again, algorithms exist that can exploit the Hessian matrix, where available [215–219]. The popular nudged elastic band method begins with a series of geometries (images) supposed to lie upon a hypothetical reaction pathway and then uses a constrained minimization to find the optimal path connecting reactants and products while minimizing the forces between the images (hence, the term nudged elastic band).

1.3.5 Molecular Dynamics

Molecular dynamics simulation is perhaps the most directly accessible of molecular modeling tools conceptually speaking. However, its use as an interpretive modeling tool is perhaps one of the most limited due to the necessity of modeling relatively long stretches of time that do not necessarily include the events of interest to the modeler. Molecular dynamics simulation involves the time propagation of some initial atomic configuration within some suitable thermodynamic ensemble. A common ensemble used is the NVT ensemble, which indicates constant number of chemical species, constant volume, and constant temperature. Temperature control is typically maintained in a molecular dynamics simulation by coupling the kinetic energy of the particles in the simulation with a virtual thermal reservoir/thermostat [220, 221]. Time propagation is most commonly achieved by applying the Born–Oppenheimer approximation (i.e., the behavior of nuclei is classical and slow compared to the motion of electrons) and classical Newtonian dynamics. Molecular dynamics simulation can be achieved by using *ab initio* forces on the particles or by using suitable interatomic potentials. The former method has appeal, in that *ab initio* methods can implicitly model changes in chemical bonding that may occur during the simulation—typically interatomic potentials do not allow changes in bond types between atoms, although recent potentials have been devised to try to overcome this [202]. Molecular

dynamics simulations of interfaces, such as appear in corrosion scenarios, are challenged by the difficulty of adopting a potential set that applies equally well to the solid state, as to the solution state. Molecular dynamics approaches have been applied to understanding the role of hydrogen embrittlement of metals [222–224]; to the structure, dynamics, and transport processes in ionic solids [225, 226]; and for understanding solvation of ions in dilute and concentrated solutions [85, 88, 90, 227].

In addition to providing a microscopic tool for observing the outcomes of physicochemical processes in extraordinary detail, molecular dynamics simulations can, in principle, provide a valuable technique for obtaining thermodynamic variables and rate constants via integration over selected portions of the molecular dynamics trajectory. Several techniques have been recently employed that allow this kind of analysis, even with the present limitations regarding length and timescales, such as time-accelerated molecular dynamics [228, 229].

1.3.6 Monte Carlo Simulation

Monte Carlo simulations take advantage of probabilistic sampling methods to investigate the equilibrium behavior of systems as a function of temperature (Metropolis Monte Carlo) or to advance the state of a reactive system through time (kinetic Monte Carlo). In Metropolis Monte Carlo simulation, the energy required to effect a discrete change to the system (i.e., in bonding configuration, addition or subtraction of species, atomic diffusion) is evaluated via either first principles, interatomic potentials, or a lookup table [230, 231]. If the discrete change is exothermic (i.e., negative energy change), then the event is allowed to proceed within the simulation. Otherwise, the Boltzmann probability for this event is compared to a randomly generated number between 0 and 1. If this probability exceeds the random number, then the change is effected within the simulation. In this way, an equilibrium state will ultimately emerge that corresponds to the predicted state of the system at that given temperature. The accuracy of such a prediction will depend upon the accuracy of the underlying potential energy surface and the extent to which the environment is adequately representative of the situation to which the results will be applied.

Kinetic Monte Carlo simulation proceeds in a somewhat different fashion, in that a list of all possible discrete reaction steps is compiled, or sometimes determined *on the fly*, for events such as atomic diffusion, dissolution, dissociation, or chemical combination, and a probabilistic method is used to select a reaction based on the relative likelihood it will occur in a collective portion of time [232]. Reactions with a high rate will be more likely selected than reactions with a slower rate. Reaction rates can be derived *ab initio*, from interatomic pair potentials, approximate functional relations, or a lookup table. Once a reaction is selected, the time step is advanced based on all possible rates for reactions involving the current configuration, and the system state is updated. A new reaction list is compiled, and the probabilistic selection process continues. In this way, a kinetic Monte Carlo simulation somewhat resembles a molecular dynamics trajectory, although the events are discrete rather than finite time step *continuous*, and typically, much greater timescales can be considered. Rather than waiting throughout the span of a molecular dynamics simulation for some significant event to occur, one can simply *step* ahead to the expected time it would take for that event to occur. In addition, the ability provided by kinetic Monte Carlo to consider competing reaction mechanisms and devise simulations with complex topological dependencies can also provide significant insights.

1.4 BRIDGING THE REALITY GAP

Just as an experiment must be well designed to provide an answer that is relevant to its practical motivation, so too must a model be well designed to mimic the physical phenomenon under consideration. For the purposes of corrosion, multiple phenomena should be given consideration beyond the immediate reactive molecular environment. These include the estimation of thermodynamic variables at realistic temperatures and pressures, the effects of solvation, control of chemical potential, electric fields and variance from charge neutrality, as well as point, line, and planar defects in the material, materials inhomogeneities, and long-range elastic effects. Although state-of-the-art efforts to incorporate these phenomena within molecular simulations will be discussed within the following chapters, a brief overview of contemporary approaches is presented in the following subsections.

