# PHASE TRANSITIONS OF FIRST ORDER IN FINITE VOLUMES WITH APPLICATIONS TO UNDERPOTENTIAL DEPOSITION OF METALS

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This review is focused on the behavior of finite macroscopic systems (as opposed to infinitely large systems) determined from microscopic interactions. The temperature is assumed to be sufficiently below the critical point so that coexistence of two or more phases can occur and the systems can undergo first-order phase transitions. We summarize the rigorous results on the finite-size behavior for a specific but wide class of models of real systems-the lattice-gas models of dimension d > 2 with a finite number of ground states for which the free energy density can be expressed via convergent cluster expansion series. The behavior is rather sensitive to the interaction of the system with its surroundings (boundary conditions). In addition to periodic boundary conditions, which is a very popular choice, weak boundary conditions are considered. The latter are much more realistic, although they rule out the presence of large interfaces or droplets (phase separation) in the systems. For boundary conditions so strong that phase separation is possible, the situation is very complex, and we provide rigorous results only for a two-dimensional Ising model. The majority of the paper, however, is devoted to an application of these finite-size results to an interesting phenomenon in electrochemistry in which first-order phase transitions may occur at metal-electrolyte interfaces as a result of the deposition of metals on surfaces of other, more noble metals at electric potentials above the Nernst threshold. This is called underpotential deposition (UPD), and, for example, copper or silver may be so deposited on a surface of gold or platinum. The presence of such transitions is associated with sharp spikes that are observed in the current vs. electric potential plots of UPD processes. The application of the finite-size results to this problem is not straightforward, for it must take into account a polycrystalline structure of the surfaces. In fact, for a single crystalline domain on the surface the theory predicts spikes that are two or more orders of magnitude taller and sharper than those observed in experiments. On the other hand, when the surface is modeled realistically as an ensemble of many crystalline domains whose individual contributions are summed up to produce an overall spike, the agreement with experiment can be rather accurate. This is demonstrated in detail for two experimental spikes associated with UPD of copper on the (111) surface of platinum and gold electrodes.

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## 1 Introduction

Phase transitions are determined by non-analyticities of the specific free energy f. When such a non-analyticity is caused by a discontinuity in a first-order derivative, the phase transition is said to be of first order. The very introduction of phase transitions is somewhat contradictory. In fact, it relies, on the one hand, on properties of the specific free energy f, a quantity characterizing only an idealized, infinitely large system (the thermodynamic limit). On the other hand, real systems are always finite. However, the finite-volume free energy is, as a rule, analytic, and no discontinuities can therefore appear in its first-order derivatives (such as the internal energy, magnetization, etc.). Instead, infinite-volume jumps are smoothed out into rounded transitions. It is expected, though, that the rounding becomes more and more abrupt as the system size increases. In addition, it is expected that the positions of the rounded transitions are in general shifted with respect to those of the infinite-volume jumps. If we consider the derivatives of second order (the heat capacity, susceptibility, etc.) or higher order, these have singularities of the  $\delta$ -function type in the thermodynamic limit. In a finite system they are changed into *sharp spikes*, and the points where the spikes are maximal are suitable to describe the above-mentioned shifts of the rounded transitions: at these points the transitions are the steepest. The phenomena connected with the asymptotic behaviour of finite systems are commonly referred to as the *finite*size effects (at or near first-order phase transitions in the case considered here). It is important to realize that they are significantly affected by boundary conditions, i.e., the influence of the system's environment.

The finite-size effects are always distinguishable in computer simulations (where the studied systems are rather small), but they might be imperceptible in experiments and practical applications (where the systems are large). If external changes to a macroscopic system are carried out sufficiently slowly, a rounding of a first-order phase transition should be sufficiently sharp so that even an extremely careful measurement could not distinguish it from a mathematical non-analyticity; any distinct rounding that could be measured would only be due to non-equilibrium effects. In some experiments, however, the rounding does not seem to tend to non-analyticities with a decreasing rate of external changes. For example, spikes in the heat capacity vs. temperature plots [1, 2] or in the current vs. voltage plots for underpotential deposition (see Figs. 4.2 and 4.3 below) are of finite heights and widths even at very slow heating/scan rates. This may be attributed to the fact that real systems are not perfectly homogeneous. Some can be composed of many small homogeneous subsystems whose contributions are distinctly rounded and mutually shifted so that, when their total is measured, clear roundings remain even in the quasistatic regime. In the present paper this idea is developed in the case of a specific application.

A deeper understanding of the effects of finite size requires a description at a microscopic level. One possible approach is to construct simplified microscopic models and to identify and include the key properties of real systems into the models so that the macroscopic behaviour of the systems can be explained. Perhaps the most popular systems of this sort are classical *lattice-gas models*, and in this paper we shall provide a concise overview of rigorous results on their finite-size behavior (see Section 2). The main focus is, however, on application of these theoretical results to a specific problem in electrochemistry concerning the description of current density vs. electric potential plots for underpotential deposition of metals on crystalline surfaces (see Sections 4 - 6). The plots usually contain sharp spikes that are associated with phase transitions at the surfaces. Therefore, combined with the fact that these transitions can be

conveniently modeled by lattice gases, they offer a marvelous area where the theoretical results can be applied. The application is not straightforward, but it requires a generalization of finitesize effects from a single system to an ensemble of systems. Since the results are not necessarily related to underpotential deposition but are of universal nature, we present them in a separate Section 3. Concluding remarks are provided in a final section.

## 2 Effects of a finite system size

In this section we shall discuss how finiteness of a system affects its behavior at the macroscopic level. Theories of the finite-size effects near first-order phase transitions go back to the 1980s when the works of Imry [3], Fisher and Berker [4], Blöte and Nightingale [5], Binder and co-workers [6, 7, 8], Privman and Fisher [9], and others appeared. These theories were in the early 1990s systematized in a *rigorous* framework by Borgs and Kotecký [10, 11]. Their results cover the finite-size effects for the cubic systems describing the coexistence of a finite number of phases with both field- and temperature-driven transitions under periodic boundary conditions. As the main tool, they used the Pirogov-Sinai theory of first-order phase transitions [12, 13, 14]. Periodic boundary conditions do not allow the description of the finite-size effects in real systems in which the influence of the surface may play a major role. Therefore, they later extended their theory to the cubic systems with free or, more generally, weak boundary conditions; i.e., those not strongly favoring any of the considered phases near the system's surface [15, 16]. Besides cubic volumes, Borgs and Imbrie [17, 18, 19] investigated systems in long cylinders. A rigorous study of finite-size effects for strong boundary conditions when a macroscopic droplet occurs in the system was carried out for a two-dimensional Ising model [20].

Of these results we will present those predicted by the rigorous theories of Borgs and Kotecký for periodic [10] and weak [15] boundary conditions as well as the rigorous results for the strong boundary conditions for the 2D Ising model [20]. We begin by specifying the statistical mechanical models to which the results can be applied.

### 2.1 Considered lattice gases

We will consider a macroscopic system in a finite d-dimensional cubic volume  $V = L^d$  of side length L represented by a rectangular lattice  $\{0, 1, ..., L\}^d$  of  $N = (L+1)^d$  sites. Modifications of the presented results to other volumes of a parallelogram shape or other lattices are quite straightforward. It will be always understood that the length L is *large*, say, several tens or hundreds (for a 3D system of  $10^{26}$  particles it is of order  $10^9$ ).

In general, lattice gases are statistical mechanical models in which lattice sites are either occupied by a particle or vacant [21,22]. Thus, their microscopic configurations are the collections  $\omega = \{\omega_1, \ldots, \omega_N\}$ , with  $\omega_i = 0$  corresponding to a vacant site *i* and  $\omega_i = 1$  to an occupied site *i*. The models can be extended to situations with two or more particle species (see Section 6 for an example). The interactions between the particles are introduced via interaction potentials,  $U_A$ , between various groups *A* of particles (pairs, triples, etc.), and the system Hamiltonian is their sum,

$$H = \sum_{A} U_A.$$
 (2.1)

Perhaps the most frequent simplification is to restrict the interactions to the nearest-neighbor pairs; the most famous example is the Ising model [23] (see Section 2.1.2 below).

### 2.1.1 Contour models

In the Borgs–Kotecký theory the starting point is not a system specified by its potentials  $U_A$ . Instead, the theory works with an abstract system whose configurations can be rewritten in a geometrical fashion as regions in V with the lowest energy (the ground state regions) that are separated by energetically unfavorable regions. The latter correspond to objects called *contours* (or polymers) [12, 14]. The partition function, Z, of such a system is then given as the sum of contour partition functions,  $Z_q$ , each corresponding to one of a finite number of ground states (labeled by the subscript q from a finite set Q),

$$Z = \sum_{q \in Q} Z_q, \tag{2.2a}$$

with

$$Z_q = e^{-\beta E_q} \Big[ 1 + \sum_{M=1,2,\dots} \sum_{\{\gamma_1,\dots,\gamma_M\}} \prod_{j=1}^M w_q(\gamma_j) \Big].$$
(2.2b)

Here  $E_q$  is the energy of the *q*th ground state,  $\beta = 1/k_BT$  is the inverse temperature,  $w_q$  are contour weights, and the second summation in  $Z_q$  is over all collections of *M* contours that lie in *V* and are mutually non-intersecting.

It may not be obvious if a given lattice gas can be reformulated as a contour model (2.2). It turns out, however, that this is so for a large group of lattice gases. The group includes, in particular, the lattice gases with translation invariant potentials  $U_A$  that are of finite range [12]. Let us discuss this point in some detail. First, we shall consider a specific lattice gas (the standard ferromagnetic Ising model) and then a lattice gas with a finite-ranged potential.

## 2.1.2 Ising model

The model was introduced to simulate the behavior of a ferromagnet, and the value  $\omega_i = 0$  $(\omega_i = 1)$  is meant to express that the site *i* 'has a spin oriented down (up).' (In fact, the values  $\sigma_i = \pm 1$  are usually used instead of  $\omega_i = 0, 1$ , as depicted in Fig. 2.5 below. This is not physically important, however, because the transformations  $\omega_i = (\sigma_i + 1)/2$  and  $\sigma_i = 2\omega_i - 1$  enable us to get from one interpretation to the other [21].) The interaction is assumed to be pairwise and limited to the nearest neighbors (n.n.). Thus, the potential  $U_A$  vanishes for all groups A of sites except when  $A = \langle i, j \rangle$  is a pair of n.n. sites *i* and *j* in which case  $U_{\langle i,j \rangle}$  has two values so that parallel spins are energetically more favorable than antiparallel ones, as in a ferromagnet. For example,  $U_{\langle i,j \rangle}$  may be set equal to  $\varepsilon$  if  $\omega_i = \omega_j$  (parallel spins) and to  $-\varepsilon$  if  $\omega_i \neq \omega_j$  (antiparallel spins), where  $\varepsilon < 0$  is an interaction energy. The Hamiltonian of the model is thus given as

$$H(\omega) = \sum_{\langle i,j \rangle} U_{\langle i,j \rangle}(\omega_i,\omega_j) = \varepsilon [N_{\text{par}}(\omega) - N_{\text{anti}}(\omega)] = -2\varepsilon N_{\text{anti}}(\omega) + \varepsilon N, \qquad (2.3)$$

where the sum goes over all n.n. pairs of sites and  $N_{\text{par}}$  ( $N_{\text{anti}}$ ) is the number of (anti)parallel n.n. pairs.

It is possible to represent each configuration  $\omega$  in the cube V in a geometric fashion using the boundaries that separate the region,  $V_{\uparrow}$ , of sites in V with 'spins up' from the region,  $V_{\downarrow}$ , of sites in V with 'spins down.' Namely,  $V_{\uparrow}$  ( $V_{\downarrow}$ ) is the union of all unit cubes in V at the centers i



Fig. 2.1. An example of contours (the lines) corresponding to a microstate in a rectangular lattice of  $10 \times 10$  sites (indicated by the dashed square) under fixed boundary conditions (i.e.,  $\omega_i = 0$  is fixed at all sites *i* outside *V*). Vacant (occupied) sites are depicted as circles (disks).

of which  $\omega_i = 1$  ( $\omega_i = 0$ ). Each connected component of the intersection  $V_{\uparrow} \cap V_{\downarrow}$  represents an energetically unfavorable region and is a contour  $\gamma$  (see Fig. 2.1 for a two-dimensional example). Since contours are constructed as the boundaries between  $V_{\uparrow}$  and  $V_{\downarrow}$ , the number of unit segments in all contours is equal to the number  $N_{\text{anti}}$  of the antiparallel n.n. sites. Therefore,

$$H(\omega) = -2\varepsilon \sum_{\gamma} \Lambda(\gamma) + \varepsilon N, \qquad (2.4)$$

where the sum is over all contours  $\gamma$  and  $\Lambda(\gamma)$  is the number of unit segments in  $\gamma$ .

There is a unique collection of contours for each configuration  $\omega$ . On the other hand, there are two possible configurations for each collection of contours. In fact, starting at a site *i*, the value  $\omega_j$  at every n.n. site *j* of *i* coincides with  $\omega_i$ , unless *j* is separated from *i* by a contour; the value  $\omega_k$  at every n.n. site *k* of *j* coincides with  $\omega_j$ , unless *k* is separated from *j* by a contour; etc. Every time we cross a contour, the value of the spin is changed. Hence, there are two configurations of spins for a given collection of contours, corresponding to two possible values of  $\omega_i$  at the starting site. Consequently, the partition function of the Ising model (2.3) can be rewritten as

$$Z = \sum_{\omega} e^{-\beta H(\omega)} = 2 e^{-\beta \varepsilon N} \left[ 1 + \sum_{M=1,2,\dots} \sum_{\{\gamma_1,\dots,\gamma_M\}} \prod_{j=1}^M e^{-2\beta |\varepsilon| \Lambda(\gamma_j)} \right];$$
(2.5)

i.e., as a sum of two identical contour partition functions (c.f. Eq. (2.2)) with the contour weights

given as

$$w(\gamma) = e^{-2\beta|\varepsilon|\Lambda(\gamma)}.$$
(2.6)

Note that Z is actually the sum of two contour partition functions that are identical. This is due to the symmetry of the Ising model (2.3) with respect to the interchange of spins  $\omega_i$  with values 0 and 1. If a symmetry-breaking term is added to the Hamiltonian (2.3), such as the term  $-h \sum_i \omega_i$  with an external magnetic field h (as in Eq. (2.76) below), the two contour partition functions would become different.

### 2.1.3 A general case

The above procedure to introduce contours for the Ising model can be extended to cover a much wider group of lattice gases. Even though contours can be tailored to a particular lattice gas (and even for a given lattice gas it is possible to introduce various definitions of contours depending on the particular aim of study), there are rather canonic definitions of contours that may be found, for example, in [12, 13, 10, 15].

To describe the procedure, let us consider the interaction potentials  $U_A$  that are translation invariant and of finite range R (i.e.,  $U_A$  vanishes once the diameter of the group A of sites exceeds R). The Hamiltonian of the system will be given by Eq. (2.1) with the summation over all A lying inside the system volume V. Given a configuration  $\omega$ , the ground-state regions  $V_0$  and  $V_1$  in the volume V contain all those sites i for which the configurations  $\omega_j$  at the sites within the distance R from i (including i itself) are all equal to 0 and 1, respectively. The remaining sites, with configurations in their R-vicinities that differ from the constant 0 or 1 configurations, should represent energetically unfavorable regions, i.e., contours. Therefore, we split these remaining sites into connected components denoted as  $\Gamma$ .

We may now rewrite the system Hamiltonian (2.1) as

$$H = \sum_{A \text{ in } V} U_A = \sum_{A \text{ in } V} \sum_{i \text{ in } A} \frac{U_A}{|A|} = \sum_{i \text{ in } V} \sum_{A \text{ contains } i} \frac{U_A}{|A|}$$
$$= \left(\sum_{q=0,1} \sum_{i \text{ in } V_q} + \sum_{\Gamma} \sum_{i \text{ in } \Gamma}\right) \sum_{A \text{ contains } i} \frac{U_A}{|A|},$$
(2.7)

where |A| is the number of sites in A. In the ground-state regions  $V_q$  the configurations are constant ( $\omega_i = q$  for all sites i in  $V_q$ ), and so

$$E_q(V_q) = \sum_{i \text{ in } V_q} \sum_{A \text{ contains } i} \frac{U_A(\omega^q)}{|A|} = \sum_{A \text{ intersects } V_q} \frac{|A \cap V_q|}{|A|} U_A(\omega^q), \qquad q = 0, 1, \quad (2.8)$$

are the energies of the ground-state regions. Note that the interaction potentials  $U_A$  in  $E_q$  are evaluated for the constant configuration  $\omega^q = \{\omega_i = q \text{ for all sites } i\}$ . In addition, we have

$$\sum_{i \text{ in } \Gamma} \sum_{A \text{ contains } i} \frac{U_A}{|A|} = \sum_{A \text{ intersects } \Gamma} \sum_{i \text{ in } A \cap \Gamma} \frac{U_A}{|A|} = \Phi_{\Gamma},$$
(2.9)

with

$$\Phi_{\Gamma} = \sum_{A \text{ intersects } \Gamma} \frac{|A \cap \Gamma|}{|A|} U_A.$$
(2.10)

Combined together, the Hamiltonian may be written as the sum [12, 14]

$$H = E_0(V_0) + E_1(V_1) + \sum_{\Gamma} \Phi_{\Gamma}.$$
(2.11)

The first two terms on the right-hand side correspond to the ground-state regions, while the sum represents the contributions due to energetically unfavored regions.

**Remark 2.1.** For all sites i in the system volume V whose distance from the boundary is larger than the interaction range R, the quantity

$$e_q(i) = \sum_{A \text{ contains } i} \frac{U_A(\omega^q)}{|A|}$$
(2.12)

is the same (independent of the exact position of i) and is equal to the specific energy of the fully vacant (q = 0) and fully occupied (q = 1) ground state. Similarly, for all sites i in V that are closer than R from an m-dimensional face of the boundary of V but farther than R from any of its lower dimensional faces, the quantity  $e_q(i)$  is identical. The ground-state energy

$$E_q = \sum_{i \text{ in } V} e_q(i) \tag{2.13}$$

in the whole system (c.f. Eq. (2.8)) may be therefore split into bulk and boundary terms. This fact will be used later in Eq. (2.55) below.

