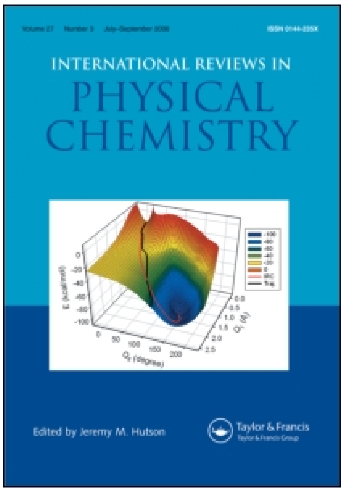

International Reviews in Physical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713724383

The question of negative capacitance and its relation to instabilities and phase transitions at electrified interfaces

Michael B. Partenskii[a]; Vladimir Dorman[a]; Peter C. Jordan[a]
[a] Department of Chemistry, Brandeis University, Waltham, MA, USA

To cite this Article Partenskii, Michael B. , Dorman, Vladimir and Jordan, Peter C.(1996) 'The question of negative capacitance and its relation to instabilities and phase transitions at electrified interfaces', International Reviews in Physical Chemistry, 15: 1, 153 — 182

To link to this Article: DOI: 10.1080/01442359609353179

URL: http://dx.doi.org/10.1080/01442359609353179

INTERNATIONAL REVIEWS IN PHYSICAL CHEMISTRY, 1996, VOL. 15, NO. 1, 153–182

The question of negative capacitance and its relation to instabilities and phase transitions at electrified interfaces

by MICHAEL B. PARTENSKII, VLADIMIR DORMAN
and PETER C. JORDAN

Department of Chemistry, Brandeis University, Waltham, MA 02254, USA

The question of negative differential capacitance (C) at electrified interfaces is critically reviewed. The importance of the thermodynamic constraints and the physical differences between systems under charge and potential control is emphasized. For a system under potential control, C can never be negative, while no such general constraint is mandated for systems under charge control. However, the appearance of a negative C domain in isolated systems can be limited by a phase transition to a non-uniform state. The occurrence of such transitions depends on the 'stiffness' of the interface. Theoretical calculations that predict $C < 0$ are analysed. We investigate a series of electromechanical analogues of the existing models of double layer, illustrating the appearance of $C < 0$ in 'rigid' systems under equilibrium conditions, and the transition to the non-uniform state in systems with moderate 'surface tension', narrowing the $C < 0$ domain. The effect of intrinsic non-homogeneity is also addressed. The appearance of domains where C is negative under charge control implies the occurrence of surface phase transitions under potential control. The characteristics of phase transitions in isolated and open systems, and the relationship between them, are considered. Some biophysical implications are discussed.

1. Introduction

The problem of negative differential capacitance (C), the so-called Cooper–Harrison (CH) catastrophe, arose in theoretical electrochemistry about two decades ago in studies of 'molecular models' of the compact layer at metal/solvent interfaces (Cooper and Harrison 1975). It initiated considerable interest, triggered in part by the sense that such behaviour is unphysical. It appeared later that the original CH catastrophe was a result of inconsistency in computation of the local electrostatic field acting on a molecular dipole. It did not resolve, however, the general question raised by those studies—the problem of the admissible sign of C.

Later work (Feldman *et al.* 1986a, b, 1987, Partenskii *et al.* 1987) showed that the question of whether C can be negative is inextricably coupled to the nature of the thermodynamic constraints on the system, i.e. whether the electrode charge (q) or the cell potential (ϕ) is the independent (controlled) variable. While C of the total interface is strictly positive for systems under ϕ-control conditions where there can be charge (electron) exchange between battery (potentiostat) and electrodes, it can become negative for an isolated system when q is the controlled thermodynamic variable. The restrictions are even less demanding for any particular part of the double layer. For instance, either compact or diffuse layer contribution, C_H or C_D, can become negative even under ϕ-control if total $C > 0$.

The possibility that $C < 0$ raised questions of what happens when systems exhibiting this anomaly under q-control are switched to ϕ-control (Feldman *et al.* 1986a, b). In brief, the appearance of domains of negative C under q-control imply the

0144-235X/96 $12·00 © 1996 Taylor & Francis Ltd

existence of surface instabilities and phase transitions under ϕ-control. These phenomena are becoming active areas of research.

It is worth noting that a physically similar question was analysed a few years before the issue of negative capacitance ever arose in electrochemistry. Without explicitly commenting on the sign of C, Crowley (1973) proposed a very elegant model of membrane rupture based on the onset of electromechanical instability under ϕ-control. Even today, just as was the case with Galvani's work on frog muscle contraction, biology can precede physics in the identification of important electrical phenomena.

In this review we first discuss the difference between ϕ- and q-control. It is shown that both types of control are experimentally realizable. We also discuss the general constraints on the differential capacitance. The existing analysis unequivocally indicates that under ϕ-control C is strictly non-negative. To date attempts at the general analysis for isolated systems (a) have been restricted to so-called 'σ-control' with local (not just average, as in q-control) charge density fixed, and (b) have considered only the simple 'primitive electrolyte' models of interfaces. We show that improved and extended, Blum, Lebovitz and Henderson's treatment (Blum *et al.* 1980) constrained as indicated, only imposes an upper bound on C^{-1} and places no restrictions on its sign.

In §3 we discuss different models which predicted, some of them falsely, the appearance of a $C < 0$ domain. Using the electromechanical analogues of the 'relaxing-gap capacitor' models of the interfaces it is shown that C can become negative under σ-control.

The possible consequences of these results for both q- and ϕ-control are discussed in §4. We show that negative C computed under σ-control can lead to a phase transformation under q-control resulting in the appearance of a non-uniform phase with both electronic and ionic density varying along the electrode plane. For the interfaces with sufficient lateral 'rigidity', the $C < 0$ domain can be detected. Finally we demonstrate that an additional, 'potential-driven' phase transition can exist if a system exhibiting regions of negative C under q-control are switched to ϕ-control. In this transition the system obtains charge from the potentiostat (q changes discontinuously) while in the isolated system the fixed charge q can only redistribute itself in the plane. We use modified electromechanical models to illustrate these differences. This analysis indicates the importance of conducting theoretical and experimental studies of surface instabilities and phase transitions both under q- and ϕ-control conditions; double layer properties and membrane electroporation provide examples where such issues must be important. The issue of capacitance anomalies and its relation to surface phase transitions is still a subject of substantial controversy and we will address some questions raised by recent analysis.

2. Electrical control and general restrictions on the differential capacitance C

To properly describe equilibrium electric properties of an interface requires careful thermodynamic and statistical mechanical analysis. We first formulate the ensembles for both types of electrical control and discuss the general statistical mechanical restrictions imposed on interfacial capacitance.

2.1. *Charge (q)- and potential (ϕ)-control*

To clarify the issue of electrical control consider a highly simplified model of an electrochemical cell consisting of two electrodes, E_1 and E_2, in contact with the ionic conductor (electrolyte). Each electrode comprises a macroscopic metal phase. We assume that the electrolyte is surface inactive, i.e. for the range of charge or voltage considered there is no charge transfer between the electrodes and electrolyte. Put differently, an applied voltage induces equilibrium redistribution of charge carriers (electrons in the electrode, ions in the electrolyte) and multipoles (induced electronic polarization, reorientation of polar groups in electrolyte, etc.) but not an electric current across the cell.