1.4.1 First-Principles Thermodynamics

The techniques of energy minimization and the calculation of the internal energy of a configuration of atoms can provide much information regarding hypothetical corrosion mechanisms, yet, in order to make more quantified statements about system behavior, it is pertinent to extrapolate from the static, 0 K configurations, to provide an estimate of the system thermodynamics at the temperatures of interest. By coupling the tools of molecular modeling with statistical mechanics, it is possible to begin constructing phase diagrams for molecular and materials systems in which competing states can coexist, depending on their position in phase space. Thermodynamic variables relevant to corrosion may include the pH, electrode potential, concentrations of ions, or gas pressures. In some cases, extrapolation of first-principles internal energies can be made using tabulated data for the variation of free energy with the variables of temperature or pressure. In other cases, it may be necessary to derive all of these terms *ab initio* by first calculating the vibrational, torsional, and rotational degrees of freedom for a molecule or materials system (or subsystem) and then determining the zero-point energy and the partition function as a means for arriving at the overall free energy. Free energies can then be adjusted for the chemical potential by using the standard Gibbs expression. This technique has been applied to both surface chemistry and bulk alloy materials [233, 234].

1.4.2 Solvation Models

Since the properties of molecules and interfaces can be significantly modified when they are solvated, it seems critical for models, particularly in aqueous corrosion, to consider the influence on the properties computed by molecular modeling techniques. The challenge posed by solvation is that the arrangement of solvent molecules about a molecule or interface is frequently dynamic, and as such, either multiple configurations should be sampled—as in a molecular dynamics or Monte Carlo approach—or a continuum approach used to mimic the solvent properties. One popular approach that has most often been employed is the polarizable continuum model for solvent [235]. The solvent is treated as a polarizable medium with a given dielectric constant, and a method is used to project the influence of this solvent on the electronic structure calculations used to determine the molecular properties. This approach provides a correction to the free energy of the system. Typically, this correction is made using parameterized data that has been shown to provide accurate solvation energies for molecules under ambient conditions. There therefore remains some uncertainty when

applying such techniques to nonambient pressures and temperatures. The representation of the solvent by explicit molecules can also be performed and may provide some particular advantages, including being able to directly model the bonded and nonbonded interactions that may develop between the molecule and material of interest and the solvent itself [184, 236]. However, one must then take proper care to sample an appropriate number of solvent configurations so that the study does not become biased toward one particular configuration that may be statistically insignificant in a thermalized system.

1.4.3 Control of Electrode Potential and the Presence of Electric Fields

Since many corrosion processes occur at the electrochemical double layer, the influence of variations in the electrode potential and the electric field should also be given consideration in advanced modeling approaches. In slab models or 2D periodic models, it is possible to apply an electric field, typically a constant electric field, across the supercell that represents the materials system, such that there exists a bias that favors the separation of charge states and the alignment of dipoles in a given direction [89, 116]. This procedure can be applied to both first-principles electronic structure codes and also to techniques that use pair potentials and charges on atom or molecular centers. An alternative approach for modeling electrode systems has been to vary the net charge on the system and make appropriate corrections to determine the role of the induced electrochemical potential in modifying the system free energy [237]. In both cases, serious consideration should be given to the relationship between the submicroscopic system, composed of molecules, atoms, and ions, and the continuum concepts of electrochemical potential.

1.4.4 Materials Defects and Inhomogeneities

Corrosion is a process that is commonly initiated at weak points at the materials/environment interface, presented by microstructural inhomogeneities such as grain boundaries, triple points, or secondary phases [238]. In many cases, the atomic-level structure of defect sites may not be well characterized or can manifest in multiple variations, such that deciding on one representation for a molecular modeling study can be challenging. At present, there are no trivial ways to simplify this problem; however, as experimental characterization techniques continue to improve the knowledge base regarding the atomic-level structure of materials defects and as computational methods expand to provide the ability to model more complex atomic configurations, this seems to be an area in which significant growth and materials insights can be expected in the near future.

1.5 MOLECULAR MODELING AND CORROSION

As indicated in Figure 1.1, the application of molecular modeling techniques to corrosion science is still in its infancy. In this first edition of *Molecular Modeling and Corrosion*, we introduce several areas in corrosion science to which molecular modeling has been successfully applied. In Chapter 2, Taylor discusses the application of molecular modeling techniques to study the reactivity of species introduced from the environment on the surface of metals and the current challenges to developing models that properly account for the defect structure of the material, as well as the configurational complexity of an aqueous phase environment. In Chapter 3, Schmickler et al. discuss the development of models

to take into account surface reactivity and to describe cathodic phenomena such as the oxygen reduction and hydrogen evolution reactions. In Chapter 4, Policastro describes the current state of the art in modeling dealloying via kinetic Monte Carlo simulation techniques. Costa and Marcus describe in Chapter 5 the application of molecular modeling to investigate the adsorption properties of organic molecules on metal surfaces—a topic relevant to the development of corrosion inhibitors, as well as understanding the response of metals to biological media. In Chapter 6, Holby and Francis discuss the application of electronic structure techniques to predict the oxidation properties of fresh metal surfaces, the precursor phases to passivity of those metals. Maurice et al. present, in Chapter 7, a review of investigations of the reactivity of metal-oxide films to environmental species that induce localized corrosion and pitting. Finally, Lu and coworkers present, in Chapter 8 of this edition, a description of the application of multiscale methods to study the challenging problem of hydrogen embrittlement, which bridges mechanical failure modes in a material with the chemical interactions between H and materials defects.

As the brief survey we have made of the aforementioned corrosion mechanisms reveals, there remain many more scientific and engineering problems that can be tackled via molecular modeling approaches. The combination of modern developments in computational architectures, algorithms, and molecular modeling approaches with the age-old problems presented by corrosion science (as well as emerging problems that develop as both existing and new materials are pushed to greater extremes) will no doubt continue to increase the application of these techniques to the field of corrosion science. As a deeper understanding of corrosion mechanisms grows through this analysis, advanced strategies will be developed for the mitigation of corrosion of materials, and the science of interfacial reactions will itself be greatly developed with gains in areas not only in the field of corrosion but in catalysis, electrochemistry, and other disciplines in which interfacial properties are of key significance.

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