Using the expression (2.11) for the Hamiltonian, the partition function is given as

$$Z = \sum_{\omega} e^{-\beta H} = \sum_{\omega} e^{-\beta E_0(V_0) - \beta E_1(V_1)} \prod_{\Gamma} e^{-\beta \Phi_{\Gamma}}.$$
(2.14)

A contour  $\gamma$  is introduced as a pair  $(\operatorname{supp} \gamma, l_{\gamma})$ , where  $\operatorname{supp} \gamma$  is a connected collection of sites and  $l_{\gamma}$  is an assignment of a label 0 or 1 to the boundary of each component of the complement to  $\operatorname{supp} \gamma$  [13]. Since  $\Phi_{\Gamma}$  depends only on the configuration at the sites in  $\Gamma$ , the partition function may be rewritten as

$$Z = \sum_{M=1,2,\dots} \sum_{\{\gamma_1,\dots,\gamma_M\}} e^{-\beta E_0(V_0) - \beta E_1(V_1)} \sum_{\omega^{(1)}} \cdots \sum_{\omega^{(M)}} \prod_{k=1}^M e^{-\beta \Phi_{\text{supp } \gamma_k}}.$$
 (2.15)

The second sum is over all collections of non-overlapping contours  $\{\gamma_k\}$  that lie inside the volume V and have labels  $l_{\gamma_k}$  that are constant on the boundaries of each component of  $V \setminus \bigcup_{k=1}^M$  supp  $\gamma_k$ . The ground-state regions  $V_0$  and  $V_1$  are all of these components that have the boundary

label 0 and 1, respectively. The last M sums are over all configurations on the supports of contours for which  $\omega_i^{(k)}$  coincides with the label  $l_{\gamma_k}$  of the contour  $\gamma_k$  if the site i is on the boundary of the contour. Observing that

$$\sum_{\omega^{(1)}} \cdots \sum_{\omega^{(M)}} \prod_{k=1}^{M} e^{-\beta \Phi_{\operatorname{supp}} \gamma_k} = \prod_{k=1}^{M} \sum_{\omega^{(k)}} e^{-\beta \Phi_{\operatorname{supp}} \gamma_k}, \qquad (2.16)$$

we obtain

$$Z = \sum_{M=1,2,\dots} \sum_{\{\gamma_1,\dots,\gamma_M\}} e^{-\beta E_0(V_0) - \beta E_1(V_1)} \prod_{k=1}^M Y(\gamma_k)$$
(2.17)

with

$$Y(\gamma_k) = \sum_{\omega^{(k)}} e^{-\beta \Phi_{\text{supp } \gamma_k}}.$$
(2.18)

The representation (2.17) of the partition function can be rewritten to have form of the sum

$$Z = Z_0 + Z_1 (2.19)$$

of two contour partition functions given as in Eq. (2.2) with the labels q = 0 and q = 1. The corresponding contour weights are [15]

$$w_q(\gamma) = Y(\gamma) e^{\beta E_q(\operatorname{supp}\gamma)} \frac{Z_{1-q}(\operatorname{Int}\gamma)}{Z_q(\operatorname{Int}\gamma)},$$
(2.20)

where  $Z_q(\text{Int } \gamma)$  is the contour partition function in the interior of the contour  $\gamma$  (in the region encircled by the contour) rather than in the whole system volume V. We can therefore conclude that a lattice gas with translation invariant potentials  $U_A$  of finite range can be reformulated as a contour model (2.2).

## 2.2 Cluster expansions. Free energy

Since the contours  $\gamma$  are introduced so as to represent the boundaries of thermal perturbations of a microstate over the ground state, the contour weights  $w_q$  should be decaying with the contour size  $\Lambda(\gamma)$ . The exponential decay

$$|w_q(\gamma)| \le e^{-c\,\beta\Lambda(\gamma)} \tag{2.21}$$

with a constant c > 0 is often assumed; it is called the *Peierls condition*. The Ising weights (2.6) satisfy the condition with  $c = 2|\varepsilon|$ . More generally, contour weights of a lattice gas at low temperatures (high  $\beta$ ) are known to satisfy the condition if the interaction potential  $U_A$  constitutes an *m*-potential—if there are finitely many microscopic configurations (the ground states) each of which minimizes  $U_A$  for any group A of particles [24, 25]. Examples of such lattice gases will be given later in Sections 5 and 6 (see Eqs. (5.1) and (6.1)). If  $U_A$  is not an *m*-potential,

the Peierls condition may be still satisfied, but this must be verified individually for the contour weights under consideration.

One-dimensional thermal perturbations need not increase their boundaries when their size grows, thus violating the Peierls condition. Therefore, in the following we shall always consider only the systems of dimension two or higher; i.e.,

$$d \ge 2 \tag{2.22}$$

will be always assumed.

As long as the Peierls condition is satisfied, the dominant contribution to each contour partition function  $Z_q$  from Eq. (2.2) is due to the *q*th ground state. This contribution is represented by the Boltzmann factor  $\exp(-\beta E_q)$ . The contours, on the other hand, yield higher-order contributions to  $Z_q$ . It is therefore convenient to write

$$Z_q = e^{-\beta E_q} \mathcal{Z}_q, \tag{2.23}$$

where  $Z_q$  is the expression in the square brackets in Eq. (2.2). To evaluate the free energy

$$F_q = -\frac{1}{\beta} \ln Z_q = E_q - \frac{1}{\beta} \ln \mathcal{Z}_q, \qquad (2.24)$$

a sort of perturbative technique that would treat the contribution  $\ln \mathbb{Z}_q$  from contours is needed. Expansions of  $\ln \mathbb{Z}_q$  via contour clusters are a very popular approach [26, 27, 28, 29]. There are different versions of cluster expansions and definitions. Here a cluster will be defined as a collection of contours that cannot be split into two parts such that every contour from one part would intersect no contours from the other one [26]. Using the clusters, the free energy may be expressed as a cluster expansion series [26, 27, 28, 29]

$$F_q = E_q - \frac{1}{\beta} \sum_{K \text{ in } V} \Phi_q(K), \qquad (2.25)$$

where the summation is over all clusters K lying in the system volume. The cluster weights  $\Phi_q(K)$  are expressed in terms of the weights of the contours of which they are composed. A general expression for  $\Phi_q(K)$  is given by Eq. (3) in [26]. For example,

$$\Phi_q(\{\gamma\}) = \ln(1 + w_q(\gamma))$$
(2.26)

is the weight of a cluster  $K = \{\gamma\}$  containing just one contour  $\gamma$ .

The cluster expansion can be used to obtain the specific free energy  $f_q = \lim_{V\to\infty} (F_q/V)$  of the system. In fact, if  $e_q = \lim_{V\to\infty} (E_q/V)$  is the specific energy of the *q*th ground state, we may write

$$f_q = e_q + \varphi_q, \tag{2.27}$$

where  $\varphi_q = -(1/\beta) \lim_{V \to \infty} (\ln Z_q)/V$  is the contribution due to contour clusters. Thus,  $f_q$  is expressed as a sum of a zero temperature term  $e_q$  and a thermal perturbations term  $\varphi_q$ . According to Eq. (2.25), we have

$$\ln \mathcal{Z}_q = \sum_{K \text{ in } V} \Phi_q(K) = \sum_{K_b \text{ in } V} \Phi_q(K_b) + \sum_{K_s \text{ in } V} \Phi_q(K_s),$$
(2.28)

where  $K_b$  ( $K_s$ ) are the bulk (surface) clusters that contain only the contours not intersecting (intersecting) the system surface. The last sum, being over the surface clusters, is proportional to the system surface and its contribution to  $\varphi_q$  vanishes. The sum over the bulk clusters may be rewritten as

$$\sum_{i \text{ in } V} \sum_{\substack{K_b \text{ contains } i, \\ K_b \text{ in } V}} \frac{\Phi_q(K_b)}{W(K_b)} = \sum_{i \text{ in } V} \Big( \sum_{K_b \text{ contains } i} - \sum_{\substack{K_b \text{ contains } i, \\ K_b \text{ not wholly in } V}} \Big) \frac{\Phi_q(K_b)}{W(K_b)},$$
(2.29)

where a cluster is said to contain a site *i* whenever *i* lies inside one or more of its contours, and  $W(K_b)$  is the number of sites in all contours contained in the cluster  $K_b$ . The last sum is over the bulk clusters that intersect the system surface, so its contribution to  $\varphi_q$  vanishes, too. Thus, we get [26, 27, 28, 29]

$$\varphi_q = -\frac{1}{\beta} \sum_{K_b \text{ contains } i} \frac{\Phi_q(K_b)}{W(K_b)}$$
(2.30)

(it is tacitly assumed that the cluster weights are translation invariant). Note that the expression for  $\varphi_q$  is independent of the site *i*, and so *i* can be arbitrarily prefixed.

Due to the Peierls condition, the cluster expansion in Eq. (2.25) converges very fast in terms of the length  $\Lambda(K)$  of a cluster that is given as the sum  $\sum_{\gamma \in K} \Lambda(\gamma)$  of lengths of its contours. Indeed, similarly to the contour weights, the cluster weights decay exponentially with the cluster length as

$$|\Phi_a(K)| \le e^{-b\,\beta\Lambda(K)} \tag{2.31}$$

with a constant b > 0 slightly smaller than the constant c in the Peierls condition (2.21). An even stronger bound is true, however, because we have [26]

$$\sum_{K \text{ contains } i} e^{b\,\beta\Lambda(K)} |\Phi_q(K)| \le 1 \tag{2.32}$$

for any prefixed site *i*. Consequently, if  $\gamma_b^0$  is the bulk contour of shortest possible length,  $\Lambda_0$ , the estimate

$$|\varphi_q| \le \frac{1}{\beta} \sum_{K_b \text{ contains } i} |\Phi_q(K_b)| \le \frac{e^{-b\beta\Lambda_0}}{\beta} \sum_{K \text{ contains } i} e^{b\,\beta\Lambda(K)} |\Phi_q(K)| \le \frac{e^{-b\beta\Lambda_0}}{\beta}$$
(2.33)

can be established (for the Ising contours from Fig. 2.1 the shortest contour is a unit cube with  $\Lambda_0 = 2d$ , which corresponds to an addition/removal of a particle at a single site). This shows that the leading contribution to  $\varphi_q$  corresponds to the bulk cluster containing just the contour  $\gamma_b^0$ . Explicitly,

$$\varphi_q = -\frac{1}{\beta} \left( \frac{\ln(1 + w_q(\gamma_b^0))}{W(\gamma_b^0)} + \cdots \right), \tag{2.34}$$

where Eq. (2.26) was taken into account. In other words, the leading cluster contributions to the free energy  $f_q$  or  $F_q$  come from the clusters of small sizes; i.e., the clusters of a few small contours.

### 2.3 Low-temperature phases and phase diagrams

When the Peierls condition (2.21) is fulfilled for a given q, then the qth ground state gives rise to a unique low-temperature phase [12]. Its typical microscopic configuration looks as a 'sea' of the qth ground state in which small isolated 'islands' of non-ground-state configurations (represented by contours) are scattered. The volume density of the islands is not equal to zero, but is of order  $\exp(-b\beta\Lambda_0)$ , where  $\Lambda_0$  is the length of the shortest bulk contour  $\gamma_b^0$  (c.f. Eq. (2.33)).

It cannot be expected that the Peierls condition is satisfied simultaneously for the contour weights  $w_q$  with all labels q, but only for those q for which the corresponding phases are stable in the system. For example, for a system with two possible phases (when there are only two different labels q) the condition holds for both phases at and very close to the coexistence of these phases, while farther away from the coexistence only one of the two phases is stable and the condition holds for this phase and fails for the other one. Which phases are stable in a given region of parameters (external fields, temperature, etc.) is determined by the single-phase free energies  $f_q$ ; i.e., they determine the phase diagram of the system. Namely, a phase q is said to be *stable* if its free energy  $f_q$  is the lowest of all free energies [12, 13]. Of course, several phases may be stable at the same time in this sense. It is thus possible to identify points, curves, surfaces, etc. in the space of parameters where one or several phases coexist. This is analogous to the construction of the ground-state diagram where the specific single-phase energies  $e_q$  are mutually compared rather than the free energies  $f_q$ . Since

$$f_q = e_q + O(e^{-b\beta\Lambda_0}) \tag{2.35}$$

by Eqs. (2.27) and (2.30), it is clear that a low-temperature phase diagram is a 'slight deformation' of the ground-state diagram, the differences being just of order  $\exp(-b\beta\Lambda_0)$ . The symbol O(x) denotes an error term of order x.

### 2.4 Periodic boundary conditions

The behaviour of a macroscopic system is strongly affected by the boundary conditions; i.e., the interaction of the system with its surroundings. The simplest case is periodic boundary conditions when surface effects are significantly suppressed by a trick: systems are defined on a d-dimensional torus (with sides of length L) rather than on a cube, as if the opposite faces of the cube were identical.

### 2.4.1 Coexistence of several phases

For periodic boundary conditions the qth ground-state energy has the form  $E_q = e_q V$ , where  $e_q$  is its specific value. Similarly, if the contour weights  $w_q$  are translation invariant, the cluster expansion (2.25) can be rewritten to yield [10]

$$F_q = f_q V + O(e^{-b\beta L}) \tag{2.36}$$

for the corresponding free energy, where  $f_q$  is its specific value given by Eqs. (2.27) and (2.30), and the second term on the right-hand side is due to the clusters of very long contours,  $\Lambda(\gamma) \ge L$ , that may even 'wrap around' the torus. The expression (2.36) can be true only if the Peierls condition is fulfilled for the contour weights  $w_q$ . Suppressing the contours whose weights do not satisfy the Peierls condition,  $f_q$  can be introduced as a sort of auxiliary, 'meta-stable' specific free energies so that [12,13]

(a) their minimum,

$$f = \min_{q \in Q} f_q, \tag{2.37}$$

is equal to the specific free energy f of the system, and

(b)  $f_q = f$  when the *q*th phase is stable, while  $f_q > f$  if the *q*th phase is unstable (see Section 2.3 above).

It is then possible to express the system partition function as [10] (c.f. Eq. (2.2))

$$Z_{\rm per} = \left(\sum_{q \in Q} e^{-\beta f_q V}\right) [1 + O(e^{-b\beta L})].$$
(2.38)

This relation is the basis for evaluating any thermodynamic quantity in a finite system of volume  $V = L^d$  with periodic boundary conditions.

Thus, let us consider a quantity

$$a_{\rm per}(y) = -\frac{1}{V} \frac{\partial F_{\rm per}(y)}{\partial y}$$
(2.39)

that is the first derivative of the system free energy  $F_{per} = -(1/\beta) \ln Z_{per}$  with respect to a parameter (an external field) denoted as y. Examples of  $a_{per}$  and y are the magnetization and magnetic field, or the particle density and chemical potential. If we introduce the single-phase quantities

$$a_q(y) = -\frac{\partial f_q(y)}{\partial y} \tag{2.40}$$

as the derivatives of the single-phase specific free energies, then  $a_{per}$  can be shown to be their convex combination [10],

$$a_{\rm per} = \sum_{q \in Q} a_q p_q + O(e^{-b\,\beta L}),\tag{2.41}$$

where the coefficients

$$p_q = \frac{e^{-\beta f_q V}}{\sum_{q'} e^{-\beta f_{q'} V}}$$
(2.42)

sum to 1. In addition, a relation analogous to Eq. (2.41) holds for derivatives of  $a_{per}$ : they are equal to the derivatives of  $\sum_{q} a_q p_q$  with the same error term  $O(\exp(-b \beta L))$ .



Fig. 2.2. The plot of the functions J(x) and P(x) that describe the jump and spike in  $a_{per}$  and its derivative, respectively. For comparison, the dashed lines depict the Gaussian error function (of the same slope at x = 0) and Gaussian bell curve (of the same height and area).

### 2.4.2 Coexistence of two phases

In the special case when there can be only two possible stable phases (when there are only two labels, q = 1 and q = 2, say), Eq. (2.41) may be further rewritten to get an explicit dependence of the quantity  $a_{per}$  on the parameter y as follows. Let us introduce the sigmoid function and its derivative

$$J(x) = \frac{1}{1 + e^{-2x}} = \frac{1 + \tanh x}{2},$$
(2.43a)

$$P(x) = 2 \frac{dJ(x)}{dx} = \frac{4}{(e^x + e^{-x})^2} = \cosh^{-2} x.$$
(2.43b)

Note that J(x) has a profile of a jump that interpolates between the values 0 and 1, while P(x) exhibits a spike of height and area equal to 1 and 2, respectively (see Fig. 2.2). Both the jump and spike are positioned at x = 0. The convex coefficients  $p_1$  and  $p_2$  have the form of the jump functions,

$$p_1 = J\left(\frac{\beta}{2}\Delta f V\right), \qquad p_2 = J\left(-\frac{\beta}{2}\Delta f V\right),$$
(2.44)

whose arguments depend on the difference  $\Delta f = f_2 - f_1$  between the single-phase free energies. If  $y_t$  is the point at which both phases coexist so that  $\Delta f(y_t) = 0$ , then the infinite-volume jump,  $\Delta a$ , of the quantity  $a_{per}$  at the transition point  $y_t$  is [10]

$$\Delta a = a_2(y_t) - a_1(y_t), \tag{2.45}$$

and the Taylor expansion around  $y_t$  yields

$$\Delta f(y) = -\Delta a \, (y - y_t) + O((y - y_t)^2). \tag{2.46}$$

Thus, using that [15]

$$|J(x_1) - J(x_2)| \le \frac{1}{2} \min\left\{\frac{1}{|x_1|}, \frac{1}{|x_2|}\right\} |x_1 - x_2|,$$
(2.47)

the error in replacing the argument of J in the coefficient  $p_2$  by

$$\Lambda = \frac{1}{2} \Delta a \left( y - y_t \right) \beta V \tag{2.48}$$

is

$$|p_2 - J(\Lambda)| = \left|J\left(-\frac{\beta}{2}\Delta f V\right) - J(\Lambda)\right| \le \frac{\left|-\frac{\beta}{2}\Delta f V - \Lambda\right|}{2|\Lambda|} = O(|y - y_t|).$$
(2.49)

If we restrict y to an interval  $|y - y_t| \le \text{const}/L$ , then Eq. (2.41) yields the expression [10]

$$a_{\text{per}} = a_1 + (a_2 - a_1)p_2 + O(e^{-b\beta L})$$
  
=  $a_1 + (a_2 - a_1)J(\Lambda) + O(L^{-1}).$  (2.50)

When y is farther away from the transition point,  $|y - y_t| \ge \operatorname{const} / L$ , then

$$\beta |\Delta f| V = \beta \left| \frac{\partial \Delta f(\tilde{y})}{\partial y} \right| |y - y_t| V \ge \operatorname{const} \beta L^{d-1} \gg 1$$
(2.51)

by the mean-value theorem, so that one of the coefficients  $p_1$  and  $p_2$  is equal to 1 and the other one to 0, the errors being extremely small, just of order  $\exp(-\cosh\beta L^{d-1})$ . The quantity  $a_{per}$  therefore very precisely coincides with  $a_1$  or  $a_2$ . The same result, although with a larger error, is predicted by Eq. (2.50). The equation can be thus applied for any y. It shows that  $a_{per}$ interpolates between the two single-phase quantities  $a_1$  and  $a_2$  as the sigmoid function, and the change from one to the other takes place at the transition point  $y_t$  within a range of order  $1/\beta V$ (see Fig. 2.3). This range becomes extremely narrow as the system size L grows.