Electrical control of the cell is maintained through the electronic subsystems of the electrodes (Parsons 1954). Either the number of electrons or their electrochemical potentials can be fixed externally. The electrochemical potential of the electrons in phase α is $\bar{\mu}_\alpha = \mu_\alpha - e\phi_\alpha$. The chemical potential μ_α (the Fermi energy) is completely specified by bulk properties of the (macroscopic) metal phase; ϕ_α is the electrostatic potential. To avoid complexities due to contact phenomena ('Volta potential') we assume both electrodes are made of the same metal and therefore have the same chemical potential. Then the difference of the electrochemical potentials equals the voltage:

$$\phi = \frac{(\bar{\mu}_1 - \bar{\mu}_2)}{e}. \tag{1}$$

The conjugate electric variable to ϕ is the electrode charge q. In studies of electrochemical interfaces it is convenient to scale properties such as C or q by the electrode surface area, S. Thus we introduce a mean surface charge density

$$\sigma = \frac{q}{S} \tag{2}$$

and a differential capacitance (per unit area) defined as

$$C = \frac{\mathrm{d}\sigma}{\mathrm{d}\phi}. \tag{3}$$

In q-control the electrode charge is the independent variable under external control and ϕ, the potential drop across the cell adjusts itself accordingly. To determine $\phi(\sigma)$ requires supplying the electrode E_1 with small amounts of charge, δq, switching a contact with a charge source (battery) for a short period of time, δt.† With no loss of generality the second electrode, E_2, can always be grounded, automatically developing a compensating charge thus preserving global electroneutrality. The change in the potential increment, $\delta\phi$, is detected in the isolated system after the charge source is disconnected and equilibrium is established. This determines both the charging plot $\phi(\sigma)$ and the differential capacity, $C^Q \equiv \delta\phi^Q/\delta\sigma$; the superscript '$Q$' refers to quantities determined under q-control.

We note here that in most theoretical studies of the double layer in the absence of specific adsorption the system is assumed uniform in the plane parallel to the electrode surface. The charge density is either presumed to be constant, as for an ion–dipole

---

† The corresponding charge increment is $\delta q = \int_0^{\delta t} j(t)\,\mathrm{d}t$ where $j(t)$ is the charging current between the battery and the electrode; the current is easily measured.

plasma contacting the charged wall (see §3.2.1 for references) or to exhibit only atomic-scale variation when image-like screening effects are included (Rosinberg *et al.* 1985, Hautman *et al.* 1989, Brodsky *et al.* 1991 and references therein; §3.1). In these cases σ-control, where the local charge density on the electrode is fixed, is equivalent to q-control. Generally, only the latter is experimentally accessible because there is no way to keep the local density on the electrode fixed. To emphasize this difference we use the superscript Σ for quantities calculated under σ-control. Further discussion of the interrelation between σ- and q-control is postponed to §4.

Now consider ϕ-control. Imagine for simplicity that each electrode is linked to its own potentiostat, P_1 or P_2, thereby fixing the value of the corresponding electrochemical potential. P_i can be a large piece of metal, the potential of which is controlled by its charge q_{P_i}. We require only that charge fluctuations between P_i and E_i do not noticeably change the potential of P_i. Thus, in ϕ-control the voltage is fixed and it determines the electric charge on the electrode. Such quantities are denoted by the superscript Φ (σ^{Φ}, C^{Φ}, etc.). In what follows, when constraints are obvious, the superscripts Q and Φ are suppressed.

The choice of control variable determines the ensemble to use in analysis. With the number of electrons fixed (q-control), the canonical ensemble is appropriate and the thermodynamic potential (per unit area) is

$$A^{Q}(\sigma, T, V) = -\frac{kT}{S}\ln Z^{Q}(\sigma, T, V) \tag{4}$$

with the partition function

$$Z^{Q}(\sigma, T, V) = \int_{(\Omega)} \exp[-\beta H^{Q}(\sigma, \Omega)]\,\mathrm{d}\Omega \tag{5}$$

where H^{Q} is the Hamiltonian of the isolated system with the specified charge, $\beta = 1/kT$, and Ω is the volume of the configurational space.† In ϕ-control the grand canonical ensemble is applicable (Hill 1956) and the thermodynamic potential (again per unit area) is

$$A^{\Phi}(\phi, V) = -\frac{kT}{S}\ln Z^{\Phi}(\phi, V) \tag{6}$$

with the partition function

$$\begin{aligned} Z^{\Phi} &= \frac{S}{e}\int \mathrm{d}\sigma Z^{Q}(\sigma, V)\exp(\sigma\phi\beta S) \\ &= \frac{S}{e}\int \mathrm{d}\sigma \int \mathrm{d}\Omega \exp -\beta[H^{Q}(\sigma, \Omega) - q\phi] \\ &= \frac{S}{e}\int \mathrm{d}\sigma \exp -\beta S[A^{Q}(\sigma, V) - \sigma\phi]. \end{aligned} \tag{7}$$

Equation (7) relates the two ensembles. The major difference between them is that in ϕ-control the system includes both the electrochemical cell (electrodes and electrolyte)

---

† Note that in general the configurational space includes all possible fluctuations of the local charge density, $\sigma(r)$, and the corresponding lateral fluctuations in the ionic subsystem, keeping the average value of σ fixed. σ-control refers to situations where these fluctuations are artificially suppressed.

and the potentiostats. The additional contribution $-q\phi$ added to H^Q in changing from an isolated to a 'global' system is simply the energy required to transfer charge q from the potentiostat to the electrode (see, for example, the discussion in Landau and Lifshitz (1960), Feldman *et al.* (1986b)).

σ plays the same role in the grand canonical ensemble as any other phase variable (e.g. dipolar orientations, ionic positions) imply adding an extra dimension to the configurational space. Thus the equilibrium thermodynamic potential accounts for all possible fluctuations of σ (or q). In the so-called 'thermodynamic' approach charge fluctuations are neglected and σ is replaced by its most probable value (Hill 1956, Huang 1963, Landau and Lifshitz 1960). The corresponding free energy functional ('Landau function', $\tilde{A}^{\Phi}$) in the global system is

$$\tilde{A}^{\Phi}(\phi,\sigma,V)=A^{Q}(\sigma,V)-\sigma\phi. \tag{8}$$

This can be formally derived from (6) by replacing the partition function (7) by the function $W(\sigma)=\exp-\beta S[A^{\Sigma}-\sigma\phi]$, the (un-normalized) probability that the electrode has charge q.

From the known potential of the isolated system $A^Q(\sigma, V)$, the equilibrium value of the charge is determined by the conditions

$$\left.\frac{\partial\tilde{A}^{\Phi}(\phi,\sigma,V)}{\partial\sigma}\right|_{\phi,V=\text{const}}=0 \tag{9}$$

and

$$\left.\frac{\partial^{2}\tilde{A}^{\Phi}(\phi,\sigma,V)}{\partial\sigma^{2}}\right|_{\phi,V=\text{const}}\geqslant 0. \tag{10}$$

In the consistent statistical approach conditions like (9) and (10) are not needed; equilibrium is implicit in the partitioning and the mean equilibrium charge density ($\langle\sigma\rangle$) on an electrode is given by

$$\langle\sigma\rangle=\frac{\int d\sigma\int d\Omega\,\sigma\exp-\beta[H^{Q}(\sigma,\Omega)-\phi\sigma S]}{Z^{\Phi}(\phi,\Omega)}. \tag{11}$$

With equations (9)–(11) we can now analyse system capacitance.

2.2. *General restrictions on* C

First consider ϕ-control. Using (3) and (11) yields

$$C^{\Phi}=\frac{\partial\langle\sigma\rangle}{\partial\phi}=\frac{S}{kT}\langle(\sigma-\langle\sigma\rangle)\rangle^{2}, \tag{12}$$

Here we suppress thermodynamic variables (e.g. T, P or V) which are fixed. This equation is a typical relation for the susceptibility, $\partial X/\partial F$, for systems with Hamiltonians of the forms $H=H_0-XF$ (Baxter 1982) (for applications to capacitance see, e.g. McCombie 1971, Nikitas 1991a, 1992a, Stafiej 1993). It is immediately apparent from (12) that differential capacitance cannot be negative under ϕ-control.

This well-known stability condition, $C^{\Phi} \geqslant 0$, was originally obtained by thermodynamic means (see for example the derivation by Landau and Lifshitz (1960) and its more recent discussion in Attard *et al.* (1992), Partenskii and Jordan (1993)).

Under q-control there is no such universal relationship although some inequalities can be derived for a quite general model presuming in addition that charge density is uniform (σ-control). Consider a parallel-plate capacitor of width L bounding a mixture of particles with multipolar moments (solvent) and charges (ions). The Hamiltonian of such a system can be expressed as

$$H^{\Sigma} = 2\pi\sigma^2 L - 4\pi\sigma \Sigma x_i q_i + H' \tag{13}$$

where the index i represents all charges whether free (ions) or bound (solvent and solute multipoles); q_i and x_i are the charge magnitudes and locations respectively and H' describes interaction between the particles and is independent of σ. Introducing this Hamiltonian in (4) we find:

$$\frac{\partial A^{\Sigma}}{\partial \sigma} = \langle v \rangle = \phi \tag{14}$$

where

$$\begin{aligned} v &= 4\pi(\sigma L - \textstyle\sum q_i x_i) \\ &= 4\pi\left(\sigma L - \left[\int_0^L \rho_{\text{ion}}(x) x \, \mathrm{d}x\right] - P_x^{\text{solvent}}\right). \end{aligned} \tag{15}$$

The integral term is the potential drop due to the distribution of ions in the cell while the last term describes the solvent's contribution, both for general points in the configurational phase space.

The inverse capacitance, the second derivative of the A^{Σ} with respect to σ, is

$$(C^{\Sigma})^{-1} = 4\pi L - \frac{S}{kT}(\langle v^2 \rangle - \langle v \rangle^2). \tag{16}$$

Therefore, for this class of models we obtain the general result

$$\frac{1}{C^{\Sigma}} \leqslant 4\pi L. \tag{17}$$

The last inequality means that the influence of the electrolyte reduces the potential drop between the electrodes which otherwise should be equal to $4\pi\sigma L$, thus reducing $(C^{\Sigma})^{-1}$. However, it puts no restrictions on the sign of C^{Σ}. The earliest attempt to derive general statistical mechanical constraints on C^{Σ} was due to Blum, Lebovitz and Henderson (BLH) who treated a purely ionic system (Blum *et al.* 1980). The original analysis was then extended to dipolar systems (Partenskii and Feldman 1989) correcting some errors in the original study. More recent discussions have been presented in Partenskii and Blum (1990), Attard *et al.* (1992) (ionic systems) and Partenskii and Jordan (1993) (molecular multipoles and ions).

The critical feature of these models is that regions occupied by the electrode and electrolyte are distinctly separate so that their interaction occurs only through the uniform electric field $4\pi\sigma$. Whether more realistic models, treating e.g. solvent polarizability or the penetration of the metal's electronic wavefunctions into the region occupied by electrolyte, exhibit similar inequalities has not been established.

Control of a thermodynamic variable implies that: (a) it can be directly altered by an external source; (b) after the change it remains fixed and measurements of the conjugate property (q in the global system and ϕ in the isolated system) are conducted after all relaxation processes are completed and equilibrium is re-established. Thus, the definition of the differential capacity (3) implies that one variable is controlled and another one adjusts itself in response and is determined at equilibrium. As discussed previously, both q- and ϕ-control are valid experimental procedures. However, this has been questioned by different authors. Thus, Nikitas (1991a) suggested that using q as a control variable is 'improper', although his recent work (Nikitas 1994) indicates a change of mind. Stafiej (1993) suggests it is paradoxical to compute the capacitance of a system under charge control since this constraint insulates a system from charge exchange with its surroundings and 'its capacity in the grand canonical sense vanishes'. It is true that fixing q requires computation via the canonical, not the grand canonical, ensemble. Nevertheless, the constructive definition of (3) (which leads to (12) in the case of ϕ-control) holds and can be used to determine C by changing σ and measuring the corresponding equilibrium ϕ. Computing capacitance under such constraints is no more paradoxical than computing the compressibility of a system by changing its volume and determining the corresponding equilibrium pressure. In addition, Stafiej (1993) asserts that capacitance calculations require explicit accounting of the electrical work required in exchanging charge between system and surroundings. We cannot agree. As long as the focus remains on equilibrium states, the thermodynamic path used in effecting the change of state (altering the control variable) is of no significance; q-control is in no way peculiar.

Quite simply, both types of electrical control are valid and achievable. We stress this point because we believe both provide insight into the relationship between capacitance anomalies and phase transitions at electrified interfaces.

3. Admissible sign of C: Capacitance anomalies at electrode/electrolyte interfaces

The traditional treatment of the Double Layer ('dl') at electrode–electrolyte interfaces is based on its separation into two series contributions: the compact ('Helmholtz') layer and the diffuse ('dif') layer, so that the inverse capacitance is

$$C_{\mathrm{dl}}^{-1} = C_{\mathrm{H}}^{-1} + C_{\mathrm{dif}}^{-1}. \tag{18}$$

The problem of negative capacitance first arose in theoretical studies of C_{H} at metal/solvent interfaces in the absence of ionic adsorption.

3.1. *Origin of the problem—molecular models of the compact layer*

In the last thirty years the study of molecular models of the compact layer at the metal–solvent interface, originated by Mott and Watts-Tobin (Watts-Tobin 1961, Mott and Watts-Tobin 1961), has become a significant topic in theoretical electrochemistry. Molecular or 'dipolar capacitor' models treat the surface layer of water molecules as a lattice of point or finite-size dipoles (for a review see Fawcett (1979), Marshall and Conway (1984)). Many studies have focused on the analysis of the response of such model lattices to electrode charging and comparison with experimental values of the compact layer capacitance, $C_{\mathrm{H}}(\sigma)$, using the technique originally devised by Grahame (1947, 1954). A major stimulus for much of this work has been the 'Cooper–Harrison (CH) catastrophe', the prediction of negative $C_{\mathrm{H}}(\sigma)$ in molecular models of the compact layer.

3.1.1. *General characteristics of a molecular capacitor* (*MC*)

Consider a parallel-plate capacitor with a two-dimensional lattice of point dipoles in the gap (the gap width is d and lattice constant is a). The potential drop across the gap is

$$\phi = F_0 d + \phi_d \tag{19}$$

where

$$\phi_d = -4\pi P_x. \tag{20}$$

Here $F_0 = 4\pi\sigma$ is the external field created by the plates of the capacitor, and the polarization, P_x is $N_s\langle p_x\rangle$ where N_s is the number of dipoles per unit area, a function of lattice geometry and a; $\langle\ldots\rangle$ denotes the statistical average. The inverse capacitance (per unit area) is

$$C^{-1} = \frac{\mathrm{d}\phi}{\mathrm{d}\sigma} = 4\pi(d - 4\pi\chi_\sigma) = 4\pi\left(1 + \frac{4\pi}{d}\chi_\phi\right)^{-1} \tag{21}$$

where

$$\chi_\sigma = N_s\frac{\mathrm{d}\langle p_x\rangle}{\mathrm{d}F_0} = \frac{N_2}{4\pi}\frac{\mathrm{d}\langle p_x\rangle}{\mathrm{d}\sigma}; \quad \chi_\phi = N_s\frac{\mathrm{d}\langle p_x\rangle}{\mathrm{d}(\phi/d)} \tag{22}$$

are the susceptibilities of the dipolar lattice. Further analysis requires determining the functional dependence of $\langle p_x\rangle$ on σ or ϕ.