It is also possible to investigate the behavior of the derivatives of  $a_{per}$ . Let us consider only the first-order derivative

$$a_{\rm per}'(y) = \frac{\partial a_{\rm per}(y)}{\partial y} \tag{2.52}$$

(if  $a_{per}$  stands for the magnetization, for example, then its derivative is the susceptibility). It can be shown that it has a very sharp and tall spike described by the peak function P (see Fig. 2.3) and it is given as [10]

$$a'_{\rm per} = \left(\frac{\Delta a}{2}\right)^2 (1 + O(L^{-1})) \beta V P(\Lambda) + \delta a'_{\rm per}$$
(2.53)

with

$$\delta a'_{\rm per} = a'_1 + (a'_2 - a'_1)J(\Lambda) + O(L^{-1}), \qquad a'_i = \frac{\partial a_i}{\partial y}.$$
 (2.54)



Fig. 2.3. A schematic dependence of  $a_{per}$  and its derivative on the parameter y as given by Eqs. (2.50) and (2.53). The single-phase quantities  $a_1$  and  $a_2$  are depicted by dashed lines,  $a_j^t$  stand for their values at the transition, and 'max' denotes a maximal value of the derivative of  $a_{per}$ . Note that the maximum position is practically equal to the transition point  $y_t$ .

The height and width of the spike (the first term in  $a'_{per}$ ) are of order  $\beta V$  and  $1/\beta V$ , respectively. The second term  $\delta a'_{per}$  in  $a'_{per}$  is of order O(1) in the system size, thus being only a small contribution to  $a'_{per}$  near the transition. It has the same form as  $a_{per}$  itself (see Eq. (2.50)), describing a sharp jump interpolating between  $a'_1$  and  $a'_2$ . It can be also shown that the maximum position,  $y_{max}$ , of  $a'_{per}$  practically coincides with the transition point  $y_t$ : the shift between them is just of order  $1/V^2$  [10].

**Remark 2.2.** In the range  $|y - y_t| \leq \text{const} / L$  near the transition point the single-phase quantities are practically constant,  $a_i(y) \approx a_i(y_t)$  and  $a'_i(y) \approx a'_i(y_t)$ , the error terms being of order 1/L. Thus, in this range it is possible to apply Eqs. (2.50) and (2.53) with  $a_i$  and  $a'_i$  taken as these constants. As already pointed out, far from the transition, when  $|y - y_t| \geq \text{const} / L$ , Eq. (2.50) shows that  $a_{\text{per}}$  reduces to one of the single-phase quantities  $a_i$  (to one of them above the transition point  $y_t$  and to the other one below  $y_t$ ). Similarly, Eq. (2.53) shows that the derivative  $a'_{\text{per}}$  reduces to one of the single-phase quantities  $a'_i$ . Indeed, while the spike function  $P(\Lambda)$ practically vanishes, the jump function  $J(\Lambda)$  in the term  $\delta a'_{\text{per}}$  becomes equal to  $\pm 1$ .

### 2.5 Weak boundary conditions

Although simple to treat, periodic boundary conditions are not realistic. Interactions of a system with its surroundings (i.e., surface effects) may significantly influence the macroscopic behavior of the system. For example, they should slightly shift the position of a phase transition jump from the transition point—by an amount of order of the surface vs. bulk ratio; i.e., of order 1/L. To

describe such surface effects, it is more proper to consider weak boundary conditions. They work with a true, cubic volume of the system, but the interactions with the surroundings are restricted so that they do not strongly favor any phase near the system surface. Thus, no large interfaces and/or droplets occur in the system. With this restriction, the system's behavior can be studied by the same perturbative techniques as for the periodic boundary conditions.

### 2.5.1 Coexistence of several phases

For weak boundary conditions the key point is to take into account also the surface contributions to the free energies  $F_q$  from Eq. (2.25). Thus, it is first assumed that the system has bulk specific energies  $e_q$  (the same as for periodic boundary conditions, of course) as well as boundary specific energies,  $e_q^{(m)}$ , associated with *m*-dimensional faces of the system volume *V* (with  $m = d - 1, \ldots, 0$ ) such that the ground-state energies can be expressed as a bulk-surface expansion (see Remark 2.1)

$$E_q = e_q V + \sum_{m=0}^{d-1} e_q^{(m)} \,\partial V_m, \tag{2.55}$$

where  $\partial V_m = 2^{d-m} {d \choose m} L^m$  is the joint *m*-dimensional area of all *m*-dimensional faces of *V*. The fact that the boundary conditions are weak is specified by requiring that the boundary specific energies do not differ much from the bulk ones [15],

$$|e_q^{(m)} - e_q| \le \gamma \tag{2.56}$$

with not too large a constant  $\gamma$ . Furthermore, an analogous bulk-surface expansion can be obtained for  $F_q$ , if the contour weights  $w_q(\gamma)$  are (a) translation invariant whenever a contour  $\gamma$  is a bulk contour (i.e., it does not touch the boundary of V) and (b) translation invariant along an m-dimensional face of V whenever  $\gamma$  does not touch any of the (m-1)-dimensional faces. In fact, then the cluster expansion in Eq. (2.25) can be rewritten to yield [15] (c.f. Eq. (2.36))

$$F_q = f_q V + \sum_{m=0}^{d-1} f_q^{(m)} \,\partial V_m + O(e^{-b\,\beta L}),\tag{2.57}$$

where  $f_q$  are given by Eqs. (2.27) and (2.30). The boundary specific free energies may be written in a form similar to that for the bulk free energies,

$$f_q^{(m)} = e_q^{(m)} + \varphi_q^{(m)}; (2.58)$$

i.e., they are sums of a zero-temperature (ground-state) term and a thermal perturbations term. The dominant surface effects are due to the (d-1)-dimensional faces: their contribution to  $F_q$  is of order  $L^{d-1}$ , while the contribution from all remaining faces of lower dimensions is by 1/L smaller. An explicit expression for  $\varphi_q^{(d-1)}$  can be found in [30]. As may be expected, its leading contribution corresponds to the cluster containing a single contour attached to a (d-1)-dimensional face whose length is the shortest. If this length is denoted as  $\Lambda_s$ , Eq. (2.32) yields the bound

$$|\varphi_q^{(d-1)}| \le \frac{e^{-b\beta\Lambda_s}}{\beta} \tag{2.59}$$

analogous to the bound (2.33). For the Ising contours from Fig. 2.1 the shortest surface contour is associated with a single-site perturbation on a (d-1)-dimensional face, yielding  $\Lambda_s = 2d - 1$ .

The Peierls condition (2.21) for the contour weights  $w_q$  must be satisfied (i.e., the *q*th phase must be stable) in order that the bulk-surface expansion (2.57) holds. As for periodic boundary conditions, this is achieved by suppressing the contours that violate the Peierls condition, and  $f_q$  and  $f_q^{(m)}$  are introduced as 'meta-stable' specific free energies. It remains true, of course, that  $\min_q f_q$  is the specific free energy of the system and that  $f_q = f$  when the *q*th phase is stable. Combining Eqs. (2.2) and (2.57), the system partition function is given as [15]

$$Z_{\text{weak}} = \left(\sum_{q \in Q} e^{-\beta F_q}\right) [1 + O(e^{-b\beta L})].$$
(2.60)

For weak boundary conditions it is this relation that determines the thermodynamic quantities for a finite system. Namely, it implies that a first derivative

$$a_{\text{weak}}(y) = -\frac{1}{V} \frac{\partial F_{\text{weak}}(y)}{\partial y}$$
(2.61)

of the system free energy  $F_{\text{weak}} = -(1/\beta) \ln Z_{\text{weak}}$  with respect to a parameter (an external field) y is the convex combination [15]

$$a_{\text{weak}} = \sum_{q \in Q} \tilde{a}_q \tilde{p}_q + O(e^{-b\beta L})$$
(2.62)

of the single-phase quantities (c.f. Eq. (2.40))

$$\tilde{a}_q(y) = -\frac{1}{V} \frac{\partial F_q(y)}{\partial y} = a_q(y) + O(L^{-1})$$
(2.63)

with the convex coefficients

$$\tilde{p}_q = \frac{e^{-\beta F_q}}{\sum_{q'} e^{-\beta F_{q'}}}.$$
(2.64)

Moreover, derivatives of  $a_{\text{weak}}$  are equal to the derivatives of  $\sum_{q} \tilde{a}_{q} \tilde{p}_{q}$  with the same error term as in Eq. (2.62).

### 2.5.2 Coexistence of two phases

When the system has only two possible stable phases to be labeled  $q_1 = 1$  and  $q_2 = 2$ , it is possible to obtain explicit dependences of the quantity  $a_{\text{weak}}$  and its derivative

$$a'_{\text{weak}}(y) = \frac{\partial a_{\text{weak}}(y)}{\partial y}$$
(2.65)

as for periodic boundary conditions. Thus, the convex coefficients

$$\tilde{p}_1 = J\left(\frac{\beta}{2}\Delta F\right), \qquad \tilde{p}_2 = J\left(-\frac{\beta}{2}\Delta F\right),$$
(2.66)

are given by the jump function from Eq. (2.43) with the arguments depending on the difference  $\Delta F = F_2 - F_1$  of the single-phase free energies. The difference does not vanish at the transition point  $y_t$ , as for periodic boundary conditions, but at a point,  $y_L$ , that is shifted from  $y_t$  by a distance of order 1/L and coincides with the position,  $y_{\text{max}}$ , of the maximal value of the derivative  $a_{\text{weak}}$  up to an error of order  $1/(\beta V)^2$  [15]. The Taylor expansion around the point  $y_L$  thus yields

$$\Delta F(y) = [\tilde{a}_1(y_L) - \tilde{a}_2(y_L)]V(y - y_L) + O((y - y_L)^2 V)$$
  
= -[\Delta a + O(L^{-1})]V(y - y\_L) + O((y - y\_L)^2 V), (2.67)

where  $\Delta a$  is the infinite-volume jump in  $a_{\text{weak}}$  at the transition point (see Eq. (2.45)). So, if the argument of J in the coefficient  $\tilde{p}_2$  is replaced by

$$\Omega = \frac{1}{2} \Delta a \left( y - y_{\max} \right) \beta V, \tag{2.68}$$

the so caused error is only (c.f. Eq. (2.47))

$$\begin{split} |\tilde{p}_{2} - J(\Omega)| &\leq \left| J \left( -\frac{\beta}{2} \Delta F \right) - J(\Omega_{0}) \right| + |J(\Omega_{0}) - J(\Omega)| \\ &\leq \frac{\left| -\frac{\beta}{2} \Delta F - \Omega_{0} \right|}{2|\Omega_{0}|} + \frac{|\Omega_{0} - \Omega|}{2} = O(L^{-1}) + O(|y - y_{L}|) + O(V^{-1}), \end{split}$$
(2.69)

where  $\Omega_0 = (\Delta a/2) (y - y_L) \beta V$  and we used that  $|J(x_1) - J(x_2)| \le |x_1 - x_2|/2$  [15]. So, if we restrict y to the interval  $|y - y_{\text{max}}| \le \text{const}/L$ , Eq. (2.62) yields the expressions [15]

$$a_{\text{weak}} = a_1 + (a_2 - a_1) J(\Omega) + O(L^{-1}).$$
(2.70)

When y is beyond this interval,  $|y - y_{\text{max}}| \ge \text{const} / L$ , then

$$\beta|\Delta F| = \beta \left| \frac{\partial \Delta F(\tilde{y})}{\partial y} \right| |y - y_L| \ge \operatorname{const} \beta L^{d-1} \gg 1$$
(2.71)

by the mean-value theorem, so that one of the coefficients  $\tilde{p}_1$  and  $\tilde{p}_2$  is equal to 1 and the other one to 0, the errors being extremely small, just of order  $\exp(-\cosh\beta L^{d-1})$ . The quantity  $a_{\text{weak}}$ therefore very precisely coincides with  $a_1$  or  $a_2$ , which follows also from Eq. (2.50) (just with a larger error term). The equation can be thus applied for any y. It shows that, similarly to periodic boundary conditions,  $a_{\text{weak}}$  interpolates between the single-phase quantities  $a_1$  and  $a_2$  as the sigmoid function, and the change from one to the other occurs within a range of order  $1/\beta V$  (see Fig. 2.4).

In addition, the derivative of  $a_{\text{weak}}$  can be expressed as [15]

$$a'_{\text{weak}} = \left(\frac{\Delta a}{2}\right)^2 (1 + O(L^{-1})) \beta V P(\Omega) + \delta a'_{\text{weak}}$$
(2.72)

with

$$\delta a'_{\text{weak}} = a'_1 + (a'_2 - a'_1) J(\Omega) + O(L^{-1}), \qquad a'_i = \frac{\partial a_i}{\partial y}.$$
 (2.73)



Fig. 2.4. A schematic dependence of  $a_{\text{weak}}$  and its derivative on the parameter y as given by Eqs. (2.70) and (2.72). The single-phase quantities  $a_1$  and  $a_2$  are depicted by dashed lines,  $a_j^t$  stand for their values at the transition, and 'max' denotes a maximal value of the derivative of  $a_{\text{weak}}$ . Note that the maximum position is shifted from the transition point  $y_t$  by an amount of order 1/L.

The first term in the derivative has the profile of a sharp and tall spike with the height and width of order  $\beta V$  and  $1/\beta V$ , respectively (see Fig. 2.4). The second term  $\delta a'_{\text{weak}}$  is of order O(1) in L and has the profile a sharp jump interpolating between  $a'_1$  and  $a'_2$  (analogously to  $a_{\text{weak}}$ ). The first term is dominant near the phase transition, while the second one is dominant farther away from the transition where  $a'_{\text{weak}}$  reduces to one of the single-phase quantities  $a'_i$ .

A major difference between the weak and periodic boundary conditions is that the position,  $y_{\text{max}}$ , of a maximal value of the derivative  $a'_{\text{weak}}$  is *shifted* with respect to the transition point  $y_t$  due to the presence of boundary interactions. The shift is of order 1/L and is given as [15]

$$y_{\max} - y_t = \frac{\tau}{\Delta a} \frac{2d}{L} \left( 1 + O(L^{-1}) \right), \tag{2.74}$$

where

$$\tau = f_2^{(d-1)}(y_t) - f_1^{(d-1)}(y_t) \tag{2.75}$$

is the difference in the surface free energies evaluated at the transition point. The jump in the quantity  $a_{\text{weak}}$  and its derivative  $a'_{\text{weak}}$  are therefore positioned not at the transition point  $y_t$  but slightly away from it (see Fig. 2.4).

## 2.6 Strong boundary conditions

In reality it may often happen that the surroundings strongly affect a system through all or a part of its surface, thus imposing the presence of large interfaces in the system; i.e., separation of phases occurs. (For example, if a half of the system is immersed in one phase and the other half in another, an interface that crosses the system may appear.) Then the above results for the finitesize behavior of macroscopic quantities cannot be applied, because the Peierls condition (2.21) (i.e., an exponential decay of contours with their size) is violated for the contours representing the interfaces.

As an example of a system with strong boundary conditions, we shall consider the wellknown Ising model [23] on a square lattice. The model was originally proposed to describe a first-order phase transition in a ferromagnet: the magnetization of the model stays positive (i.e., a spontaneous magnetization,  $m^* > 0$ , appears) even if an external magnetic field vanishes, provided the temperature is sufficiently low, below its critical value [31] (as will be assumed in the following).

The configurations of the standard Ising model in a finite lattice of  $N = (L+1) \times (L+1)$  sites are the collections  $\sigma = \{\sigma_1, \ldots, \sigma_N\}$  of 'spins' with  $\sigma_i = \pm 1$  representing a 'spin up/down' at a site *i* (see Fig. 2.5). Note that  $\omega_i = (\sigma_i + 1)/2$  coincide with the occupation numbers of a lattice gas. The interactions between the spins are limited to the nearest-neighbor (n.n.) sites. Thus,  $U_A$  is set equal to  $-\mathcal{J}\sigma_i\sigma_j$  when A is a pair of n.n. spins *i* and *j* and to 0 when A is any other group of spins ( $\mathcal{J} > 0$  is an interaction coupling parameter). The minus sign corresponds to a ferromagnetic behavior when two equal n.n. spins interact with a lower energy than two unequal n.n. spins. Taking into account an external (positive or negative) magnetic field *h*, the model has the Hamiltonian

$$H_V(\sigma) = -\mathcal{J}\sum_{\text{n.n. in }V} \sigma_i \sigma_j - h \sum_{i \text{ in }V} \sigma_i + \mathcal{J}\sum_{\text{boundary }i} n_i \sigma_i.$$
(2.76)

The first summation is over all n.n. sites *i* and *j* in the system volume, the second one over all sites *i* in the volume (a positive/negative field *h* favors up/down 'spins'), and the third one over those sites *i* near the system boundary that have n.n. sites outside the system (whose number is denoted as  $n_i$ ). The latter corresponds to the boundary conditions in which all 'spins' outside the system are fixed to be down ( $\sigma_j = -1$ , yielding  $-\sigma_i \sigma_j = \sigma_i$ ) and the interaction coupling  $\mathcal{J}$  is the same as for n.n. sites in the system bulk.

When the field h is non-zero, boundary effects are negligible in the bulk of a macroscopic system, and there is a unique phase in an infinite system—the minus/plus phase for h negative/positive. Boundary conditions could play an important role only when the magnetic field depends on the system size,  $h = h_L$ , so that it decreases to 0 with a growing L. The chosen minus boundary conditions force the system along its surface to be in the minus phase. Thus, a negative  $h_L$  would ally with the boundary conditions and lead to the minus phase. An intriguing case is, therefore, when  $h_L$  is positive and draws the system toward the plus phase. The influence of the magnetic field  $h_L$  (which is a bulk effect) is comparable to that of the minus boundary conditions (a surface effect) when  $h_L = B/L$ . Then the behavior of the Ising system is as follows [32].

If B is less than a certain positive value,  $B_0$ , then the minus boundary conditions prevail and select the minus phase in the (finite but large) system. On the other hand, if  $B > B_0$ , then the magnetic field is the dominant effect and a single droplet of the plus phase is created inside the system, with the minus phase being near the system boundary (see Fig. 2.6). The droplet touches the boundary of the system along four equally long segments. Its shape is a squeezed version of the usual equilibrium crystal (Wulff) shape (the one minimizing the interfacial surface tension,



Fig. 2.5. A microscopic configuration for the Ising model in a rectangular lattice of  $10 \times 10$  sites (indicated by the dashed square) under fixed minus boundary conditions ( $\sigma_i = -1$  outside V). Note that this is the same configuration as that for the lattice gas in Fig. 2.1.

assuming that its volume is fixed [33]). In terms of the magnetization  $m = m(h_L)$  these results imply that, as the system size L grows, it tends to  $-m^*$  for  $B < B_0$  and to

$$m_B = m^* - \frac{\kappa}{4B^2} \tag{2.77}$$

for  $B \ge B_0$  (see Fig. 2.6), where the parameter  $\kappa$  is a function of the specific surface tension.