3.1.2. *Ising-type molecular capacitor in Mean Field Approximation* (*MFA*)

We limit consideration to Ising-type n-state models with dipoles aligned normal to the lattice plane, $p_x \equiv ps_x$; the vector s_x is limited to equally spaced discrete values between 1 and -1. Since the appearance of a CH catastrophe does not depend on the number of states, n, we particularize to $n = 2$.† Each dipole induces a surface charge distribution in the plates of the capacitor which expels its electric field from the interior of the conductor. The local electric field acting on a specific dipole in the gap is

$$F = F_0 + F' + F_d; \tag{23}$$

the three contributions are the external field $F_0 = 4\pi\sigma$, the field induced by the central dipole ($F' = 4p_x\zeta(3)/d^3 \sim 4{\cdot}81p_x/d^3$), and the field F_d due to the remainder of the dipolar lattice and the associated images. This last term has been a subject of considerable controversy. To illustrate the source of the dispute, we investigate F_d in some detail. To compute it we use the MFA; all lattice dipoles but the one at the origin are assigned the mean moment $\langle p_x\rangle$. In this approximation the contribution of the bare lattice (excluding images) to the local field, F_d^0, is

$$F_d^0 = -\langle p_x\rangle\Sigma r_{1i}^{-3} = -\frac{n_L^0 J\langle s_x\rangle}{p}; \tag{24}$$

the sum runs over all lattice sites. Here $J = p^2/a^3$ is the interaction energy between parallel nearest neighbours; $n_L^0 = a^3\Sigma_i r_{1i}^{-3}$ is the effective number of nearest neighbours,

---

† Marshall and Conway (1984) showed that the critical issue is consistency in the description of the electrostatic field in the MC. This can be directly addressed in a simple two-state model. Further modifications such as treating the finite size dipoles, the possibility of their lateral orientation, 'chemical' ordering at $\sigma = 0$, cluster formation and electronic polarizability, while making the molecular models much more realistic (see, for instance, Damaskin and Frumkin (1974), Fawcett (1978, 1979), Macdonald (1954, 1987), Macdonald and Barlow (1962), Parsons (1975, 1980), Parsons and Reeves (1985), Schmickler (1983), Guidelli (1990)), have no qualitative influence on the basic CH problem.

~ 9 and ~ 11 for square and hexagonal lattices respectively (Topping 1927). Similarly the electric field of a screened lattice (where the effect of images on the effective number of nearest neighbours is treated) can be represented as

$$F_d = -\frac{n_L J\langle s_x\rangle}{p} \tag{25}$$

For the two-state model the contribution F' is independent of the dipolar state and can be ignored (for both orientations $s_x^2 = 1$).†

In this approximation the electrostatic energy per dipole is $-p(F_{0x}+F_{dx})s_x$ and the average polarization is determined by the equation (Watts-Tobin 1961, Bockris and Reddy 1972)

$$\langle s_x\rangle = \tanh E(F_0, \langle s_x\rangle) \tag{26}$$

with $E = (pF_0/kT) - Jn_L\langle s_x\rangle/kT$. Using equation (22) yields

$$\chi_\sigma = \frac{p^2 N_s}{kT\cosh^2(E) + Jn_L} \tag{27}$$

where E depends on F_0 both explicitly and through $\langle s_x\rangle$. $\chi_\sigma(F_0)$ is symmetric; it reaches a maximum when $F_0 = 0$ and approaches 0 as $F_0 \to \infty$.

Following CH (Cooper and Harrison 1975) we now consider the possibility of C becoming negative. From (21) this requires that $4\pi\chi_\sigma > d$ which, from (27), is most likely when $E \to 0$, i.e. when F_0 (or σ) is small. Here we find

$$\chi_\sigma = \frac{p^2 N_s}{kT + Jn_L}; \tag{28}$$

$$C^{-1}(\sigma) = 4\pi\left(d - 4\pi\frac{p^2 N_s}{kT + Jn_L}\right). \tag{29}$$

3.1.3. *Effective number of nearest neighbours and the CH catastrophe*

From (29) we see that C becomes negative when

$$n_L < \frac{4\pi a^3 N_s}{d} - \frac{kT}{J}. \tag{30}$$

This is the result known as the 'CH catastrophe'. For a hexagonal lattice $N_s^{\text{hex}} = 2/(3^{1/2}a^2)$ and for water in the compact layer at ~ 300 K, $kT/J \sim \frac{1}{2}$ (Fawcett 1979). Thus we obtain

$$n_L^{\text{hex}} < \frac{8\pi a}{3^{1/2}d} - \frac{1}{2}. \tag{31}$$

Letting $a = d$ (reasonable for this description of the compact layer) the 'catastrophe' condition for this MC is

$$n_L^{\text{hex}} < 14{\cdot}2. \tag{32}$$

---

† It cannot be neglected even for $n = 2$ in electrostrictive molecular models (Feldman and Partenskii 1991) where d is variable. It also cannot be omitted in models with $n > 2$ because s_x^2 then depends on the dipolar state. Consider for illustration the continuous (infinite spin) model (Styller 1995). Then the susceptibility at low F_0 equals $\chi = p^2/(\alpha(p)kT + n_L J)$ where $\alpha(p)$ accounts for the contribution F' in the local field (23). If F' is neglected, then $\alpha = \alpha(0) = 3$. With this contribution included α varies between $\alpha(0) = 3$ and $\alpha(\infty) = 1$. For all reasonable values of kT, a and p the effect of F' is not important.

CH suggested that due to the screening of the dipolar field (the effect of images) n_L^{hex} is actually substantially smaller, < 11. In this case the inequality (32) is readily satisfied and at small electrode charges the capacitance becomes negative. The central issue is determining n_L, the effective number of nearest neighbours. Some authors treat this as an adjustable parameter, while others employ various models and approximations (see Fawcett (1979), Guidelli (1990) for reviews).

Before proceeding several points must be stressed. First of all the potential drop, ϕ, is determined as a potential difference between planes $x = 0$ and $x = d$. This requires that both surfaces are equipotential, i.e. they are the surfaces of the ideal conductors. Consequently, any distribution of charge in the compact layer induces charges (or a surface charge distribution) in these planes. Therefore, the only proper way to treat F_d (or n_L) is to account for all 'images' of the dipolar lattice in both plates of the capacitor. Otherwise, the calculation of the electric field will not be consistent with the definition of the potential drop (19), which can give rise to serious ambiguities. Models of the compact layer, no matter how detailed, e.g. accounting for water polarizability, the possible presence of second and further absorbed layers, the finite size of the water dipoles (e.g. Guidelli (1990)), cannot clarify the issue of CH catastrophe unless image effects are treated consistently.†

Another source of difficulty is that real MCs are of finite lateral area. However, the problem of a dipolar lattice between finite conductive plates has not been solved (a treatment of the local field of a dipolar lattice in a finite spherical capacitor has been outlined (Partenskii and Feldman 1989)). Thus theoretical analyses typically are limited to infinite MCs. Corresponding infinite electrostatic sums depend on the order of summation which requires very careful consideration.

3.1.4. *Summation problem in the local field computation*

To compute n_L, two distinct limiting approximations have been employed (Partenskii and Feldman 1989). The first is the co-called 'chain' (c-) approach. Here each dipole p_{ix} in the parallel-plate capacitor is substituted by an infinite dipolar chain normal to the x-plane, consisting of the original dipole and its infinite set of images. Defining $f_{ix}(\rho)$ as the x-component of the field of such a chain in the plane $x = 0$ at a distance ρ from site i, the dipolar field is

$$F^{\text{ch}} = \sum_i f_{ix} \tag{33}$$

For $\rho > d f_{ix}$ decays asymptotically as $e^{-2\pi\rho/d}$ (Partenskii and Feldman 1989). Instead of a $1/\rho^3$ contribution of the dipoles as in the bare (unscreened) lattice, the screening arising in the c-picture leads to sharp exponential decay effectively decreasing n_L. Direct calculations indicate that $n_{L,\text{ch}}^{\text{hex}} \sim 1{\cdot}09$ and $n_{L,\text{ch}}^{\text{sq}} \sim 0{\cdot}79$ for $d = a$ (as compared to the bare lattice values of ~ 11 and ~ 9 respectively). The third neighbour's contribution is practically negligible. Comparing with (32) we see that the dramatic 10-fold decrease in the effective number of nearest neighbours inevitably leads to the CH

---

† Both plates of the molecular capacitor are made of an ideal conductor. This can fairly imitate reality only in the limit of high ionic concentration in the electrolyte. Under normal conditions the 'ionic plate' of the surface capacitor is diffusive and extended in the x-direction. To improve the model one might want to account for this effect in calculating the electrostatic field. Nevertheless, whatever model of the 'electrolyte plate' is used, image effects have to be treated consistently within the framework of the model to obtain an unambiguous answer to the question of the existence of $C < 0$.

catastrophe. This agrees with Schmickler's suggestion (Schmickler 1983) that for a lattice with sufficiently large spacing a, the dipoles are practically independent and the CH catastrophe is unavoidable.

This intuitive picture collapses if the co-called 'plane' (p-) approach is used. Here images are represented by infinite dipolar lattices, and the fields of the lattices are summed up. It should be stressed that for any finite lattice array the fields calculated by either the c- or p-summation methods must be and are equivalent. To illustrate the difference between these approaches for the infinite lattice surround the central dipole by a circle of radius $R \gg a$. Because the chain fields converge rapidly, the internal contribution to F_d from the dipoles occupying the area $\rho \leqslant R$ is equal to F_d^{ch},

$$F_n^{\text{in}} = F_{\text{d}}^{\text{ch}}. \tag{34}$$

In the chain picture the contribution from $\rho > R$ naturally vanishes. To determine this outer contribution, F_d^{out}, in the p-approach, note that at distances large compared to a the lattice is effectively continuous and may be treated as a uniform dipolar layer with polarization $P_x = N_s\langle p_x\rangle$. Therefore in the p-approach the field F_d^{out} arises from a stack of infinite dipolar layers (the original one and its infinite set of images) with coordinates $\rho > R$, $x_i = id$ $(i = 0, \pm 1, \pm 2, \ldots)$, and as long as $R \gg (d, a)$ (Partenskii and Feldman 1989)

$$F_d^{\text{out}} = \frac{-4\pi P_x}{d}. \tag{35}$$

The total field is

$$\begin{aligned} F_d^{\text{pl}} &= F^{\text{in}} + F^{\text{out}} \\ &= F^{\text{ch}} - \frac{4\pi P_x}{d}, \end{aligned} \tag{36}$$

which, with (25), yields a relation between the effective number of nearest neighbours calculated on the basis of the c- and p-approaches:

$$n_L^{\text{pl}} = n_L^{\text{ch}} + \frac{4\pi N_s a^3}{d}. \tag{37}$$

Comparison with (30) now demonstrates that in the p-approach the capacitance is always positive while the c-approach leads to the CH 'catastrophe'. Thus the appearance of $C < 0$ is intimately related to the way in which calculation is done. The following arguments demonstrate that only the p-approach is consistent with equations (19)–(22).

Consider ϕ. By construction the field of each infinite chain leads to a potential drop of exactly zero. Regardless of the number of chains, even in the infinite limit $\phi_d^{\text{ch}} = 0$. On the other hand

$$\phi_d^{\text{ch}} \equiv \int_{-d/2}^{d/2} F_{dx}^{\text{ch}}\, dx.$$

Performing the same integration on F_d^{pl}, equation (36), it follows that $\phi_d^{\text{pl}} = -4\pi P_x$. Therefore, the total potential (19), is

$$\phi^{\text{ch}} = 4\pi\sigma d \tag{38}$$

$$\phi^{\text{pl}} = 4\pi\sigma d - 4\pi P_x. \tag{39}$$

In other words, only the p-approach agrees with (19) and (20). Does it mean that the c-approach is always wrong? Not at all. It simply refers to a very different physical situation. Consider a finite capacitor with disc plates of radius R confining a dipolar lattice of radius R'. Initially they are equal. Suppose that both radii increase at fixed N_s, and approach infinity. Consider two cases: (a) $R'/R = 1$ and (b) $R'/R = O(1/R')$. In both cases the mean density of dipolar moment relative to lattice area is $P_x^{\text{lat}} = N_s\langle p_x\rangle$. But when averaged over the area of the plates $P_x^{\text{pl}} = P_x^{\text{lat}} = N_s\langle p_x\rangle$ in (a) and $P_x^{\text{pl}} \sim R'^2/R^2 \to 0$ in case (b). It is now clear that the p-approach is related to (a), when both lattice and plates have the same 'strength', while the c-approach corresponds to (b) where the lattice, being large (even infinitely large), has vanishingly small strength compared to the plates and P_x is effectively zero. In this sense both approaches agree with (19) but in c-summation the average polarization is actually zero. Both limiting cases can be reproduced in finite system calculations. The p-approach describes a lattice occupying the whole area between the plates while the c-approach describes a lattice 'island' large compared to a and d but vanishingly small if compared with the area of the plate.

The local electric field in the MC, equation (23), can now be represented as

$$\begin{aligned} F &= 4\pi(\sigma-\sigma_d)+F^{\text{ch}} \\ &= \frac{\phi}{d}+F^{\text{ch}} \end{aligned} \tag{40}$$

with $\sigma_d = P_x/d$. This expression, with slight modifications (e.g. sometimes neglecting F_{ch} which, as already seen, is justified, especially for $a > d$), has been used by a number of authors (Watts-Tobin 1961, Mott and Watts-Tobin 1961, Levine *et al.* 1969, Marshall and Conway 1984, 1987, 1992). This approach has been criticized by Nikitas (1987). In a gedanken experiment he considered a process in which dipoles, previously separated by large distances so that interaction can be neglected, approach each other. Nikitas suggests that 'the term $4\pi\sigma_d$ begins to contribute when the dipoles approach each other...Therefore we have to conclude that the term $4\pi\sigma_d$ is related to the dipole–dipole interaction energy only'. On the basis of such arguments he suggests that σ_d in (40) should be substituted by $\sigma_d/2$. As we have seen, bringing dipoles together only contributes to the appearance of F^{ch}; the uniform contribution being an intensive property (Marshall and Conway 1987), cannot be changed in this process. Assume, for instance, a 'diluted' dipolar lattice (the first stage of the process (Nikitas 1987)). Then we take N dipoles and start bringing them closer together keeping all other dipoles fixed. As is clear from the previous discussion, this process does not influence the contribution $4\pi\sigma_d$ (F^{out} is fixed by the whole bulk of the lattice); only the local dipole–dipole interaction is affected.

Where does the additional uniform contribution come from? How does it happen that with a fixed charge density σ on the plates of a capacitor the local field is determined by the smaller density $\sigma-\sigma_d$? Where does part of the charge density disappear? To answer this question consider another gedanken experiment based on the discussion of MacDonald (1954). Suppose at the outset the dipolar capacitor is under the fixed voltage $\phi = 0$. The lattice induces a *non-uniform* charge distribution $\sigma(y,z)$ in the plates. The average charge density can be defined as $\sigma^{\text{av}} = N_s\int\sigma(y,z)$ where the integral is taken over the unit cell. On the other hand it can equally well be identified as the density 'screening' the dipolar lattice smeared over the plane. It means that $\sigma^{\text{av}} = -P_x/d = \sigma_d$. Now, disconnect the MC from the potentiostat and charge its plates to an overall density σ. To do this requires increasing the average density by $\sigma-\sigma_d$. Now the picture is clear! The charge of the electrode consists of two parts: non-uniform, with mean density σ_d, responsible for the term F^{ch} in the local electric field, and a uniform contribution $\sigma-\sigma_d$ responsible for the potential drop ϕ, equation (19), and for the major part of the local field (if $a \gtrsim d$). Analysis of the finite spherical MC (Partenskii and Feldman 1989) yields similar results. Note that retrospective justification for the use of the MFA is given by the fact that the nearest neighbours' contribution is small compared to the mean field term.