For the Ising model (2.76) with the strong minus boundary conditions, the macroscopic quantities of interest in a finite volume  $V = L^2$  are the magnetization,  $m_{\rm str}$ , and susceptibility,  $\chi_{\rm str} = \partial m_{\rm str}/\partial h$ , as its derivative. Their behaviour reflects the above-described balance between the competing influences of the magnetic field and minus boundary conditions. Considering the magnetic field to be constrained to an interval  $|h - B_0/L| \leq c/L$  with a positive c, we have [20]

$$m_{\rm str}(h) = -m^* + [m_{Lh} - (-m^*)] J(\Psi) + O(L^{-1/5})$$
(2.78)

and

$$\chi_{\rm str}(h) = \left(\frac{m_{Lh} - (-m^*)}{2}\right)^2 \beta V P(\Psi) + \delta \chi_{\rm str}(h)$$
(2.79)

with

$$\delta\chi_{\rm str}(h) = \frac{\chi_{Lh}}{1 + e^{-2\Psi}} + O(L^{-1/5}), \qquad \chi_B = \frac{\partial m_B}{\partial B} = \frac{\kappa}{2B^3}.$$
(2.80)



Fig. 2.6. As the Ising system size L grows, its magnetization  $m(h_L)$  with  $h_L = B/L$  converges to  $-m^*$  for  $B < B_0$  and to  $m_B$  for  $B \ge B_0$ . The minus phase is stable in the former case, while a squeezed Wulff shaped droplet of the plus phase is immersed in the minus phase in the latter case.

Thus, the behavior of the magnetization and susceptibility (see Fig. 2.7) is again described by the jump and spike functions J and P from Eq. (2.43) with the argument

$$\Psi = \frac{1}{2} \Delta m (h - h_{\max}) \beta V, \qquad \Delta m = m_{B_0} - (-m^*).$$
(2.81)

The position  $h_{\text{max}}$  of the jump in the magnetization and of the susceptibility spike is *shifted* with respect to the transition point  $h_t = 0$  by an order of 1/L,

$$h_{\max} - h_t = \frac{B_0}{L} \left( 1 + O(L^{-1/5}) \right).$$
(2.82)

These expressions for  $m_{\text{str}}$  and  $\chi_{\text{str}}$  are very similar to those for  $a_{\text{weak}}$  and  $a'_{\text{weak}}$  from Eqs. (2.70) and (2.72) considered for weak boundary conditions, with  $a_1$  and  $a_2$  corresponding here to  $-m^*$  and  $m_{Lh}$ . The key difference is that (a) near the transition  $m_{Lh}$  and  $\chi_{Lh}$  significantly vary with h and cannot be approximated by constants and (b) the error terms are of a higher order here.



Fig. 2.7. A schematic dependence of the magnetization and susceptibility on the magnetic field near  $h = B_0/L$  for the Ising model with minus boundary conditions as given by Eqs. (2.78) and (2.79). The symbol 'max' denotes a maximal value of the susceptibility.

## 3 Finite-size effects for a large ensemble of systems

Sometimes the studied system,  $S_0$ , may be composed of a large number of finite subsystems, S, so that the macroscopic behavior of the system is a cumulative result of the behavior of its subsystems. This will be the situation for the current density measured in underpotential deposition experiments that is studied below in Section 4: a typical electrode surface is polycrystalline, consisting of many separate finite crystalline domains.

To describe the macroscopic properties of the system  $S_0$  of dimension two or higher  $(d \ge 2)$ in a simple way, we shall adopt the assumption that the subsystems S are mutually *independent* (non-interacting). This is quite a crude simplification that may be, nevertheless, thought of as a first approximation. The partition function of the system is then the product of the partition functions of the individual subsystems and its free energy is the sum of the individual free energies,

$$Z_0 = \prod_S Z_S, \qquad F_0 = \sum_S F_S, \tag{3.1}$$

where  $F_0 = -(1/\beta) \ln Z_0$  and  $F_S = -(1/\beta) \ln Z_S$ . Consequently, specific macroscopic quantities of the system are weighted *averages* of their subsystems equivalents. In fact, for the first and second derivatives

$$a_0 = -\frac{1}{V_0} \frac{\partial F_0}{\partial y}, \qquad a'_0 = \frac{\partial a_0}{\partial y}$$
(3.2)

of the system free energy and their equivalents

$$a_S = -\frac{1}{V_S} \frac{\partial F_S}{\partial y}, \qquad a'_S = \frac{\partial a_S}{\partial y}$$
(3.3)

in the subsystems we get

$$a_0 = -\frac{1}{V_0} \frac{\partial}{\partial y} \sum_S F_S = \sum_S \frac{V_S}{V_0} a_S = \langle a_S \rangle, \qquad (3.4a)$$

$$a_0' = \frac{\partial}{\partial y} \sum_S \frac{V_S}{V_0} a_S = \sum_S \frac{V_S}{V_0} a_S' = \langle a_S' \rangle, \tag{3.4b}$$

where the weighted average is defined as

$$\langle \cdot \rangle = \sum_{S} \cdot w_{S}, \qquad w_{S} = \frac{V_{S}}{V_{0}}.$$
 (3.4c)

Note that the weights  $w_S$  are equal to the fractions of the subsystems volumes  $V_S$  in the volume  $V_0$  of the whole system  $S_0$ .

We may now apply the results from Section 2 to describe the subsystems quantities  $a_S$  and  $a'_S$ . Then, as soon as the weights  $w_S$  are known (either from experiment or theory), we may use Eq. (3.4) to evaluate, at least numerically, the quantities  $a_0$  and  $a'_0$  characterizing the whole system.

## 3.1 Alternative expressions

To evaluate  $a_0$  and  $a'_0$  and to analyze their behavior, it is convenient to rewrite the weighted averages over subsystems in Eq. (3.4) in an alternative form. The form must be determined, of course, by the factors that make  $a_S$  and  $a'_S$  change from one subsystem to another. As the results from Section 2 show, these factors are the subsystem size L (or volume  $V_S$ ) and boundary conditions. The subsystem size L affects the maximum position  $y_{\text{max}}$  (which is inversely proportional to L) and the rounding of the phase transition (i.e., the width of the jump in  $a_S$  and spike in  $a'_S$  as well as the height of the spike—all via the subsystem volume  $V_S = L^d$ ). The influence of boundary conditions is also twofold: they determine

- (a) the maximum position  $y_{\text{max}}$ ;
- (b) the single-phase quantities  $a_i$  as functions of the parameter y, depending on whether phase separation (i.e., the presence of macroscopic interfaces) occurs in a subsystem or not.

The results from Section 2 are insufficient, however, to precisely describe (a) and (b) for strong boundary conditions with *varying* strengths of boundary interactions. For weak boundary conditions, on the other hand, the results are very detailed. Therefore, we shall simplify the forth-coming discussion by restricting our attention to one type of boundary conditions—the weak ones.

**Remark 3.1.** Actually, shapes of the subsystems should be also taken into account whenever the shapes may vary significantly. We shall assume, for simplicity, that this is not the case. Therefore, all subsystems will have cubic volumes  $V_S = L^d$  (with various sizes L) in the following, and thus any effects from possibly varying subsystems shapes will be neglected.

For weak boundary conditions the influence of the boundary conditions with various strengths is given by a single parameter, the surface free energy difference  $\tau$ , that affects the maximum position  $y_{\text{max}}$  (see Eq. (2.74)) but not the single-phase quantities  $a_i = -\partial f_i / \partial y$ . Thus, we shall apply Eqs. (2.70) and (2.72) for  $a_S$  and  $a'_S$ , respectively, in the following. Consequently, near a first-order transition between two phases, we have

$$a_S \approx a_1 + (a_2 - a_1)J_S, \qquad a'_S = \hat{a}'_S + \delta a'_S$$
 (3.5a)

with

$$\hat{a}'_S \approx \frac{\Delta a}{\Delta y_S} P_S, \qquad \delta a'_S \approx a'_1 + (a'_2 - a'_1)J_S,$$
(3.5b)

where  $\Delta a \neq 0$  is the jump at the transition point  $y_t$  (see Eq. (2.45)) and

$$\Delta y_S = \frac{4}{\Delta a \,\beta V_S}, \qquad a'_i = \frac{\partial a_i}{\partial y}. \tag{3.5c}$$

The jump and spike functions are given as (see Eq. (2.43))

$$J_S = J(\Omega_S) = \frac{1}{1 + e^{-2\Omega_S}} = \frac{1 + \tanh \Omega_S}{2},$$
(3.5d)

$$P_S = P(\Omega_S) = \left(\frac{2}{e^{\Omega_S} + e^{-\Omega_S}}\right)^2 = \cosh^{-2}\Omega_S,$$
(3.5e)

where

$$\Omega_S = 2 \frac{y - y_{\text{max}}}{\Delta y_S}, \qquad y_{\text{max}} \approx y_t + \frac{2d\tau}{\Delta a} \frac{1}{L}.$$
(3.5f)

The point  $y_{\text{max}}$  is the position of a maximal value of the derivative  $a'_S$  and  $|\Delta y_S|$  is the half-width of the spike function  $P_S$ . Note that the derivative  $a'_S$  is expressed as a sum of an *excess* part  $\hat{a}'_S$ (described by the spike function  $P_0$ ) and a *baseline* part  $\delta a'_S$  (described by the jump function  $J_0$ ), the former being of order  $V_S$  and the latter being much smaller, ranging between  $V_S$  independent quantities  $a'_1$  and  $a'_2$ .

We may classify all subsystems according to their size L and their value of the surface free energy difference  $\tau$  and obtain an alternative expression for the weighted averages from Eq. (3.4) as *double* weighted *averages*. Namely, we observe that for any function  $g_S = g_S(L, \tau)$  of subsystems we have

$$\langle g_S \rangle = \sum_{S} \frac{V_S}{V_0} g_S = \sum_{L} \sum_{\tau} \sum_{\substack{S: \text{ size } L \text{ and } \\ \text{ surf. diff. } \tau}} \frac{V_S}{V_0} g_S(L,\tau) = \sum_{L} \frac{L^d}{V_0} \sum_{\tau} g_S(L,\tau) N_L w_{\tau}$$

$$= \sum_{L} N_L \frac{L^d}{V_0} \sum_{\tau} w_{\tau} g_S(L,\tau),$$
(3.6)

where  $N_L$  is the number of all subsystems with size L and  $w_{\tau}$  is the fraction of the subsystems of size L whose value of the surface free energy difference is equal to  $\tau$ . It thus follows that

$$a_0 = \langle \langle a_S \rangle_\tau \rangle_L \qquad a'_0 = \langle \langle a'_S \rangle_\tau \rangle_L, \tag{3.7a}$$

where  $a_S = a_S(L, \tau)$  and  $a'_S = a'_S(L, \tau)$  are given by Eq. (3.5) and the two weighted averages are given as

$$\langle \cdot \rangle_L = \sum_L \cdot w_L, \qquad \langle \cdot \rangle_\tau = \sum_\tau \cdot w_\tau.$$
 (3.7b)

The size weights

$$w_L = N_L \frac{L^d}{V_0} \tag{3.8}$$

are the fractions of the total system volume occupied by all subsystems of size L.

Using Eqs. (3.5) and (3.7), it is possible to rewrite the quantities for the whole system in a form *analogous* to that for the subsystems,

$$a_0 \approx a_1 + (a_2 - a_1)J_0, \qquad a'_0 = \hat{a}'_0 + \delta a'_0,$$
(3.9a)

where

$$\hat{a}'_0 \approx \frac{\Delta a}{\Delta y_0} P_0, \qquad \delta a'_0 \approx a'_1 + (a'_2 - a'_1)J_0$$
(3.9b)

and

$$\Delta y_0 = \frac{4}{\Delta a \,\beta V_0}, \qquad J_0 = \langle \langle J_S \rangle_\tau \rangle_L, \qquad P_0 = \left\langle \frac{L^d}{V_0} \,\langle P_S \rangle_\tau \right\rangle_L. \tag{3.9c}$$

The reason why the fraction  $L^d/V_0$  appears in  $P_0$  is that

$$\left\langle \left\langle \hat{a}_{S}^{\prime} \right\rangle_{L} = \left\langle \left\langle \frac{\Delta a}{\Delta y_{S}} P_{S} \right\rangle_{\tau} \right\rangle_{L} = \frac{\Delta a}{\Delta y_{0}} \left\langle \left\langle \frac{L^{d}}{V_{0}} P_{S} \right\rangle_{\tau} \right\rangle_{L}$$
(3.10)

as follows from the definitions of  $\Delta y_S$  and  $\Delta y_0$ .

We shall now study the properties of the functions  $J_0$  and  $P_0$  that describe the jump in  $a_0$  and the spike in its derivative  $a'_0$ , respectively. It is sufficient to focus just on the spike function  $P_0$ , because the jump function can be easily obtained from  $P_0$  by integration,

$$J_0(y) = \frac{1}{\Delta y_0} \int_{\mp\infty}^y P_0(\tilde{y}) \, d\tilde{y} = \frac{1}{\Delta a} \int_{\mp\infty}^y \hat{a}'_0(\tilde{y}) \, d\tilde{y},\tag{3.11}$$

where the minus/plus signs correspond to the case when  $\Delta a$  is positive/negative.

### 3.2 Surface effects

Let us consider the subsystems with a fixed size L, whose number was denoted by  $N_L$ , and let us study the average  $\langle P_S \rangle_{\tau}$  of the spike functions  $P_S$  over the surface free energy differences  $\tau$ . It is understood that the values of  $\tau$  are constrained to a finite interval,

$$\tau_0 - \Delta \tau \le \tau \le \tau_0 + \Delta \tau, \tag{3.12}$$

so that the boundary conditions remain weak (see Eq. (2.56)).

We shall assume that the subsystems are created in a *random* process (this will be the case studied in Section 4 below). Thus, the boundary conditions for various subsystems are irregular, and this is the reason why  $\tau$  changes from one subsystem to another. To approximate this situation by the boundary conditions in which the boundary interactions have *fixed* values, we identify these values with arithmetic averages of the random ones. Then the weights  $w_{\tau}$  can be approximated to have the Gaussian form [34] (see Fig. 3.1)

$$w_{\tau_j} \approx \rho(\tau_j) \,\delta\tau \tag{3.13a}$$

with

$$\rho(\tau) = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{1}{2}\left(\frac{\tau-\tau_0}{\sigma}\right)^2}, \qquad \sigma = \frac{\Delta\tau}{\sqrt{2dL^{d-1}}},$$
(3.13b)

where  $\tau_j = \tau_0 - \Delta \tau + j \, \delta \tau$  (with  $j = 1, ..., N_L$ ) are the values of  $\tau$  for the individual subsystems of size L and  $\delta \tau = 2\Delta \tau / (N_L - 1) \approx 2\Delta \tau / N_L$  is the distance between two adjacent values. The fluctuation (standard deviation)  $\sigma$  of  $\tau$  is inversely proportional to the square root of the subsystem boundary, because  $\tau$  is a random boundary quantity.

If we approximate the spike function  $P_S = \cosh^{-2} \Omega_S$  by the Gaussian  $\exp(-\pi \Omega_S^2/4)$  that has the same area and height, we get

$$\langle P_S \rangle_{\tau} = \sum_{j=1}^{N_L} w_{\tau_j} \cosh^{-2} \Omega_S(\tau_j) \approx \int_{\tau_0 - \Delta \tau}^{\tau_0 + \Delta \tau} \rho(\tau) \cosh^{-2}[\Omega_S(\tau)] d\tau$$

$$\approx \frac{1}{\sqrt{2\pi}\sigma} \int_{\tau_0 - \Delta \tau}^{\tau_0 + \Delta \tau} e^{-\frac{1}{2} \left(\frac{\tau - \tau_0}{\sigma}\right)^2} e^{-\pi \left(\frac{y - y_{\max}(\tau)}{\Delta y_S}\right)^2} d\tau;$$
(3.14)

having in mind that the studied ensemble of subsystems (i.e.,  $N_L$ ) is large, making  $\delta \tau$  practically vanishing. Evaluating the last integral, we get

$$\langle P_S \rangle_{\tau} \approx \frac{\Delta y_S}{\Delta y} X e^{-x^2}$$
(3.15)

with

$$X = \frac{1}{2} \left[ \operatorname{erf}(c(x+x_0)) - \operatorname{erf}(c(x-x_0)) \right],$$
(3.16)



Fig. 3.1. The Gaussian weights  $w_{\tau_j}$  from Eq. (3.13) on the interval  $\tau_0 - \Delta \tau \leq \tau_j \leq \tau_0 + \Delta \tau$  for  $N_L = 100$  and L = 10. The values  $\tau_j$  (with  $j = 1, ..., N_L$ ) are chosen to be spread equidistantly with a mutual distance  $2\Delta \tau/(N_L - 1)$ . The maximal value is max  $= \delta \tau/\sqrt{2\pi} \sigma$ .

where

$$x = \sqrt{\pi} \, \frac{y - y_{\max}(\tau_0)}{\Delta y}, \qquad c = \frac{\Delta y_{\tau}}{\Delta y_S} > 0, \qquad x_0 = \frac{\Delta \tau \, \Delta y}{\sqrt{2} \, \sigma |\Delta y_{\tau}|} > 0. \tag{3.17}$$

Within the interval  $|x| \leq x_0$  with  $x_0 \geq \Delta \tau / \sqrt{2} \sigma = \sqrt{dL^{d-1}} \gg 1$  the factor X is very precisely equal to 1. Thus, for all x where the Gaussian  $\exp(-x^2)$  is non-vanishing we have  $X \exp(-x^2) \approx \exp(-x^2)$ , and it follows that

$$\langle P_S \rangle_{\tau} \approx \frac{\Delta y_S}{\Delta y} e^{-\pi \left(\frac{y - y_{\max}(\tau_0)}{\Delta y}\right)^2},$$
(3.18a)

where we used that  $y_{\max}(\tau) = y_t + B\tau$  with  $B = 2d/\Delta a L$  and introduced

$$\Delta y = \sqrt{\Delta y_S^2 + \Delta y_\tau^2}, \qquad \Delta y_\tau = \sqrt{2\pi} \,\sigma B = \sqrt{\frac{\pi d}{L^{d+1}}} \,\frac{2\Delta\tau}{\Delta a}. \tag{3.18b}$$

Note that  $y_{\max}(\tau_0)$  is the maximum position of the spike function  $P_S$  for the value  $\tau = \tau_0$  and  $|\Delta y_S|$  is its half-width (c.f. Eq. (3.5)). Moreover,  $|\Delta y_{\tau}|$  is the half-width of the range over which the dominant, high-weighted spike functions  $P_S$  (those corresponding to  $\tau$  between  $\tau_0 - \sqrt{2\pi} \sigma$  and  $\tau_0 + \sqrt{2\pi} \sigma$ ) are spread. Indeed, since  $y_{\max}(\tau) = y_t + B\tau$ , a change in  $\tau$  makes a spike  $P_S$  shift proportionally to this change, but its profile is unaffected. Thus, spikes with different  $\tau$  have identical shapes (including their heights and widths), their maxima are just mutually shifted (see Fig. 3.2(a)). If the range of values  $\tau$  is  $|\tau - \tau_0| \leq \sqrt{2\pi} \sigma$ , then the spikes are spread over the range  $|y - y_{\max}(\tau_0)| \leq |\Delta y_{\tau}|$ .