It is now clear that CH catastrophe arises as a result of inconsistency in the treatment of the electric field and the potential drop in the molecular capacitor. Does it prove that the appearance of $C < 0$ is physically impossible or unrealistic (Cooper and Harrison 1975, Parsons and Reeves 1985, Marshall and Conway 1984, Borkowska and Stafiej 1985, Macdonald 1987)? In the following sections we show that the answer to this question is no and that it gives rise to a number of exciting problems and phenomena.

3.2. *Problem of* C < 0 *beyond the molecular models: Ionic and electronic contributions to the double layer capacitance and 'relaxing gap capacitor' models*

3.2.1. *Negative capacitance in the theory of the diffuse layer*

The theory of diffuse layer capacitance C_{dif} is traditionally based on local statistical models where ionic charge density is a local function of potential. For such models C_{dif} can never become negative (Partenskii *et al.* 1987). The Gouy–Chapman (GC) model (Bockris and Reddy 1972) for a 1:1 electrolyte is illustrative:

$$C_{\mathrm{dif}}^{\mathrm{GC}} = a(b+\sigma^2)^{1/2} \tag{41}$$

with $a = q/2kT$, $b = 2\theta kT\varepsilon/\pi$, where θ is the ionic concentration in the bulk electrolyte and ε is the bulk dielectric constant. Another feature of GC-type models is that $\rho_i(r)$ is always a monotonous function of the coordinate.

Very different results are found in studies that go beyond the local statistical approach. Early analyses of 'primitive' models (uniform continuum solvent) of the electrical double layer at charged surfaces using either the hypernetted chain approximation (HNCA) at high electrode density (Henderson *et al.* 1979, Carnie *et al.* 1981) or the mean spherical approximation (MSA) at high ionic concentration (Blum 1977) indicated that C_{dif} might possibly become negative. These results were attributed to noticeable oscillations found in the computed ionic density profiles, observations which were confirmed shortly thereafter by Monte Carlo simulation (Torrie and Valleau 1982). Rather surprisingly, this work did not stimulate further analysis of the possibility that $C < 0$ and its possible consequences, probably because of the apparent derivation of a general result that seemed to demonstrate the impossibility of negative differential capacitance for the primitive model double layer under σ-control (Blum *et al.* 1980). Since negative C is initially counterintuitive, the BLH results apparently demonstrating its impossibility were readily accepted; they were used later (Schmickler and Henderson 1989) to veto any appearance of $C^{\Sigma} < 0$ even for double layer computations conducted far beyond the primitive model of BLH (Kim *et al.* 1989).

Later studies (Partenskii and Feldman 1989, Partenskii and Blum 1990, Attard *et al.* 1992, Partenskii and Jordan 1993) (see also discussion in §2.2) revealed subtle errors in the original BLH analysis. A correct treatment leads to equation (16) with no limitations on the sign of C_{dif} calculated with fixed σ. Recent research provides several examples that negative $\partial\phi/\partial\sigma$ can occur in limited σ domains. Examples include a Monte Carlo simulation of the electrical double layer in a primitive model of 1:2 electrolytes (Torrie 1992) and an integral equation analysis of the influence of ionic polarizability on the properties of the double layer (Wei *et al.* 1993), which indicates that the appearance of a negative slope in $\phi_{\mathrm{dl}}(\sigma)$ plots reflects the 'true behaviour of plausible theoretical models'.

3.2.2. *Metal electrons in double layer theory and the negative* C *problem*

The problem of the allowed sign of the differential capacitance becomes even more apparent in the microscopic approach which considers the metal electrons' contributions to the properties of the double layer. To begin we summarize some important features. We introduce centroids of charge located at the electrode (electrons, e) and in the electrolyte (ions, i) characterizing the effective positions of the corresponding 'plates' of the interfacial capacitor and determined (see e.g. Lang (1973)) as centres of gravity of induced charge density profiles, $\delta n^{\sigma}_{\mathrm{i,e}}(x)$,

$$x_{\mathrm{i,e}} = \frac{\int_{-\infty}^{+\infty} \delta n^{\sigma}_{\mathrm{i,e}}(x) x \, dx}{\sigma_{\mathrm{i,e}}} \tag{42}$$

where $\sigma_{\mathrm{e}} = -\sigma_{\mathrm{i}} = \sigma$; $x_{\mathrm{e}} = 0$ corresponds to the electrode surface location in the 'perfect conductor' approximation.

Until the early 1980s metals were usually described in double layer theories using 'sharp boundary' models (SBM). The simplest (and most popular) is the 'perfect conductor model' of classical electrostatics. Near the plane surface of such a conductor the potential changes linearly with distance and attains fixed values crossing the boundaries. Modification of this model was generally based on a non-self-consistent Thomas–Fermi type approach originated by Rice (Rice 1928, Macdonald 1964, Tsong and Muller 1969, Macdonald *et al.* 1980). Its applications to double layer analysis gave rise to some ambiguities including the co-called 'Rice paradox' (Kornyshev and Vorotyntsev 1981, Kornyshev 1985).

The transition to the modern microscopic theory of the double layer was stimulated by the development of the self-consistent theory of metal surface electron properties and especially the studies of surface electronic screening of the electrostatic field (Lang 1973, 1983, Partenskii 1979, Feldman *et al.* 1986b, Kornyshev 1989). Three results of this approach are important for our purposes.

1. Near $\sigma = 0$, x_{e} is positive, in the range of 0·5 to 1·2 Å for different metals.
2. The 'electron plate' moves with charging, approaching the metal interior for positive values of σ and moving outside it if $\sigma < 0$.
3. Depending on σ, the tail of the metal surface electron charge distribution, which projects into the compact layer, influences the equilibrium location and polarization of solvent molecules in the compact layer.†

The external location of the 'electron plate' at $\sigma = 0$ ($x_{\mathrm{e}}(0) > 0$) caused by the screening of the external field by the electron 'tail' outside the metal naturally resolves the problems raised by the application of SBM, including the Rice paradox. The dependence of the surface electron distribution on charge and its influence on the properties of solvents adds new sophisticated features to the characteristics of the

---

† It also affects the location and partial charge of ions in the presence of specific adsorption.

compact layer lacking in previous solvent-oriented models. The study of these phenomena originated by the pioneering work of Badiali *et al.* (1983a–c) represents a new era in physical electrochemistry and has been carefully reviewed (Schmickler and Henderson 1986, Feldman *et al.* 1986b, Kornyshev 1989, Amokrane and Badiali 1993).

Negative C_H was first given serious consideration in this context in Partenskii and Vorobjev (1984). This analysis addressed the problem of abnormally high C in contacts of some metals (Au, Pt) with solid electrolyte–silver ion conductors (e.g. Ag_4RbI_5, α-AgCl, AgBr). According to the traditional view the total C_{dl} could not exceed the 'compact' contribution:

$$C_{dl} \leqslant C_H \text{ (conventional condition).} \tag{43}$$

In the SBM approach (Macdonald *et al.* 1980) C_H is estimated as

$$4\pi C_H = \frac{\varepsilon_H}{x_H - x_e}. \tag{44}$$

Here ε_H is a compact layer permittivity and x_H is the effective width of the compact ('Stern') layer. For the systems considered $\varepsilon_H \sim 3$, $x_H \sim 1{\cdot}26$ Å (the ionic radius for Ag^+) (Macdonald *et al.* 1980). The estimates of C_H based on these data lead to $C \lesssim 20\ \mu F\ cm^{-2}$, a result more than an order of magnitude less than the experimental values (Raleigh 1976, Remez and Chebotin 1984). Early attempts at resolving the problem presumed either effectively 'shortening' the compact layer by electron tunnelling from electrode to Ag^+ ions (Macdonald *et al.* 1980) or introducing ionic profiles with 'over-screening' either due to ionic density oscillations (Dogonadze and Chizmadzhev 1964) or to 'superequivalent' adsorption (Raleigh 1976).