The ratio

$$\frac{\Delta y_{\tau}}{\Delta y_{S}} = \frac{\beta \Delta \tau}{2} \sqrt{\pi dL^{d-1}} \ge \beta \Delta \tau \sqrt{L} \gg 1$$
(3.19)

at low temperatures even for subsystems of small sizes. Thus, the high-weighted spikes  $P_S$  are spread over an interval that is much wider than any of the spikes. Consequently,  $\Delta y \approx |\Delta y_{\tau}|$ , and the average

$$\langle P_S \rangle_\tau \approx \frac{\Delta y_S}{\Delta y_\tau} e^{-\pi \left(\frac{y - y_{\max}(\tau_0)}{\Delta y_\tau}\right)^2} = \frac{\Delta y_S}{B} \rho \left(\frac{y - y_t}{B}\right) \qquad (\text{if } \Delta y_S \ll \Delta y_\tau) \tag{3.20}$$

has the same shape as the weight function  $\rho$ , but it is re-scaled to have the height  $\Delta y_S / \Delta y_\tau$ and half-width  $\approx |\Delta y_\tau|$ . Recalling that each  $P_S$  has the height 1 and half-width  $\approx |\Delta y_S|$ , we conclude that the average  $\langle P_S \rangle_\tau$  is rather different from a spike function  $P_S$  associated with a single subsystem: it is *substantially smaller and wider* (see Fig. 3.2). This latter fact is important because the spikes measured in experiments are much smaller and wider than the spikes predicted for a single subsystem by Eq. (3.5).

It is interesting to note that the details of the shape of the subsystem spikes  $P_S$  are rather irrelevant for the resulting average  $P_L$ , for it is determined primarily by the shape of the weight function  $\rho$ . The relevant property is that the spikes  $P_S$  are much sharper that the interval over which they are spread for various  $\tau$ . This shows that the result Eq. (3.20) is quite robust.

**Remark 3.2.** In general, without assuming the Gaussian or other specific form of the weights  $w_{\tau}$ , we may write [35]

$$\langle P_S \rangle_{\tau} = \sum_{\tau} w_{\tau} \cosh^{-2} \Omega_S(\tau) \approx \int_{-\infty}^{\infty} \rho(\tau) \cosh^{-2} [K_S(\tau - \tau_S)] d\tau$$
  
=  $\langle P_S \rangle_{\tau}^a + \langle P_S \rangle_{\tau}^b + \langle P_S \rangle_{\tau}^c,$  (3.21)

where  $K_S = 2B/\Delta y_S = d\beta L^{d-1}$  and  $\tau_S = (y - y_t)/B$ . The first term is

$$\langle P_S \rangle^a_{\tau} = \rho(\tau_S) \int_{-\infty}^{\infty} \cosh^{-2} [K_S(\tau - \tau_S)] d\tau = \frac{2}{K_S} \rho(\tau_S).$$
 (3.22)

The second term is

$$\langle P_S \rangle_{\tau}^b = \int_{|\tau - \tau_S| \le \epsilon} [\rho(\tau) - \rho(\tau_S)] \cosh^{-2} [K_S(\tau - \tau_S)] d\tau$$

$$\leq \sup_{|\tau - \tau_S| \le \epsilon} |\rho(\tau) - \rho(\tau_S)| \int_{-\infty}^{\infty} \cosh^{-2} [K_S(\tau - \tau_S)] d\tau \le \frac{2}{K_S} \bar{\rho}' \epsilon$$
(3.23)

with  $\bar{\rho}' = \sup_{\tau} |d\rho(\tau)/d\tau|$ . Finally, the third term is

$$\langle P_S \rangle_{\tau}^c = \int_{|\tau - \tau_S| \ge \epsilon} [\rho(\tau) - \rho(\tau_S)] \cosh^{-2} [K_S(\tau - \tau_S)] d\tau$$

$$\leq \sup_{\tau} |\rho(\tau) - \rho(\tau_S)| \int_{|\tau - \tau_S| \ge \epsilon} 4e^{-2K_S |\tau - \tau_S|} d\tau \le \frac{4}{K_S} \bar{\rho} e^{-2K_S \epsilon}$$

$$(3.24)$$



Fig. 3.2. (a) The spike functions  $P_S(\tau_j) = \cosh^{-2} \Omega_S(\tau_j)$  for  $j = 20, 30, \ldots, 80$ , taking L = 10,  $N_L = 100, \Delta a = 1, \beta \Delta \tau = 2$ , and d = 2. (b) The same spike functions multiplied by the Gaussian weights  $\lambda(\tau_j)$  from Fig. 3.1. (c) The average  $\langle P_S \rangle_{\tau}$  computed numerically from its definition (the full line) and from the approximation (3.20) (the dashed line). (d) The average  $\langle P_S \rangle_{\tau}$  is smaller and wider than the spike function  $P_S(\tau_0)$  by the factor  $\Delta y_S / \Delta y_{\tau}$  equal to 7.9 for the considered values of parameters.

with  $\bar{\rho} = \sup_{\tau} \rho(\tau)$ , where we used the bound  $\cosh^{-2} x \leq 4 \exp(-2|x|)$ . Thus, combining all three terms, choosing  $\epsilon = L^{-3/4}/\beta$ , and estimating  $\bar{\rho}' \sim \bar{\rho}/\sigma \sim \bar{\rho}\sqrt{L}$ , we get

$$\langle P_S \rangle_{\tau} \approx \frac{2}{K_S} \left[ \rho(\tau_S) + O(\bar{\rho}\sqrt{L}\epsilon) + O(\bar{\rho}\,e^{-2K_S\epsilon}) \right]$$

$$= \frac{\Delta y_S}{B} \left[ \rho\left(\frac{y-y_t}{B}\right) + O\left(\frac{\bar{\rho}}{\beta L^{1/4}}\right) + O(\bar{\rho}\,e^{-4L^{1/4}}) \right].$$

$$(3.25)$$

This is the same result as that obtained for the special case of a Gaussian weight function  $\rho$  in Eq. (3.20).

#### 3.3 The resulting spike and jump

To evaluate the resulting spike represented by the baseline part (c.f. Eq. (3.9))

$$\hat{a}_{0}^{\prime} = \frac{\Delta a}{\Delta y_{0}} \left\langle \frac{L^{d}}{V_{0}} \left\langle P_{S} \right\rangle_{\tau} \right\rangle_{L} = \left(\frac{\Delta a}{2}\right)^{2} \frac{\beta}{V_{0}} \sum_{L} N_{L} L^{2d} \left\langle P_{S} \right\rangle_{\tau}, \tag{3.26}$$

it is necessary to know the number  $N_L$ . Even if it is available from experiment, it may have a very complex form and  $P_0$  could be then calculated from Eq. (3.26) only in a numerical way. We will therefore obtain  $P_0$  and describe its basic features for a general  $N_L$ , so that the fitting of  $P_0$  to experimental data will be straightforward to calculate whenever  $N_L$  is known or estimated for a given experiment.

The resulting spike can be expressed from Eqs. (3.20) and (3.26) as

$$\hat{a}'_{0} \approx \frac{\Delta a^{2}}{2\sqrt{\pi d} \,\Delta \tau V_{0}} \sum_{L} N_{L} \,L^{(3d+1)/2} \,e^{-z_{L}^{2}}, \qquad z_{L} = \sqrt{d \,L^{d-1}} \left( L \,\frac{y-y_{t}}{b\Delta \tau} - r \right), \quad (3.27)$$

where  $b = 2d/\Delta a$  and  $r = \tau_0/\Delta \tau$ . Thus,  $P_0$  is a sum of spikes whose maxima are located at  $y_{\max}(\tau_0) = y_t + rb\Delta \tau/L$  (where  $z_L = 0$ ). As the subsystem length L increases, these maximum positions get closer and closer to the phase-transition point  $y_t$ . The mutual distances between the spikes are not equal, however, because  $y_{\max}(\tau_0)$  decreases inversely with L. The spikes are therefore accumulated on one side of  $y_t$  (either below it, if r is negative, or above it, if r is positive). Consequently,  $P_0$  as a sum of these spikes will in general exhibit an *asymmetric* spike, which is usually the case observed in experiments. This asymmetry is a pure finite-size effect, requiring no asymmetries in the weights  $w_L$  or  $w_{\tau}$  (in fact, here we consider these weights to be symmetric).

Let us now describe basic properties of the spike exhibited by  $\hat{a}'_0$  as given by Eq. (3.27).

(a) Its area, A, is, according to Eq. (3.9), equal to the double weighted average of the area of  $(\Delta a/\Delta y_0)(L^d/V_0)P_S$ . The latter area is equal to  $(\Delta a/\Delta y_0)(L^d/V_0)|\Delta y_S| = |\Delta a|$ , yielding

$$A = \langle \langle |\Delta a| \rangle_{\tau} \rangle_{L} = |\Delta a|. \tag{3.28}$$

(b) Its maximum position, y\*, is obtained from the condition (dP<sub>0</sub>/dy)<sub>y=y\*</sub> = 0. If we express y\* in the same form as y<sub>max</sub>(τ<sub>0</sub>),

$$y^* = y_t + \frac{b\tau_0}{L^*}$$
(3.29)

with a suitable length  $L^*$ , then the condition may be rewritten as the equation

$$\sum_{L} N_L L^{2d+1} z_L^* e^{-(z_L^*)^2} = 0$$
(3.30)

with

$$z_L^* = z_L(\psi^*) = r\sqrt{d\,L^{d-1}}\,\Big(\frac{L}{L^*} - 1\Big).$$
(3.31)

From this equation the length  $L^*$  can be obtained.

(c) Once the size  $L^*$  and, thus, the maximum position  $y^*$  of the spike  $\hat{a}'_0$  have been calculated, its *height* is given as

$$Ht = \hat{a}_0'(y^*) \approx \frac{\Delta a^2}{2\sqrt{\pi d} \,\Delta \tau V_0} \sum_L N_L \, L^{(3d+1)/2} \, e^{-(z_L^*)^2}.$$
(3.32)

(d) To describe *asymmetry* of the spike function, let us consider an asymmetry factor,  $0 < \alpha < 1$ , equal to the ratio of the area under the spike that lies below the maximum position  $y^*$  to the spike's total area A. From Eq. (3.27) we get

$$\alpha = \frac{1}{A} \int_{-\infty}^{y^*} \hat{a}'_0(y) \, dy \approx \frac{1}{V_0} \sum_L N_L L^d \, \frac{1 \pm \operatorname{erf} z_L^*}{2}, \tag{3.33}$$

where erf is the Gauss error function and the plus/minus sign corresponds to a positive/negative  $\Delta a$ . When  $\alpha$  is smaller than 1/2 (larger than 1/2), most of the spike's area lies above (below) its maximum position; if  $\alpha = 1/2$ , the areas below and above  $y^*$  are equal.

According to Eqs. (3.11) and (3.33), the jump function  $J_0$  and asymmetry factor  $\alpha$  are related as  $J_0(y^*) = \alpha$  for  $\Delta a$  positive and as  $J_0(y^*) = 1 - \alpha$  for  $\Delta a$  negative. Thus, Eq. (3.33) can be also used to calculate the jump function  $J_0$  for any y, if we replace  $z_L^*$  by  $\pm z_L$  in it,

$$J_0 \approx \frac{1}{V_0} \sum_L N_L L^d \, \frac{1 + \text{erf} \, z_L}{2}.$$
(3.34)

The same expression follows, of course, if we integrate Eq. (3.27) according to Eq. (3.11).

## 3.4 Fitting to experimental data: Four fitting parameters

The spike  $\hat{a}'_0$  and jump  $J_0$ , as given by Eqs. (3.27) and (3.34), respectively, depend on seven parameters:  $\Delta a$ ,  $\Delta \tau$ ,  $V_0$ ,  $N_L$ ,  $y_t$ , r, and  $\tau_0$ . The number  $N_L$  of subsystems of a given size and the total volume  $V_0$  are assumed to be provided from experimental data (or be plausibly estimated), and  $\tau_0 = r \Delta \tau$ . Thus, there are actually four independent parameters that may vary from experiment to experiment over significant ranges: the phase-transition point  $y_t$ , the value of the phase transition jump  $\Delta a$ , half-width  $\Delta \tau$ , and ratio r. Their values can be uniquely determined by fitting four properties of the spike  $\hat{a}'_0$ —its area, maximum position, height, and asymmetry—to an experimental spike, using the following procedure.

- 1. The value of the phase transition jump  $\Delta a$  is determined as the area of the spike  $\hat{a}'_0$ . The spike is obtained from experiment as the difference  $a'_0 \delta a'_0$  between the derivative  $a'_0$  and its 'baseline' part  $\delta a'_0$ .
- 2. Solving Eq. (3.30) for various r yields the dependence  $L^*(r)$ . Then the asymmetry factor  $\alpha(r)$  can be calculated from Eq. (3.33). By fitting  $\alpha(r)$  to an experimental value, the ratio r is obtained.
- 3. Plugging  $L^*(r)$  and r into Eq. (3.32), we obtain the height Ht of the spike  $\hat{a}'_0$  in the form  $\text{Ht} = \text{const} / \Delta \tau$ . The experimental value of the height thus yields the half-width  $\Delta \tau$ .

4. According to Eq. (3.29), we have  $y_t = y^* - 2dr\Delta\tau/\Delta a L^*$ . Using the already determined parameters and experimental value of the maximum spike position  $y^*$ , we get the phase-transition point  $y_t$ .

Knowing all parameters, the spike  $\hat{a}'_0$  and jump  $J_0$  are finally obtained from Eqs. (3.27) and (3.34), respectively. We will apply this procedure to a specific experimental situation in Section 4 where the spikes and jumps will be associated with the current and surface coverage, respectively, measured during deposition of metals on electrode surfaces.

## 4 Current spikes due to phase transitions at electrode-electrolyte interfaces

Bulk electrodeposition from a solution of a given metal ion,  $M^{+z}$ , onto an electrode surface consisting of atoms of the same metal M occurs at the thermodynamically reversible (Nernst) potential. Above this value the bulk deposition does not take place. Another type of deposition may be possible, however. Namely, deposition of metal ions  $M^{+z}$  (such as copper or silver) on a substrate of a foreign, more noble metal  $S \neq M$  (such as gold or platinum). This is called *underpotential deposition* (UPD). The reason for its occurrence is that the interaction between metal M and the substrate metal S is thermodynamically more advantageous than that between M and M. Consequently, only a submonolayer or a single *monolayer* of metal M can be so deposited on the substrate metal S (bulk deposition is absent because it is thermodynamically disadvantageous to deposit M on itself). In addition, the deposited (sub)monolayers are often observed to form *ordered two-dimensional phases* commensurate with the geometrical alignment of the substrate metal atoms (see Fig. 4.1).

In UPD experiments the measured quantity is the *current density*,  $I_0$ , as a function of an externally controlled *electric potential*,  $\psi$ , by which an electrode is polarized. A plot of  $I_0$  vs.  $\psi$  is called a *voltammogram*. The potential is usually varied with time at a constant rate,  $\nu = d\psi/dt = \text{const}$ , within a finite interval in cycles. Namely, when  $\psi$  is decreased at a rate  $\nu$  from an initial to a final value, the ion is being *deposited* on the electrode surface. Reversing  $\psi$  at the final value and returning it at the rate  $\nu$  back to its initial value, the ion is being *stripped* off of the electrode surface. A new cycle may begin subsequently.





Fig. 4.1. Bulk vs. underpotential deposition (a schematic picture).



Fig. 4.2. Voltammogram for the UPD of copper on Pt(111) from 1 mM Cu<sup>2+</sup> and 0.1 M H<sub>2</sub>SO<sub>4</sub> (adapted from [46]). The scan rate is  $\nu = 1 \text{ mV} \cdot s^{-1}$ . The triplet 111 stands for the crystallographic Miller indices *hkl*.

Faradaic current. It occurs due to electrochemical reactions in the experimental cell and the corresponding charge transfer at the electrode surfaces. The other one is the capacitive current that occurs due to (dis)charge of the electrical double layer capacitance of the electrode. This current does not involve chemical reactions. It is responsible for accumulation (removal) of charge on and near the electrode.

If a metallic (sub)monolayer is suddenly deposited on a crystalline electrode, one or more sharp spikes appear in the associated voltammogram (see Figs. 4.2 and 4.3). Such a spike can be interpreted as corresponding to a *phase transition* at the electrode surface [36]. In the cases when the (sub)monolayer is ordered, it may be expected that 2D lattice-gas models could be used to simulate the associated UPD process in a reliable way. This was first shown in the pioneering studies of Blum and Huckaby. They were able to introduce a lattice-gas model [37] that successfully described the structure of phases experimentally observed in the UPD of Cu on Au(111) [37,38,39,40]. (The triplet 111 stands for the crystallographic Miller indices *hkl*.) Their description of voltammogram spikes was not entirely satisfactory, however, because their theoretical spikes were infinitely tall and sharp and they resolved the problem by adding a qualitative 'switching function' [37,41]. The UPD studies based on Monte Carlo simulations for lattice gases produced voltammogram spikes of finite height and non-zero width that were in qualitative agreement with experiment, but the simulated spikes were still too tall and sharp [42,43,44,45].



Fig. 4.3. Voltammogram for the UPD of copper on Au(111) from 1 mM Cu<sup>2+</sup> and 0.05 M H<sub>2</sub>SO<sub>4</sub> (adapted from [47]). The scan rate is  $\nu = 1 \text{ mV} \cdot s^{-1}$ . The triplet 111 stands for the crystallographic Miller indices *hkl*.

In this section we discuss the key features of our statistical mechanical theory [35, 48] from which voltammogram spikes corresponding to first-order phase transitions can be obtained. To illustrate the theoretical results, in Sections 5 and 6 we will show how the theory can be applied to experimental data.

## 4.1 Current density and coverage

We shall consider an electrode surface with a flow of current in it. The two contributions to the current (see Remark 4.1 above) will be as follows: (1) the Faradaic part is assumed to be exclusively due to the discharge of a *single* type of ion, and (2) capacitive contributions will be neglected. Moreover, we will consider only the *stripping* part of the deposition process (when  $\nu > 0$ ). The reason is that non-equilibrium effects should be rather less important in stripping processes that in the deposition ones, and therefore our equilibrium analysis can be applied at slow scan rates (in the 'quasistatic' limit  $\nu \rightarrow 0$ ). Under these conditions the current density at the electrode interface can be expressed as [38]

$$I_0(\psi) = -\kappa e_0 \gamma \nu \,\frac{\partial \Theta_0(\psi)}{\partial \psi}\,,\tag{4.1}$$



Fig. 4.4. A schematic picture of current density spikes from the individual crystals on an electrode surface.

where  $\kappa$  is the number of adsorption sites on the electrode surface per unit area,  $e_0$  is the elementary charge,  $\gamma$  is the effective electrovalence of the ion deposited on the electrode surface, and  $\Theta_0$  is the surface coverage of the ion. The minus sign in Eq. (4.1) ensures that the current density  $I_0$  is positive for a stripping process (when  $\Theta_0$  decreases). The quantity  $\gamma$  is considered independent of  $\psi$ , and it relates the applied electric potential  $\psi$  to the chemical potential of the ion in a linear fashion [39],

$$\mu(\psi) = -e_0 \gamma(\psi - \psi_0), \tag{4.2}$$

where the constant  $\psi_0$  is a reference potential. The coverage  $\Theta_0$  is defined as the statistical average value of the fraction of adsorption sites occupied by the ion. Thus,

$$\Theta_{0}(\psi) = \frac{1}{Z_{0}(\psi)} \sum_{\omega} \frac{N(\omega)}{N_{0}} e^{-\beta [H_{0}(\omega) - \mu(\psi) N(\omega)]}$$
$$= -\frac{1}{e_{0}\gamma\beta N_{0}} \frac{\partial}{\partial\psi} \log Z_{0}(\psi), \qquad (4.3)$$

where the sum runs over the microscopic configurations  $\omega$  on the electrode surface,  $N(\omega)$  is the number of occupied adsorption sites in a given  $\omega$ , and  $N_0$  is the total number of adsorption sites.

We shall now invoke the observation that an electrode surface has a polycrystalline structure; i.e., it consists of a large number of finite crystalline domains that we shall call *crystals*. It is therefore natural to assume that each crystal makes a contribution to the overall current density in dependence on its size, shape, and boundary conditions (see Fig 4.4). Consequently, a voltammogram spike is an *averaged result* of the contributions coming from all crystals [49, 34, 35].

It might seem redundant to take into account the polycrystalline structure of electrode surfaces: it should be possible to obtain a voltammogram spike as a result of a first-order phase transition in a single, 'typical' crystal. This approach turns out to be erroneous, however. In fact, for a crystal of a typical size (few hundreds of sites) the current density would exhibit a spike about a hundred times taller and sharper than the experimental one [49, 34]. On the other hand, if the polycrystalline structure of electrode surfaces is considered, then the spikes from various crystals are mutually shifted and of varying heights and widths so that their resulting average can very well fit the profile of a real voltammogram spike. The crucial point is that the individual spikes are shifted with respect to each other (otherwise the average would still be too tall and sharp), so that periodic boundary conditions are inappropriate to consider.

Therefore, we shall imagine that a large ensemble of crystals, C, lying on the electrode surface is given and that boundary conditions for all crystals are fixed. The boundary conditions represent the interaction of the crystals with those parts of the electrode surface that separate the crystals from each other (i.e., with the defect regions on the electrode surface). To be able to apply the theory of finite-size effects for an ensemble of systems from Section 3, the boundary conditions will be assumed to be weak. In addition, as long as the crystals are not too oblong, their shapes are not a key factor [35], and we shall suppose that all crystal are of a uniform, parallelogram shape. Finally, using the approximation that the crystals are mutually non-interacting, the partition function  $Z_0$  for the whole ensemble of crystals becomes the product of the partition functions of individual crystals, yielding [34]

$$\Theta_0(\psi) = \langle \Theta_C(\psi) \rangle_C, \qquad I_0(\psi) = \langle I_C(\psi) \rangle_C \tag{4.4}$$

with

$$\langle \cdot \rangle_C = \sum_C \cdot w_C, \qquad w_C = \frac{N_C}{N_0}.$$
 (4.5)

The weights  $w_C$  are equal to the fractions of all adsorption sites contained in individual crystals. Hence, the electrode coverage  $\Theta_0$  and current density  $I_0$  are averages of the coverages  $\Theta_C$  and current densities  $I_C$  from the crystals. The latter are given as (c.f. Eqs. (4.1) and (4.3))

$$\Theta_C(\psi) = -\frac{1}{e_0 \gamma \beta N_C} \frac{\partial \log Z_C(\psi)}{\partial \psi}, \qquad (4.6a)$$

$$I_C(\psi) = -\kappa e_0 \gamma \nu \, \frac{\partial \Theta_C(\psi)}{\partial \psi},\tag{4.6b}$$

with the crystal partition function

$$Z_C(\psi) = \sum_{\omega_C} e^{-\beta [H_0(\omega) - \mu(\psi) N(\omega)]},$$
(4.7)

(the summation is over the microscopic configurations  $\omega_C$  in the crystal).

Comparing Eqs. (4.4) and (4.6) with Eq. (3.4), we conclude that the description of the current density  $I_0$  and coverage  $\Theta_0$  is a specific two-dimensional case of the general situation studied in Section 3. We may therefore apply the results given there to obtain voltammogram spikes associated with the first-order phase transitions that correspond to sudden depositions of

(sub)monolayers of metals on electrode surfaces. To be able to apply the general results easily, we will use Table 4.1 where the correspondence between the general quantities from Section 3 and the quantities studied here is provided. Let us first describe the results in a single crystal and then on the whole electrode surface.

### 4.2 Rounding of phase transitions in a single crystal

Using Table 4.1 and Eq. (3.5), the coverage and current density in a crystal C, as functions of the electric potential  $\psi$ , may be expressed as

$$\Theta_C \approx \theta_1 + (\theta_2 - \theta_1) J_C, \qquad I_C = \hat{I}_C + \delta I_C, \tag{4.8a}$$

where

$$\hat{I}_C \approx \frac{1}{4} \kappa \nu (e_0 \gamma \Delta \theta)^2 \beta L^2 P_C, \qquad \delta I_C \approx \kappa \nu (e_0 \gamma)^2 [\theta_1' + (\theta_2' - \theta_1') J_C]$$
(4.8b)

with the derivatives  $\theta'_i = \partial \theta_i / \partial \mu$ . The jump and spike functions are given as

$$J_C = J(\Omega_C) = \frac{1}{1 + e^{-2\Omega_C}} = \frac{1 + \tanh \Omega_C}{2},$$
(4.8c)

$$P_C = P(\Omega_C) = \left(\frac{2}{e^{\Omega_C} + e^{-\Omega_C}}\right)^2 = \cosh^{-2}\Omega_C,$$
(4.8d)

with

$$\Omega_C = 2 \, \frac{\psi - \psi_{\max}}{\Delta \psi_C}, \qquad \psi_{\max} \approx \psi_t - \frac{4\tau}{e_0 \gamma \Delta \theta} \, \frac{1}{L}, \qquad \Delta \psi_C = -\frac{4}{e_0 \gamma \Delta \theta \, \beta L^2}. \tag{4.8e}$$

We use  $\Delta \theta = \theta_2(\mu_t) - \theta_1(\mu_t)$  to denote the infinite-volume jump in the coverage at the transition point  $\mu_t$ . Note that the current density  $I_C$  is a sum of two contributions—the *excess* and *baseline* current densities  $\hat{I}_C$  and  $\delta I_C$ , respectively. In addition,  $\kappa \nu e_0 \gamma |\Delta \theta|$  and  $|\Delta \psi_C|$  are equal to the *area* and *half-width*, respectively, of the spike in the excess crystal current density  $\hat{I}_C$ .

## 4.3 Boundary effects

Boundary conditions for the individual crystals on the electrode surface are determined by various defects separating the crystals. Thus, random boundary conditions seem to be the most suitable. To treat averaging over this randomness for all crystals of a given size L, it was suggested [34] that practically the same result should be obtained when (a) the boundary conditions are fixed to have constant values of interaction energies along the boundary of every crystal, and (b) the constant values vary from crystal to crystal. The boundary average is thus represented by the average  $\langle \cdot \rangle_{\tau}$  over the values of the specific surface free energies  $\tau$ . While  $\tau$  has a definite value for every crystal, it may be different for different crystals, ranging within an interval  $|\tau - \tau_0| \leq \Delta \tau$  (c.f. Eq. (3.12)). The connection between  $\tau$  and the interaction energies will become clear later on when specific lattice-gas models will be considered to simulate UPD process from a microscopic viewpoint.

General quantity	corresponds to	UPD quantity	Remark
subsystem S		crystal $C$	
volume $V_S$		crystal size $N_C$	
y		$\psi$	
$a_i = -\frac{\partial f_i}{\partial y}$		$-e_0\gamma\theta_i$	$ heta_i = -rac{\partial f_i}{\partial \mu}$
$\Delta a = a_2(y_t) - a_1(y_t)$		$-e_0\gamma\Delta\theta$	$\Delta \theta = \theta_2(\mu_t) - \theta_1(\mu_t)$
$a_S$		$-e_0\gamma\theta_C$	
$a'_i = \frac{\partial a_i}{\partial y}$		$(e_0\gamma)^2\theta_i'$	$ heta_i' = rac{\partial  heta_i}{\partial \mu}$
$a'_S = \frac{\partial a_S}{\partial y}$		$\frac{1}{\kappa\nu}I_C$	
$\hat{a}'_S$		$\frac{1}{\kappa\nu}\hat{I}_C$	
$\delta a'_S$		$\frac{1}{\kappa\nu}\delta I_C$	

Tab. 4.1. The correspondence between the general quantities from Section 3 and the quantities studied for UPD. The chemical potential  $\mu$  is the linear function of the electric potential  $\psi$  as given by Eq. (4.2).

Classifying all crystals according to their length L and value of  $\tau$ , the electrode coverage and current density from Eq. (4.4) may be expressed as the double averages (c.f. Eq. (3.7))

$$\Theta_0 = \langle \langle \Theta_C \rangle_\tau \rangle_L \qquad I_0 = \langle \langle I_C \rangle_\tau \rangle_L, \tag{4.9}$$

with

$$\langle \cdot \rangle_L = \sum_L \cdot w_L, \qquad \langle \cdot \rangle_\tau = \sum_\tau \cdot w_\tau.$$
 (4.10)

The weights

$$w_L = N_L \frac{L^2}{N_0} \tag{4.11}$$

are the fractions of the total electrode surface occupied by all crystals of length L (whose number is  $N_L$ ), and the weights  $w_{\tau}$  are the fractions of the crystals of length L whose value of the surface free energy difference is equal to  $\tau$ .

In [34] the local-limit theorem was invoked to argue that the weights  $w_{\tau}$  could be approximated by a Gaussian probability distribution  $\rho(\tau)$  (see Eq. (3.13)). Hence,  $w_{\tau} = \rho(\tau) \,\delta\tau$ , where  $\delta\tau$  is the distance between adjacent values of  $\tau$ . Since  $\tau$  is a random quantity associated with the crystal boundary, the fluctuation (standard deviation) in the Gaussian distribution is proportional to the square root of the crystal boundary,  $\sigma = \Delta \tau / 2\sqrt{L}$ . The mean value is identified with  $\tau_0$ .

Introducing

$$\Delta\psi_{\tau} = \frac{\sqrt{8\pi}\,\Delta\tau}{e_0\gamma\Delta\theta\,L^{3/2}}\tag{4.12}$$

and observing that the ratio

$$\frac{\Delta\psi_{\tau}}{\Delta\psi_{C}} = \beta\Delta\tau\sqrt{\frac{\pi}{2}} L \gg 1 \tag{4.13}$$

at low temperatures even for crystals of small lengths, Eq. (3.20) implies that

$$\langle \cosh^{-2}\Omega_C \rangle_{\tau} \approx \frac{\Delta\psi_C}{\Delta\psi_{\tau}} e^{-\pi \left(\frac{\psi - \psi_{\max}(\tau_0)}{\Delta\psi_{\tau}}\right)^2}.$$
(4.14)

Thus, the  $\tau$  average of the crystal current density  $I_C$  exhibits a spike that is *much shorter and* wider than that exhibited by  $I_C$  itself. This is important for fitting theoretical voltammogram spikes to experimental ones: the latter are about a hundred times shorter and wider that the spikes from a single crystal of typical lengths L (say, 10 or 15) [49].

## 4.4 Rounding of phase transitions on an electrode surface

If we now apply Table 4.1 and Eqs. (3.9), (3.11), (3.27), and (3.34), we may express the coverage and current density for the whole electrode as

$$\Theta_0(\psi) \approx \theta_1 + (\theta_2 - \theta_1) J_0(\psi), \qquad I_0(\psi) = \hat{I}_0(\psi) + \delta I_0(\psi), \tag{4.15a}$$

where

$$\hat{I}_{0}(\psi) \approx \frac{\kappa \nu (e_{0} \gamma \Delta \theta)^{2}}{\sqrt{8\pi} \,\Delta \tau N_{0}} \sum_{L} N_{L} \,L^{7/2} \,e^{-[z_{L}(\psi)]^{2}},\tag{4.15b}$$

$$\delta I_0(\psi) \approx \kappa \nu (e_0 \gamma)^2 \left[ \theta_1' + (\theta_2' - \theta_1') J_0(\psi) \right], \tag{4.15c}$$

and

$$J_0(\psi) \approx \frac{1}{N_0} \sum_L N_L L^2 \, \frac{1 + \text{erf} \, z_L(\psi)}{2}.$$
(4.15d)

The factor

$$z_L(\psi) = \sqrt{2L} \left[ \frac{e_0 \gamma \Delta \theta}{4\Delta \tau} (\psi_t - \psi) L - r \right], \qquad r = \frac{\tau_0}{\Delta \tau}.$$
(4.16)

In addition, applying Eqs. (3.28) – (3.33), the excess current density  $\hat{I}_0$  has the area

$$A = \int_{-\infty}^{\infty} \hat{I}_0(\psi) \, dy = \kappa \nu e_0 \gamma |\Delta \theta|, \tag{4.17a}$$

position of its maximal value at

$$\psi^* = \psi_t - \frac{4\tau_0}{e_0 \gamma \Delta \theta \, L^*},\tag{4.17b}$$

height

$$Ht = \hat{I}_0(\psi^*) \approx \frac{\kappa \nu (e_0 \gamma \Delta \theta)^2}{\sqrt{8\pi} \,\Delta \tau N_0} \sum_L N_L \, L^{7/2} \, e^{-(z_L^*)^2}, \tag{4.17c}$$

and asymmetry factor

$$\alpha = \frac{1}{A} \int_{-\infty}^{\psi^*} \hat{I}_0(\psi) \, dy \approx \frac{1}{N_0} \sum_L N_L L^2 \, \frac{1 \mp \operatorname{erf} z_L^*}{2}. \tag{4.17d}$$

The minus/plus sign in the expression for  $\alpha$  corresponds to a positive/negative  $\Delta \theta$  (whose sign is opposite to that of  $\Delta a$ ), the shorthand

$$z_{L}^{*} = r\sqrt{2L} \left(\frac{L}{L^{*}} - 1\right), \tag{4.18}$$

and

$$\sum_{L} N_L L^5 z_L^* e^{-(z_L^*)^2} = 0$$
(4.19)

is the equation whose solution is the length  $L^*$ .

### 4.5 Fitting to a voltammogram spike

There are four adjustable parameters in the theoretical results from Eq. (4.15) that can be used to obtain a voltammogram spike. Namely, the electrovalence  $\gamma$ , half-width  $\Delta \tau$  of the range of values  $\tau$ , phase-transition potential  $\psi_t$ , and ratio r (from which we get the mean value  $\tau_0 = r\Delta \tau$ ). The values of these four parameters are adjusted from given experimental data as follows (see Section 3.4).

First,  $\gamma$  is determined from the area A of the excess spike  $I_0$  that is obtained from experiment as the difference between the voltammogram spike  $I_0$  and its baseline part  $\delta I_0$ . (The phase transition jump  $\Delta \theta$  is known from experiment.)

Second, by solving Eq. (4.19) for various r, we get the dependence  $L^*(r)$ , and  $\alpha(r)$  is then calculated. When this  $\alpha(r)$  is fitted to an experimental value, r is obtained.

Third, using  $L^*(r)$  and r, we calculate  $Ht = const / \Delta \tau$  and get  $\Delta \tau$  by fitting the experimental value of the height.

Finally, from the already determined parameters and experimental value of the maximum spike position, we get the phase-transition point  $\psi_t = \psi^* + 4r\Delta\tau/e_0\gamma\Delta\theta L^*$ .

To apply the procedure, it is necessary to know the size distribution  $N_L$ . This is hardly available from experiment. Nevertheless, a simple theoretical mechanism was suggested in [49] to describe the distribution. It is based on the assumption that the crystals of a parallelogram shape are formed due to line defects that occur on an electrode surface with a certain probability, P. Let us choose a crystal corner and either of its edges that meet at the corner. The probability that the site next to the corner as well as all sites on the half-line perpendicular to the edge and pointing inside the crystal are part of the crystal is equal to 1 - P. Thus, the fraction of crystals of size L on the electrode surface is proportional to  $((1 - P)^L P)^2$ . Consequently, the fraction of adsorption sites that lie in the crystal of size L is proportional to  $L^2((1 - P)^L P)^2$ . Introducing  $p = (1 - P)^2$  and evaluating the normalization constant, we get [49]

$$N_L = N_0 \,\frac{(1-p)^3}{p(1+p)} \,p^L \tag{4.20a}$$



Fig. 4.5. The model weights  $w_L$  from Eq. (4.20) for the probability P of line defects 0.2, 0.15, and 0.1.

and

$$w_L = N_L \frac{L^2}{N_0} = \frac{(1-p)^3}{p(1+p)} L^2 p^L.$$
(4.20b)

This model weights are plotted in Fig. 4.5. For small sizes  $w_L$  increases (proportionally to the crystal area) and, after reaching its maximum (at  $L_{\text{max}} = 2/|\ln p| \approx (1+p)/(1-p)$ ), it vanishes (at an exponential rate). This should represent a general behavior of the weights. Note that the mean size and its fluctuation for these weights are approximately equal to  $(3/2)L_{\text{max}}$  and  $(\sqrt{3}/2)L_{\text{max}}$ , respectively. Physically interesting values of p should be  $0.8 \le p \le 0.9$  (i.e.,  $0.05 \le P \le 0.1$ ) for which the mean value of the crystal size L is between 14.4 and 28.5.