Displacement of the 'electronic plate' due to charging naturally resolves the problem. C_H is then represented as

$$4\pi C_H = \frac{\varepsilon_H}{x_H - x_e - \sigma(dx_e/d\sigma)} \tag{45}$$

$x_e(\sigma)$ has been calculated for different models of the compact layer (Partenskii *et al.* 1981, Partenskii and Vorobjev 1984). In all cases C_H reaches a vertical asymptote and becomes negative at moderate cathodic charges corresponding to the condition $x_e + \sigma(dx_e/d\sigma) \geqslant x_H$. It is important that when C_H crosses the asymptote, the capacitor gap is finite and positive, $x_H - x_e > 0$, in clear contradiction with the conventional view, (44). It also shows that (43) does not hold, and that the total C_{dl} can exceed C_H, results resolving the above-mentioned contradictions.

On the basis of these findings calculations of Feldman *et al.* (1985) were reexamined (Feldman *et al.* 1986b, 1987) and it was found that the narrow domains with $C_H < 0$ were originally overlooked since an overly large σ step was chosen. The possibility of $C_H < 0$ also follows from self-consistent quantum mechanical calculations (Halley *et al.* 1985, Halley and Price 1987). In a study by Badiali *et al.* (1983a) the anomalous domain was missed because an overly large gap between the electrode and the solvent molecules was introduced and its dependence on σ was ignored. In other instances the negative C branch was suppressed as unphysical (Schmickler and Henderson 1984, 1986) (see also Kim *et al.* (1989), Schmickler and Henderson (1989) for discussion). The clear illustration of the appearance and admissibility of $C_{dl} < 0$ when the charge density σ is fixed is provided by the 'relaxing-gap capacitor' models considered below.

3.3. *Electromechanical models of charge-induced relaxation in the double layer*

3.3.1. *The double layer as a relaxing-gap capacitor*

Quite generally the potential drop across the double layer can be represented as

$$\phi = 4\pi\sigma[x_i(\sigma) - x_e(\sigma)] - 4\pi P_x \tag{46}$$

where P_x is the overall polarization of the solvent across the interface (including the contribution of induced and permanent dipole moments). Then, using (3) we find

$$(4\pi C)^{-1} = l(\sigma) - \sigma\frac{\mathrm{d}l}{\mathrm{d}\sigma} - \frac{\mathrm{d}P_x}{\mathrm{d}\sigma} \tag{47}$$

where $l(\sigma) = x_i(\sigma) - x_e(\sigma)$ is the effective gap of the interfacial capacitor. From these equations the double layer is described as a capacitor with a relaxing gap $l(\sigma)$. The effects associated with the relaxation of the effective gap are well-known. In particular, they determine the $C(\sigma)$ behaviour in metal–semiconductor contacts and in p–n junctions (Sze 1969) and in the theory of the diffuse layer at metal–electrolyte boundaries (Bockris and Reddy 1972). As mentioned previously, the use of GC-type models in the vast majority of studies suppresses the possibility of $C < 0$.

3.3.2. *Electromechanical models. Admissibility of* C < 0 *under* σ*-control*

Consider an imaginary attempt to alter the equilibrium electron and ion density profiles causing the displacement of x_e and x_i from their equilibrium positions. The corresponding increase in energy (e.g. in the value of density functional used to describe electron–solvent systems (Feldman *et al.* 1985, Halley *et al.* 1985)) can be expressed through the effective restoring force opposing the variation of l from its equilibrium value. In turn, the restoring force can be expressed through some effective elastic constant. This is analogous to an 'elastic capacitor'—a system with some (generally, anharmonic) coupling between the 'plates' and a gap varying with charging (Partenskii and Kim 1986, Feldman *et al.* 1986a, Partenskii *et al.* 1987). A few comments are necessary.

1. The 'elastic capacitor' is designed to illustrate and explain capacity anomalies that appear in microscopic simulation in terms of mechanical or thermodynamic equilibrium. The advantage of these models is their exact solvability while in microscopic calculations there is always room for doubts (and as seen, doubt often prevailed over the computational evidence).
2. The 'elasticity' in these models can be related to very different interactions in microscopic prototypes. It includes classical and non-classical (exchange) electrostatic forces in ion–electron systems, entropic ('lattice gas') effects, Lennard-Jones and van der Waals-type interactions between solvent molecules and metal, etc. In the same way, 'interfacial relaxation' involves displacement of the electronic plate, shift in the equilibrium position of adsorbed molecules, redistribution of ions and solvent molecules in electrolyte, variation of the area of interface, etc. Thus, the use of macroscopic terminology should not create the illusion that models are unrelated to a real interface (in the same way as a macroscopic elastic constant can be expressed through the microscopic properties of matter).
3. Electromechanical models are not designed to reproduce all features of microscopic behaviour. For instance, small negative charging causes expansion of the surface 'gap' pushing away the monolayer of water molecules adjacent to

the electrode (Feldman *et al.* 1985, Halley *et al.* 1985). Also, at large anodic charges the gap increases because x_e continues moving inside the metal (approaching the fixed slope determined by the sum rule of Theophylou (1972)) while the 'ionic plate' slows down due to interaction of waters with the metal ions' hard cores, and, possibly, due to 'lattice saturation' effects in the diffuse layer. These models were invented to illustrate phenomena typical of existing microscopic models in certain charge ranges, and to focus attention on their possible appearance in a wide class of models.

Consider an isolated capacitor the plates of which can move with charging ('relaxing capacitor' (RC)). We write its energy in the form

$$E(\sigma, l) = E_0(l) + 2\pi\sigma^2 l, \quad l > 0 \tag{48}$$

where the first term is the coupling energy, and the second the electrostatic energy. The conditions for stable equilibrium of an isolated RC are

$$\frac{\partial E}{\partial l} = \frac{dE_0}{dl} + 2\pi\sigma^2 = 0 \tag{49}$$

$$\frac{\partial^2 E}{\partial l^2} = \frac{d^2 E_0}{dl^2} > 0. \tag{50}$$

The potential drop between the plates is given by

$$\phi = 4\pi\sigma l(\sigma) \tag{51}$$

where $l(\sigma)$ satisfies equations (49) and (50). The inverse differential capacitance is (Partenskii *et al.* 1987)

$$(4\pi C)^{-1} = l(\sigma) - \frac{4\pi\sigma^2}{d^2E_0/dl^2}. \tag{52}$$

Suppose now that charging causes gap contraction such that $l \to 0$ as σ approaches a finite value $\bar{\sigma}$. This condition is sufficient for C to become negative in some charge range, because it is negative at $\bar{\sigma}$

$$(4\pi C)^{-1} = -4\pi\bar{\sigma}^2 / \frac{d^2E_0}{dl^2} < 0.$$

While sufficient, this condition may not be necessary.