Using the size distribution from Eq. (4.20), the dependences  $L^*(r)$  and  $\alpha(r)$  can be obtained by solving Eq. (4.19) and Eq. (4.17d), respectively (see Fig. 4.6). Evaluation of the remaining quantities (the area A, height Ht, jump function  $J_0$ , and excess current density  $\hat{I}_0$ ) can be done only when a specific experiment is considered (so that  $\kappa, \nu, \Delta\theta$ , and  $\psi^*$  are known).

In Sections 5 and 6 we shall consider two examples of UPD processes and apply the above theoretical results to obtain the corresponding voltammogram spikes, using the weights  $w_L$  from Eq. (4.20).



Fig. 4.6. The dependence of (a) size  $L^*$  and (b) asymmetry factor  $\alpha$  on the ratio r as calculated from Eqs. (4.19) and (4.17d), respectively, for the range  $-1 \le r \le 1$  and  $p = (1-P)^2$  with P = 0.1, 0.15, 0.2.

## 5 Example 1: Underpotential deposition of Cu on Pt(111)

As a first example, let us consider the voltammogram spike that was measured during the stripping part of the underpotential deposition of Cu on Pt(111) [46] (see Fig. 4.2). The spike corresponds to a first-order phase transition when a full monolayer of deposited ions is completely stripped off of the electrode surface [49]. This corresponds to a transition between a fully occupied and a fully vacant phase, the former being commensurate with the (111) surface whose adsorption sites constitute a triangular lattice.

## 5.1 Lattice-gas model

To model the considered UPD process, we may consider crystals that have a parallelogram shape of  $N_C = L \times L$  adsorption sites (see Fig. 5.1) and use the standard, one-component lattice gas on a triangular lattice with an attractive interaction energy,  $\varepsilon < 0$ , between a pair of n.n. ions in the crystal [49]. It is known that at  $\mu = \mu_t = 3\varepsilon$  a first-order phase transition between a fully occupied and a fully vacant phase occurs for this lattice gas below the critical temperature  $\beta > \beta_c = (\ln 3)/|\varepsilon|$ . The surface coverage has a jump from  $(1 - m^*)/2$  for the vacant phase to  $(1 + m^*)/2$  for the occupied phase, where  $m^* > 0$  is the Ising spontaneous magnetization (see Section 2.6). The boundary conditions are chosen so that each adsorption site outside the crystal is occupied by an ion that interacts with any n.n. ions inside the crystal with an attractive boundary energy,  $\eta$ , different from  $\varepsilon$ . The Hamiltonian of this lattice gas is given as (c.f. Eq. (2.76))

$$H_C(\omega) = \varepsilon \sum_{\text{n.n. in } C} \omega_i \omega_j - \mu \sum_{i \text{ in } C} \omega_i + \eta \sum_{\text{boundary } i} n_i \omega_i.$$
(5.1)

The first summation is over all n.n. sites i and j in the crystal, the second one over all sites i in the crystal, and the third one over the sites i on the crystal boundary ( $n_i$  is the number of its n.n. ions outside the crystal). To ensure that the boundary conditions are weak, it is necessary



Fig. 5.1. A crystal of a parallelogram shape with  $7 \times 7$  adsorption sites (the dashed lines) with fixed constant boundary conditions. The bulk and surface interaction energies  $\varepsilon$  and  $\varepsilon_s$ , respectively, are indicated for a pair of n.n. ions. The contours are the Ising contours from Fig. 2.1 adapted to a triangular lattice.

that [49]

$$\left|\frac{\eta}{\varepsilon} - \frac{1}{2}\right| \le \frac{1}{6};\tag{5.2}$$

i.e., the boundary energy  $\eta$  is close to half of the bulk energy.

At low temperatures the specific bulk and surface energies for the fully vacant and occupied phases for the model (5.1) are (c.f. Eq. (2.57)) [49, 30]

$$f_{\rm vac} \approx -\frac{1}{\beta} e^{\beta\mu}, \qquad \qquad f_{\rm occ} \approx 3\varepsilon - \mu - \frac{1}{\beta} e^{\beta(6\varepsilon - \mu)}, \qquad (5.3a)$$

$$f_{\rm vac}^{(1)} \approx -\frac{1}{\beta} e^{\beta(\mu-2\eta)}, \qquad \qquad f_{\rm occ}^{(1)} \approx 2\eta - \varepsilon - \frac{1}{\beta} e^{\beta(4\varepsilon-\mu+2\eta)}, \qquad (5.3b)$$

where the exponentials represent small corrections due to thermal perturbations. Thus, the singlephase coverages and their derivatives are

and the coverage jump and difference in the specific surface free energies at the transition are

$$\Delta \theta = \theta_{\rm occ}(\mu_t) - \theta_{\rm vac}(\mu_t) \approx 1 - 2e^{-3\beta|\varepsilon|} > 0,$$
(5.3e)

$$\tau = f_{\rm occ}^{(1)}(\mu_t) - f_{\rm vac}^{(1)}(\mu_t) \approx 2\eta - \varepsilon + \frac{2}{\beta} \sinh[\beta(\varepsilon - 2\eta)] e^{-2\beta|\varepsilon|}, \tag{5.3f}$$

respectively.

### 5.2 Crystal coverage and current density

Applying Eqs. (4.8) and (5.3) and introducing the shorthand notations

$$u(\psi) = e^{-e_0\gamma\beta(\psi-\psi_t)}, \qquad x = e^{-\beta|\varepsilon|} \ll 1,$$
(5.4)

the coverage and current density in a crystal C, as functions of the electric potential  $\psi$ , may be expressed as

$$\Theta_C \approx J_C, \qquad I_C = \hat{I}_C + \delta I_C,$$
(5.5a)

with

$$\hat{I}_C \approx \frac{1}{4} \kappa \nu (e_0 \gamma)^2 \beta L^2 P_C, \tag{5.5b}$$

$$\delta I_C \approx \kappa \nu (e_0 \gamma)^2 \beta x^3 \Big[ u + \Big(\frac{1}{u} - u\Big) J_C \Big], \tag{5.5c}$$

where

$$\Omega_C = \frac{e_0 \gamma}{2} \left( \psi_{\max} - \psi \right) \beta L^2, \qquad \psi_{\max} \approx \psi_t - \frac{4(2\eta - \varepsilon)}{e_0 \gamma} \frac{1}{L}.$$
(5.6)

Note that we neglected the lowest thermal perturbations terms in the single-phase coverages, coverage jump, and surface free energy difference, approximating them as  $\theta_{\text{vac}} \approx 0$ ,  $\theta_{\text{occ}} \approx 1$ ,  $\Delta \theta \approx 1$ , and  $\tau \approx 2\eta - \varepsilon$ , respectively. On the other hand, we took the lowest thermal perturbations into account in the coverage derivatives, so that  $\theta'_{\text{vac}} \approx \beta x^3 u$  and  $\theta'_{\text{occ}} \approx \beta x^3/u$ , and the baseline part  $\delta I_C$  is evaluated explicitly (rather than approximated as  $\delta I_C \approx 0$ ).

### 5.3 Electrode coverage and current density: Experiment vs. theory

The theoretical expressions for the electrode coverage  $\Theta_0$  and current density  $I_0$  are given by Eq. (4.15) in which we may approximate  $\Delta \theta \approx 1$ . Before the four fitting parameters  $\gamma$ , r,  $\Delta \tau$ , and  $\psi_t$  are adjusted to fit the experimental spike from Fig. 4.2, we need to determine its baseline and excess current densities  $\delta I_0$  and  $\hat{I}_0$ , respectively. This in turn requires to know the jump function  $J_0$  and single-phase coverages  $\theta_{occ}$  and  $\theta_{vac}$ . According to Eqs. (4.1) and (4.17), we have

$$\Theta_0(\psi) = \frac{\int_{\psi}^{\infty} I_0(\tilde{\psi}) d\tilde{\psi}}{\int_{-\infty}^{\infty} I_0(\psi) d\psi}.$$
(5.7)

Thus, using the current density  $I_0$  from the stripping part of the voltammogram (see Fig. 5.2(a)), the coverage  $\Theta_0$  can be evaluated by a numerical calculation from Eq. (5.7) (see Fig. 5.2(b)). Fitting the coverage values within the intervals  $0.2 V \le \psi \le 0.27 V$  and  $0.36 V \le \psi \le 0.42 V$  by quadratic polynomials,

$$\theta_{\rm occ} \approx -3.94\psi^2 + 1.51\psi + 0.85, \qquad \theta_{\rm vac} \approx 1.18\psi^2 - 1.72\psi + 0.64,$$
(5.8)



Fig. 5.2. (a) The stripping part of the voltammogram for the UPD of copper on Pt(111) from Fig. 4.2. (b) The corresponding coverage  $\Theta_0$  (the full curve), and the coverages for the occupied and vacant phases (the dashed curves). (c) The resulting jump function  $J_0$ .

we then obtain the coverages for the occupied and vacant phases, respectively (see Fig. 5.2(b)). The jump function  $J_0$  is determined from the first relation in Eq. (4.15) (see Fig. 5.2(c)). The same equation shows that the baseline current density

$$\delta I_0(\psi) = i_{\text{vac}} + (i_{\text{occ}} - i_{\text{vac}})J_0, \tag{5.9}$$

with

$$i_{\rm occ} = -\frac{A_0}{|\Delta\theta|} \frac{\partial\theta_{\rm occ}}{\partial\psi} \approx 3.89\psi - 0.74, \qquad i_{\rm vac} = -\frac{A_0}{|\Delta\theta|} \frac{\partial\theta_{\rm vac}}{\partial\psi} \approx -1.16\psi + 0.85,$$
(5.10)

where  $A_0 = 0.430 \,\mu A.V.cm^{-2}$  is the area under the low voltage spike and the coverage jump  $\Delta \theta \approx 1$ . The excess current density is then determined as the difference  $\hat{I}_0 = I_0 - \delta I_0$  (see Fig. 5.3).



Fig. 5.3. (a) The current density  $I_0$  corresponding to the stripping part of the voltammogram for the UPD of copper on Pt(111) from Fig. 4.2 and its splitting into the excess and baseline parts  $\hat{I}_0$  and  $\delta I_0$ . (b) A detail of the plot from (a).

We may now adjust the four parameters  $\gamma$ , r,  $\Delta \tau$ , and  $\psi_t$  so that the theoretical formula for the excess current density  $\hat{I}_0$  in Eq. (4.15) would fit the  $\hat{I}_0$  that we have just determined from experiment. We will employ the size distribution  $w_L$  from Eq. (4.20) with p = 0.81 (i.e., P = 0.1) and the fitting procedure described in Section 4.5. The values

$$\kappa e_0 = 241.1 \,\mu C.cm^{-2}, \qquad \nu = 1 \,\,\mathrm{mV}.s^{-2}, \qquad \Delta \theta \approx 1$$
(5.11)

are known from experiment ( $\kappa$  is chosen so as to correspond to the Cu–Cu distance 2.77 Å [50]). The experimental  $\hat{I}_0$  from Fig. 5.3 has the area, maximum position, height, and asymmetry factor equal to

$$A = 0.356 \,\mu A.V.cm^{-2},$$
  

$$\psi^* = 0.320 \,V,$$
  

$$Ht = 19.23 \,\mu A.cm^{-2},$$
  

$$\alpha = 0.327,$$
  
(5.12)

respectively. From the area A and Eq. (4.17a) we get

$$\gamma = 1.48. \tag{5.13}$$

Using the dependence  $\alpha(r)$  from Fig. 4.6(b), the value of the asymmetry factor determined from experiment occurs when

$$r = -0.158,$$
 (5.14)

which corresponds to  $L^* = 27.51$  in Fig. 4.6(a). These r and  $L^*$  yield  $e_0 \Delta \tau \text{Ht} = 5.50 \,\mu A.V.cm^{-2}$  from Eq. (4.17c). Thus, to get the correct height, we must have

$$\Delta \tau = 286.2 \, meV, \tag{5.15a}$$

yielding

$$\tau_0 = r\Delta\tau = -45.2\,meV.\tag{5.15b}$$

Using now the position of the spike maximum, the phase-transition voltage is

$$\psi_t = 0.315 \, V \tag{5.16}$$

by Eq. (4.17b).

Finally, the parameters  $\gamma$ , r,  $\Delta \tau$ , and  $\psi_t$  being adjusted, we use Eq. (4.15) to calculate the theoretical  $\psi$  dependences for the excess current density  $\hat{I}_0$ , jump function  $J_0$ , total coverage  $\Theta_0$ , baseline current density  $\delta I_0$ , and total current density  $I_0$  (see Fig. 5.4). Their agreement with the experimental dependences from Figs. 5.2 and 5.3 is rather good.

### 5.4 Interaction energies

The mean value  $\tau_0$  and range half-width  $\Delta \tau$  are related to the interaction energies  $\varepsilon$  and  $\eta$  in the considered lattice-gas model (5.1) as follows [34,35]. Recalling that  $\tau \approx 2\eta - \varepsilon$  in the model, the randomness in the boundary conditions corresponds to that of the boundary interaction energy  $\eta$ . To describe it, we express  $\eta$  as proportional to the bulk interaction,  $\eta = \vartheta \varepsilon$ , where  $0 \le \vartheta \le 1$  is the total occupancy of the deposited ion in the defect regions surrounding a given crystal C. (Thus,  $\vartheta$  is the number of defect sites along the boundary of C occupied by the ion divided by the number of all defect boundary sites). Approximating the occupancies at the individual defect sites to be independent, we may invoke the local limit theorem to estimate the probability of  $\vartheta$  having a specific value by a Gaussian distribution. Its mean value and variance are equal to the probability,  $0 \le \vartheta_0 \le 1$ , that a given defect site is occupied and to  $D^2 = \vartheta_0(1 - \vartheta_0)/4L$ , respectively. Therefore,  $\tau$  should have the mean value  $\tau_0 = E(\tau) \approx 2E(\eta) - \varepsilon$  and variance  $\sigma^2 = \operatorname{var}(\tau) \approx 2\operatorname{var}(\eta) = 2(\varepsilon D)^2$ . Writing  $\eta_0 = E(\eta) = \vartheta_0\varepsilon$  for the mean boundary interaction energy (the one associated with the mean single-site occupancy  $\vartheta_0$ ) and recalling that  $\sigma = \Delta \tau / 2\sqrt{L}$ , we get [34,35]

$$\tau_0 = 2\eta_0 - \varepsilon, \qquad \Delta \tau = \sqrt{2\eta_0(\varepsilon - \eta_0)}. \tag{5.17}$$

For the values of  $\tau_0$  and  $\Delta \tau$  from Eq. (5.15) adjusted so as to fit the experimental data, the bulk and mean boundary interaction energies are

$$\varepsilon = -407.2 \, meV, \qquad \eta_0 = -226.2 \, meV, \tag{5.18}$$

respectively. Note that  $\eta_0/\varepsilon = 0.56$  so that the condition (5.2) for the boundary conditions to be weak is satisfied.



Fig. 5.4. The theoretical  $\psi$  dependences for the (a) excess current density  $\hat{I}_0$ , (b) total current density  $I_0$ , (c) jump function  $J_0$ , (d) total coverage  $\Theta_0$ , and (e) baseline current density  $\delta I_0$  as calculated from Eq. (4.15) and their comparison with the experimental ones from Figs. 5.2 and 5.3.

## 6 Example 2: Underpotential deposition of Cu on Au(111)

As a second example, we consider the voltammogram that was measured for the underpotential deposition of copper on the (111) surface of a gold electrode in the presence of a sulfate electrolyte [47] (see Fig. 4.3). The voltammogram has two distinct spikes and a broad foot region near the spike at higher potentials. The following scenario of this deposition process was suggested [51, 40, 52, 34]. Let C and S denote that a site is occupied by copper and sulfate, respectively, and let O denote a vacant site. In addition, let XYZ denote a phase with a  $\sqrt{3} \times \sqrt{3}$ structure in which one triangular sublattice of the electrode surface is covered by X, one sublattice by Y, and the remaining sublattice by Z. The spike at lower potentials corresponds to a first-order phase transition between the phase CCC (a full monolayer of copper) and the phase SCC (sulfate covers a triangular sublattice and the remaining sites are occupied by copper). The high voltage spike corresponds to the transition between the SCC phase and the SCO phase (one sublattice is covered by sulfate, one by copper, and the remaining sublattice is vacant). Finally, the foot region corresponds to the transition between the SCO phase and the OOO (a fully vacant) phase. Note that the jump in the copper coverage at each of these three transitions is  $\Delta \theta \approx -1/3$ . The structure of the four phases is shown in Fig. 6.1.

In the following we shall consider only the low voltage spike. Theoretical results for the whole voltammogram, including the high voltage spike and foot region, are quite complex and can be found in [34,48].



Fig. 6.1. The structure of the CCC, SCC, SCO, and OOO phases.

### 6.1 Lattice-gas model

We again consider crystals that have a parallelogram shape of  $N_C = L \times L$  adsorption sites. To model the considered UPD process, we shall employ the two-component lattice gas of Huckaby, Blum, and Legault [37,39,40] on the two-dimensional triangular lattice. The lattice gas has three n.n. interactions:

- (a) two S ions are excluded from occupying n.n. sites,
- (b) a pair of n.n. C's interact with a repulsive energy  $\varepsilon_{C1} > 0$ ,
- (c) an adsorbed C interacts with a n.n. adsorbed S with an attractive energy  $\varepsilon_{S1} < 0$ .

These interactions are sufficient to obtain the structure of the observed phases [39]. They are not sufficient, however, to establish that the involved phase transitions are of first order. To this end, two next nearest-neighbor (n.n.n.) interactions are included [34]:

- (d) a pair of n.n.n. C's interact with an attractive energy  $\varepsilon_{C2} < 0$ ,
- (e) a pair of n.n. S's interact with an attractive energy  $\varepsilon_{S2} < 0$ .

Note that two n.n.n. sites are neighbors on one of the three triangular sublattices of the (111) surface. The boundary conditions are chosen so that a fixed configuration SCC is present outside the crystal, because SCC can be weak with respect to all four phases CCC, SCC, SCO, and OOO that appear in the scenario of the deposition process. The boundary interactions are limited to n.n. neighbors XY and, if X lies inside the crystal and Y outside, they interact with an attractive or repulsive energy  $\eta_{XY}$ . A n.n. pair of S's is excluded, as in the bulk.

Let us use  $N_{XY1}$ ,  $N_{XX2}$ , and  $N_X$  to denote the number of n.n. XY pairs, n.n.n XX pairs, and sites occupied by X, respectively, in a given microscopic configuration. Moreover, let  $\tilde{N}_{XY}$ stand for the number of n.n. XY sites such that X is in the crystal and Y outside it. Then the Hamiltonian of the considered lattice gas is given as [34]

$$H_C(\omega) = \varepsilon_{C1} N_{CC1} + \varepsilon_{S1} N_{CS1} + \varepsilon_{C2} N_{CC2} + \varepsilon_{S2} N_{SS2} - \mu_C N_C - \mu_S N_S + \eta_{CC} \tilde{N}_{CC} + \eta_{CS} \tilde{N}_{CS} + \eta_{SC} \tilde{N}_{SC}.$$
(6.1)

The chemical potentials  $\mu_X$  are linear functions of the applied electric potential (c.f.Eq. (4.2)),

$$\mu_C(\psi) = -e_0 \gamma_C(\psi - \psi_C), \qquad \mu_S(\psi) = -e_0 \gamma_S(\psi - \psi_S), \tag{6.2}$$

where  $\gamma_C$  and  $\gamma_S$  are the effective electrovalences and  $\psi_C$  and  $\psi_S$  are the reference potentials of copper and sulfate, respectively. As the potential  $\psi$  varies, the chemical potentials form a line,  $\ell$ , in the  $(\mu_C, \mu_S)$  plane given as

$$\mu_S = \frac{\gamma_S}{\gamma_C} \mu_C + e_0 \gamma_S (\psi_S - \psi_C) = K \mu_C + Q, \tag{6.3}$$

where K is its slope and Q its  $\mu_S$  intercept.

The ground state diagram of the lattice gas from Eq. (6.1) is shown in Fig. 6.2. Recalling that, at temperatures well below the critical point, the phase diagram is a 'slight deformation' of



Fig. 6.2. The ground-state diagram of the lattice gas (6.1) when  $\varepsilon_{S1} < -\varepsilon_{C1}$ . The values  $\mu_{C1} = 3(\varepsilon_{S1} + \varepsilon_{C2})$ ,  $\mu_{C2} = 3(\varepsilon_{C1} + \varepsilon_{S1} + \varepsilon_{C2})$ ,  $\mu_{C3} = 3\varepsilon_{C2}$ ,  $\mu_{C4} = 3(\varepsilon_{C1} + \varepsilon_{C2})$ ,  $\mu_{C5} = 6\varepsilon_{C1} + 3\varepsilon_{C2}$ , and  $\mu_{S1} = 3\varepsilon_{S2}$ ,  $\mu_{S2} = 3(\varepsilon_{S2} - \varepsilon_{C1})$ ,  $\mu_{S3} = 3(\varepsilon_{C1} + 2\varepsilon_{S1} + \varepsilon_{S2})$ ,  $\mu_{S4} = 6\varepsilon_{S1} + 3\varepsilon_{S2}$  [34]. The degeneracy of the ground states is indicated in parentheses.

the ground-state one and that typical microscopic configurations of low-temperature phases have the structure as their ground states (see Section 2.3), it is clear that the lattice gas can be used to describe the above-mentioned scenario for the considered UPD process in which the phases CCC, SCC, SCO, and OOO are stable one after the other as the potential  $\psi$  is increased. In addition, the CCC–SCC, SCC–SCO, and SCO–OOO phase transitions are of first order, because the copper coverage has a jump (of absolute value 1/3) at each of them.

As already mentioned, we shall focus on the CCC-SCC transition associated with the low voltage spike. For the CCC and SCC phase the specific bulk and surface energies are

$$f_{CCC} = 3\varepsilon_{C1} + 3\varepsilon_{C2} - \mu_C + o, \tag{6.4a}$$

$$f_{SCC} = \varepsilon_{C1} + 2\varepsilon_{S1} + 2\varepsilon_{C2} + \varepsilon_{S2} - \frac{2}{3}\mu_C - \frac{1}{3}\mu_S + o, \qquad (6.4b)$$

$$f_{CCC}^{(1)} = -\varepsilon_{C1} - 2\varepsilon_{C2} + \frac{4}{3}\eta_{CC} + \frac{2}{3}\eta_{CS} + o,$$
(6.4c)

$$f_{SCC}^{(1)} = -\frac{1}{3}\varepsilon_{C1} - \frac{2}{3}\varepsilon_{S1} - \frac{4}{3}\varepsilon_{C2} - \frac{2}{3}\varepsilon_{S2} + \frac{2}{3}\eta_{CC} + \frac{2}{3}\eta_{CS} + \frac{2}{3}\eta_{SC} + o, \qquad (6.4d)$$

where the terms o represent small corrections of order  $\exp(-c\beta)$  due to thermal perturbations. Thus, the single-phase copper coverages are

$$\theta_{CCC} = -\frac{\partial f_{CCC}}{\partial \mu_C} = 1 + o, \qquad \qquad \theta_{SCC} = -\frac{\partial f_{SCC}}{\partial \mu_C} = \frac{2}{3} + o. \tag{6.4e}$$

Their derivatives with respect to either chemical potential are all of order *o*. The coverage jump and difference in the specific surface free energies at the transition are

$$\Delta \theta = \theta_{SCC}(\mu_t) - \theta_{CCC}(\mu_t) = -\frac{1}{3} + o > 0, \qquad (6.4f)$$

$$\tau = f_{SCC}^{(1)}(\mu_t) - f_{CCC}^{(1)}(\mu_t) = \frac{2}{3} \left( \varepsilon_{C1} - \varepsilon_{S1} + \varepsilon_{C2} - \varepsilon_{S2} - \eta_{CC} + \eta_{SC} \right) + o, \quad (6.4g)$$

respectively.

## 6.2 Crystal coverage and current density

Since the model has two chemical potentials, the coverage and current density in a crystal C are given as

$$\Theta_C(\psi) = \frac{1}{\beta N_C} \frac{\partial \log Z_C(\mu_C(\psi), \mu_S(\psi))}{\partial \mu_C},$$
(6.5a)

$$I_C(\psi) = -\kappa e_0 \gamma_C \nu \, \frac{\partial \Theta_C(\psi)}{\partial \psi}.$$
(6.5b)

Applying Eq. (4.8) with  $\theta_1 = \theta_{CCC}$  and  $\theta_2 = \theta_{SCC}$  and Eq. (6.4), the coverage and current density in a crystal C, as functions of the electric potential  $\psi$ , may be expressed as [34]

$$\Theta_C \approx 1 - \frac{1}{3} J_C, \qquad I_C = \hat{I}_C + \delta I_C, \tag{6.6a}$$

with

$$\hat{I}_C \approx \frac{1-K}{36} \kappa \nu (e_0 \gamma_C)^2 \beta L^2 P_C, \tag{6.6b}$$

$$\delta I_C \approx \kappa \nu (e_0 \gamma_C)^2 (o + o J_C), \tag{6.6c}$$

where

$$\Omega_C = \frac{(1-K)e_0\gamma_C}{6} \left(\psi - \psi_{\max}\right)\beta L^2 \tag{6.7}$$

and

$$\psi_{\max} \approx \psi_t + \frac{8(\varepsilon_{C1} - \varepsilon_{S1} + \varepsilon_{C2} - \varepsilon_{S2} - \eta_{CC} + \eta_{SC})}{(1 - K)e_0\gamma_C} \frac{1}{L}.$$
(6.8)

The phase transition point  $\psi_t$  is determined from the condition  $f_{CCC} = f_{SCC}$ , and Eq. (6.4) yields

$$\psi_t \approx \psi_C - \frac{6(\varepsilon_{C1} - \varepsilon_{S1}) + 3(\varepsilon_{C2} - \varepsilon_{S2}) + Q}{(1 - K)e_0\gamma_C}$$
(6.9)

with  $\psi_t$  being below  $\psi_C - (6\varepsilon_{C1} + 3\varepsilon_{C2})/e_0\gamma$  (so that  $\mu_C$  stays above  $\mu_{C5}$  from Fig. 6.2).



Fig. 6.3. (a) The stripping part of the voltammogram for the UPD of copper on Au(111) from Fig. 4.3 for voltages  $0.018 V \le \psi \le 0.13 V$ . (b) The corresponding coverage  $\Theta_0$  (the full curve), and the coverages for the occupied and vacant phases (the dashed curves). (c) The resulting jump function  $J_0$ .

### 6.3 Electrode coverage and current density: Experiment vs. theory

Using the data from the stripping part of the voltammogram in Fig. 4.3 for the UPD of copper on Au(111), the coverage  $\Theta_0$  can be evaluated from Eq. (5.7) (see Fig. 6.3(b)). The low voltage current density spike lies within the range  $0.018 V \le \psi \le 0.13 V$  and is shown in Fig. 6.3(a). Fitting the coverage values within the intervals  $0.018 V \le \psi \le 0.045 V$  and  $0.09 V \le \psi \le$ 0.13 V by quadratic polynomials,

$$\theta_{CCC} \approx 1.00 + 0.06\psi - 10.58\psi^2, \qquad \theta_{SCC} \approx 0.70 - 0.24\psi - 2.75\psi^2, \tag{6.10}$$

we then obtain the coverages for the CCC and SCC phases, respectively (see Fig. 6.3(b)). The jump function  $J_0$  is determined from the first relation in Eq. (4.15) (see Fig. 6.3(c)). The same



Fig. 6.4. (a) The current density  $I_0$  corresponding to the stripping part of the voltammogram for the UPD of copper on Au(111) from Fig. 4.3 and its splitting into the excess and baseline parts  $\hat{I}_0$  and  $\delta I_0$ . (b) A detail of the plot from (a).

equation shows that the baseline current density is

$$\delta I_0(\psi) = i_{SCC} + (i_{CCC} - i_{SCC})J_0 \tag{6.11}$$

with

$$i_{CCC} = -\frac{A_0}{|\Delta\theta|} \frac{\partial\theta_{CCC}}{\partial\psi} \approx 12.40\psi - 0.04, \tag{6.12a}$$

$$i_{SCC} = -\frac{A_0}{|\Delta\theta|} \frac{\partial\theta_{SCC}}{\partial\psi} \approx 3.22\psi + 0.14, \tag{6.12b}$$

where  $A_0 = 0.195 \,\mu A.V.cm^{-2}$  is the area under the low voltage spike and the coverage jump  $\Delta \theta \approx -1/3$ . The excess current density is then the difference  $\hat{I}_0 = I_0 - \delta I_0$  (see Fig. 6.4).

We may now adjust the four parameters  $\gamma$ , r,  $\Delta \tau$ , and  $\psi_t$  so that the theoretical formula for the excess current density  $\hat{I}_0$  in Eq. (4.15) would fit the one determined from experiment. We will again employ the size distribution  $w_L$  from Eq. (4.20) with p = 0.81 (i.e., P = 0.1), the fitting procedure described in Section 4.5, and the experimental values [34]

$$\kappa e_0 = 222.4 \,\mu C.cm^{-2}, \qquad \nu = 1 \,\mathrm{mV}.s^{-2}, \qquad \Delta \theta \approx -1/3.$$
 (6.13)

The experimental  $\hat{I}_0$  from Fig. 5.3 has the area, maximum position, height, and asymmetry factor equal to

$$A = 0.146 \,\mu A.V.cm^{-2},$$
  

$$\psi^* = 0.054 \,V,$$
  

$$Ht = 10.50 \,\mu A.cm^{-2},$$
  

$$\alpha = 0.269,$$
  
(6.14)

respectively. From the area A and Eq. (4.17a) we get

$$\gamma = 1.97. \tag{6.15}$$

The dependence  $L^*(r)$  and  $\alpha(r)$  are determined just by the size distribution  $w_L$  and not the considered UPD process, so their plots within the range  $-1 \le r \le 1$  from Fig. 4.6 can be applied. To fit the value of the asymmetry factor determined from experiment, we get

$$r = 0.261,$$
 (6.16)

which corresponds to  $L^* = 25.08$ . These r and  $L^*$  yields  $e_0 \Delta \tau \text{Ht} = 0.843 \,\mu A.V.cm^{-2}$  from Eq. (4.17c). Thus, to get the correct height, we must have

$$\Delta \tau = 80.3 \, meV, \tag{6.17a}$$

yielding

$$\tau_0 = r\Delta\tau = 21.0 \, meV. \tag{6.17b}$$

Using now the position of the spike maximum, the phase-transition voltage is

$$\psi_t = 0.049 \, V \tag{6.18}$$

by Eq. (4.17b).

Using the adjusted parameters  $\gamma$ , r,  $\Delta \tau$ , and  $\psi_t$ , we calculate the theoretical  $\psi$  dependences for the excess current density  $\hat{I}_0$ , jump function  $J_0$ , total coverage  $\Theta_0$ , baseline current density  $\delta I_0$ , and total current density  $I_0$  from Eq. (4.15) (see Fig. 6.5). Their agreement with the experimental dependences from Figs. 6.3 and 6.4 is rather good.

### 6.4 Interaction energies

Let us obtain the relation between the mean value  $\tau_0$  and range half-width  $\Delta \tau$  and the interaction energies in the considered lattice-gas model (6.1). The randomness in the boundary conditions is again represented by that of the boundary interactions given in this model by the energies  $\eta_{CC}$ ,  $\eta_{CS}$ , and  $\eta_{SC}$ . We describe the latter via the total occupancies  $0 \leq \vartheta_C \leq 1$  and  $0 \leq \vartheta_S \leq$ 1 of the deposited copper and sulfate, respectively, in the defect regions surrounding a given crystal C. Namely, we express the boundary interaction energies to be proportional to the bulk n.n. interaction energies as [34]

$$\eta_{CC} = \vartheta_C \,\varepsilon_{C1}, \qquad \eta_{CS} = \vartheta_S \,\varepsilon_{S1}, \qquad \eta_{SC} = \vartheta_C \,\varepsilon_{S1}. \tag{6.19}$$

Referring to the local limit theorem, the probability that  $\vartheta_C$  and  $\vartheta_S$  have given values is estimated by a product of two Gaussian distributions, one for  $\vartheta_C$  and one for  $\vartheta_S$ . Their mean values are equal to the probabilities,  $0 \le \vartheta_C^0 \le 1$  and  $0 \le \vartheta_S^0 \le 1$ , that a given defect site is occupied by copper and sulfate, respectively. Their variances are  $D_C^2 = \vartheta_C^0(1 - \vartheta_C^0)/(2/3)4L$  and  $D_S^2 = \vartheta_S^0(1 - \vartheta_S^0)/(1/3)4L$ , respectively (in the SCC boundary conditions one third of the outer sites is occupied by sulfate and two thirds by copper).



Fig. 6.5. The theoretical  $\psi$  dependences for the (a) excess current density  $\hat{I}_0$ , (b) total current density  $I_0$ , (c) jump function  $J_0$ , (d) total coverage  $\Theta_0$ , and (e) baseline current density  $\delta I_0$  as calculated from Eq. (4.15) and their comparison with the experimental ones from Figs. 6.3 and 6.4.

Recalling the expression for  $\tau$  in Eq. (6.4), the mean value of  $\tau$  should be

$$\tau_0 \approx \frac{2}{3} \left( \varepsilon_{C1} - \varepsilon_{S1} + \varepsilon_{C2} - \varepsilon_{S2} - \eta_{CC}^0 + \eta_{SC}^0 \right), \tag{6.20}$$

where  $\eta_{CC}^0 = \vartheta_C^0 \varepsilon_{C1}$  and  $\eta_{SC}^0 = \vartheta_C^0 \varepsilon_{S1}$  are the mean boundary interaction energies. Its variance should be  $\sigma^2 = \operatorname{var}(\tau) \approx (2/3)[(\varepsilon_{C1}D_C)^2 + (\varepsilon_{S1}D_S)^2]$ . Since  $\sigma = \Delta \tau / 2\sqrt{L}$ , we get [34]

$$\Delta \tau = \left[ \eta_{CC}^{0}(\varepsilon_{C1} - \eta_{CC}^{0}) + 2\eta_{SC}^{0}(\varepsilon_{S1} - \eta_{SC}^{0}) \right]^{1/2}.$$
(6.21)

It is not possible to uniquely determine the six energies  $\varepsilon_{C1}$ ,  $\varepsilon_{S1}$ ,  $\varepsilon_{C2}$ ,  $\varepsilon_{S2}$ ,  $\eta_{CC}^0$ , and  $\eta_{SC}^0$  from the two adjusted values of  $\tau_0$  and  $\Delta \tau$ . This can be done only when not only the low voltage spike but also the high voltage spike and its foot region from the voltammogram are fitted by theoretical formulas. We shall not carry out this analysis here, it was presented in [34]. There the values  $\varepsilon_{C1} = 18.7 \text{ meV}, \varepsilon_{S1} = -100 \text{ meV}, \varepsilon_{C2} = -4.5 \text{ meV}, \varepsilon_{S2} = -9 \text{ meV}, \eta_{CC}^0 = 14.0 \text{ meV},$ and  $\varepsilon_{SC}^0 = -75.1 \text{ meV}$  were obtained.

## 7 Conclusions

The main goal of this review was to describe macroscopic behavior, as determined by microscopic interactions, in systems that are large, but finite rather than infinite, and to illustrate how this can be applied to obtain voltammogram spikes measured in electrochemical experiments.

In Section 2 we began by presenting rigorous results on finite-size effects valid for a wide group of models—the contour models—of dimension  $d \ge 2$  at temperatures well below the critical point where first-order phase transitions could occur. We showed that lattice-gas models that are often employed in various applications could be rewritten as contour models and that low-temperature cluster expansion series could be used to obtain the models' free energy, phases, and phase diagrams. Since the finite-size behavior is very sensitive to boundary conditions, we considered three cases (periodic, weak, and strong boundary conditions) and presented the results for each case separately. For weak and strong boundary conditions the surface effects caused a shift of the actual position of the finite-volume transition from the infinite-transition point (for periodic boundary conditions the shift is negligible). For strong boundary conditions there was, in addition, a significant dependence of single-phase quantities on the external fields due to the presence of phase separation in the system.

We then used the rigorous results in the case of weak boundary conditions to obtain the coverage and current density in dependence on the applied electric potential measured in underpotential deposition experiments. The key idea behind the results is that surfaces of electrodes used in the experiments have a polycrystalline structure, being composed of a large number of single-crystalline domains. In Section 3 we first presented the results that are of general nature and could be applied to a system of dimension  $d \ge 2$  that is composed of many subsystems. We expressed a quantity related to the whole system as a double average of the quantities related to the individual subsystems. One average was over the subsystem sizes and one over the surface free energy differences in the subsystems. After evaluating the latter average, we provided results for a general distribution of subsystem sizes that could be calculated in a numerical way. We described a procedure to fit experimental data with theoretical results, using only four adjustable parameters.

Finally, in Sections 4 – 6, we focused on first-order phase transitions that might occur at an electrode–electrolyte interface due to a sudden UPD deposition of a metal on the electrode surface. We pointed out that sharp spikes were known to be present in the voltammograms (the current vs. electric potential plots) when such transitions took place. As two examples, we showed voltammograms for UPD of copper on the (111) surface of platinum and gold electrodes. Applying the general results from Section 3 to this two-dimensional phenomenon, we obtained rather good agreement between theoretical and experimental spikes. The fitting procedure was described in detail for both experiments, and we were even able to obtain the corresponding values of the microscopic interaction energies in the models that simulate the two UPD processes.

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