Consider the 'elastic capacitor (EC)' (Feldman *et al.* 1986a) with

$$E_0 = \frac{k}{2}(l - l_0)^2 \tag{53}$$

designed to illustrate the origin of $C < 0$ in a density-functional model of metal/solid electrolyte interface (Partenskii and Vorobjev 1984). In dimensionless units

$$w = \frac{E}{kl_0^2}, \quad w_0 = \frac{E_0}{kl_0^2}, \quad z = \frac{l}{l_0}, \quad v = \frac{\phi}{(4\pi k l_0^3)^{1/2}}, \quad s = \left(\frac{4\pi}{kl_0}\right)^{1/2}\sigma \tag{54}$$

and using the equilibrium conditions (49) and (50), we find

$$w_0 = \frac{(1-z)^2}{2}, \quad z(s) = 1 - \frac{s^2}{2}; \quad \phi(s) = s - \frac{s^3}{2}; \quad C^{-1} = \frac{dv}{ds} = 1 - \tfrac{3}{2}s^2. \tag{55}$$

It follows that $C^{-1} \leqslant 0$ for $|s| > s_0 = (2/3)^{1/2}$. At the same time $\partial^2 w/\partial l^2 = 1 > 0$ which means that the system is stable for any charge $|s| \leqslant 2^{1/2}$ which corresponds to $l \geqslant 0$. In other words, a negative C branch exists in the range $2^{1/2} \geqslant s \geqslant (3/2)^{1/2}$.

We can now show that the condition that $l \to 0$ as $\sigma \to \bar{\sigma}$ is not necessary. The system can be prevented from direct contact between the plates by putting a 'block' in the region $0 < z_{st} < \frac{2}{3}$ so that $z = 0$ ($l = 0$) is not accessible. Nevertheless, the negative C branch still exists.

We note here that the first elastic capacitor model was constructed by Crowley (1973) to account for electrical breakdown of bimolecular lipid membranes. The coupling energy for his model can be cast in the form

$$w_0^{\text{Crowley}} = z \ln z - z + 1 \tag{56}$$

if kz_0^2 in (54) is substituted by Yz_0 where Y is Young's modulus. Crowley did not discuss the differential capacitance of his model membrane. But it can easily be shown that in his model C becomes negative for $|s| > 1$ and $z < \exp(-0{\cdot}5) \sim 0{\cdot}61$.

The 'anomaly' appears naturally for various types of coupling, involving different kinds of anharmonic behaviour (Feldman *et al.* 1986b, 1987, Partenskii *et al.* 1987, Partenskii and Jordan 1993). To interpret the results of microscopic modelling of the metal–solvent interface (Feldman *et al.* 1985, 1987) anharmonic models with bistability are useful. Bistability arises, for example, when there is a cubic term in the dimensionless energy w_0

$$w_0 = \frac{(z-1)^2}{2} + \frac{a(z-1)^3}{3} \tag{57}$$

for $a > 0{\cdot}5$. The RC loses stability at $|s_{cr}| = (2a)^{-1/2}$ and the relaxing plate jumps to a new position defined by the 'block'. This peculiarity is useful for discussing the interrelation of instabilities in isolated and open systems. Figure 1 illustrates the state diagram for the anharmonic relaxing capacitor. It shows that the 'softening' of the bond ($a > 0$) leading to bistability also facilitates the appearance of $C < 0$ ($|s_0|$ decreases) although the negative branch exists over a wide range of a including $a < 0$.

Figures 2(*a*) and 2(*b*) compare the extremals, $v(s)$, and the capacitance, $C(s)$, for a simple EC, (55), and an EC with an additional short-range repulsion between the plates giving rise to 'bistable' extremals (see discussion §4.2.1). Overall, negative capacity, typically appearing in microscopic 'electronic' models of the compact layer and in some non-local statistical models of the diffuse layer, also arises in a variety of electromechanical models. Being exactly soluble, these latter prove that in isolated systems C can be negative for stable systems under fixed σ conditions.

3.3.3. *Models coupling different types of relaxation*

3.3.3.1. *Molecular capacitor with the relaxing gap.* As shown in §3.1, consistent calculation of the local field in the MC does not allow C to become negative. On the other hand, divergences and negative values of C are typical for the relaxing gap capacitor. What happens if these two models are combined? To investigate this, an elastic capacitor model was combined with an Ising-type molecular capacitor (Feldman and Partenskii 1991), a unification already proposed in Watts-Tobin's paper (Watts-Tobin 1961) introducing the molecular models. He noticed that possible electrostriction of the water layer can also affect the double layer capacitance. After more than thirty years of research all that needs to be added is noting that effective gap relaxation is not so much a result of compressibility, but a combined effect of the shift in water's

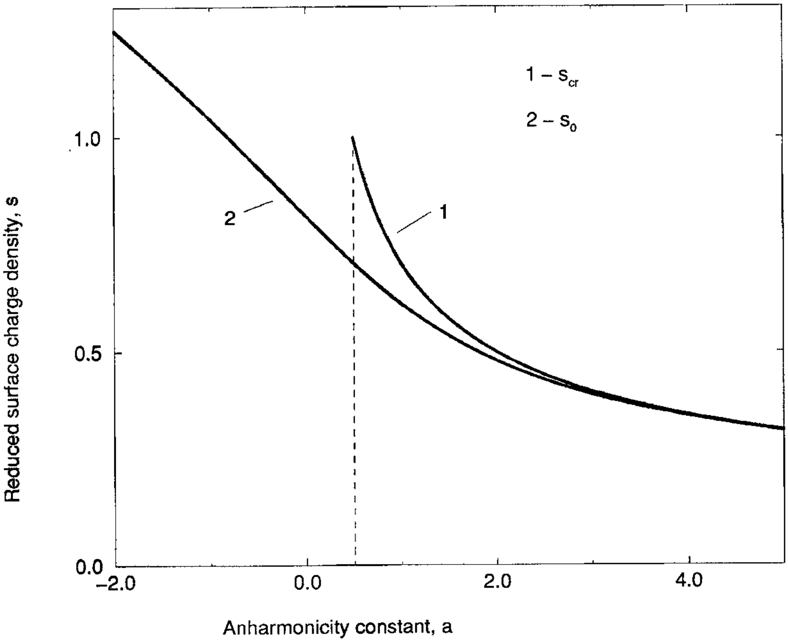

Figure 1. The influence of the anharmonic contribution to the interplate coupling w_0, equation (57), on the stability and negative capacitance in the elastic capacitor. Curve 1, s_{cr}, indicates the locus of points where the RC is physically unstable and undergoes collapse from a finite z to $z = 0$; this curve terminates at the point where the onset of this instability requires zero interplate separation. Curve 2, s_0, indicates the locus of points where $C^{-1} = 0$, i.e. the conditions for the appearance of a negative C branch. As is apparent, increasing anharmonicity facilitates the appearance of a negative C branch (it requires smaller s).

equilibrium position at the electrode and the displacement of the electronic 'plate' x_e (Price and Halley 1983, 1995, Halley *et al.* 1985, Feldman *et al.* 1985, Halley and Price 1987, Feldman *et al.* 1987).

Neglecting F_x^{ch} in (40), which is justified for $a > d$ (§3.1), the Hamiltonian (per unit area) can be represented as (Partenskii and Feldman 1989)

$$H^{\Sigma}(\sigma, l) = 2\pi\sigma^2 l - 4\pi\sigma P_x + 2\pi\frac{P_x^2}{l} + \frac{k}{2}(l-l_0)^2 + V_{\text{rep}}(l) - 2\zeta(3) n_s \frac{p^2}{l^3}.$$

The last contribution is the interaction of dipoles with their images and V_{rep} is the short-range repulsion between the plates preventing them from collapsing. The corresponding free energy functional was minimized both with respect to the polarization $\langle s_x \rangle$ and the gap width l for constant σ and T, with the result that capacitance divergence and a negative branch appear at all temperatures; increasing T shifts the critical point σ_0 toward lower charge.

3.3.3.2. *Combined effect of electronic and GC-type ionic relaxation.* As mentioned before, with electronic contributions taken into consideration C_{H} can become negative for moderate ranges of charge both for metal–solvent and metal–solid electrolyte interfaces. At the same time the diffuse layer capacitance treated in GC-type local statistical models is always positive (§3.2.1). The natural question is whether the

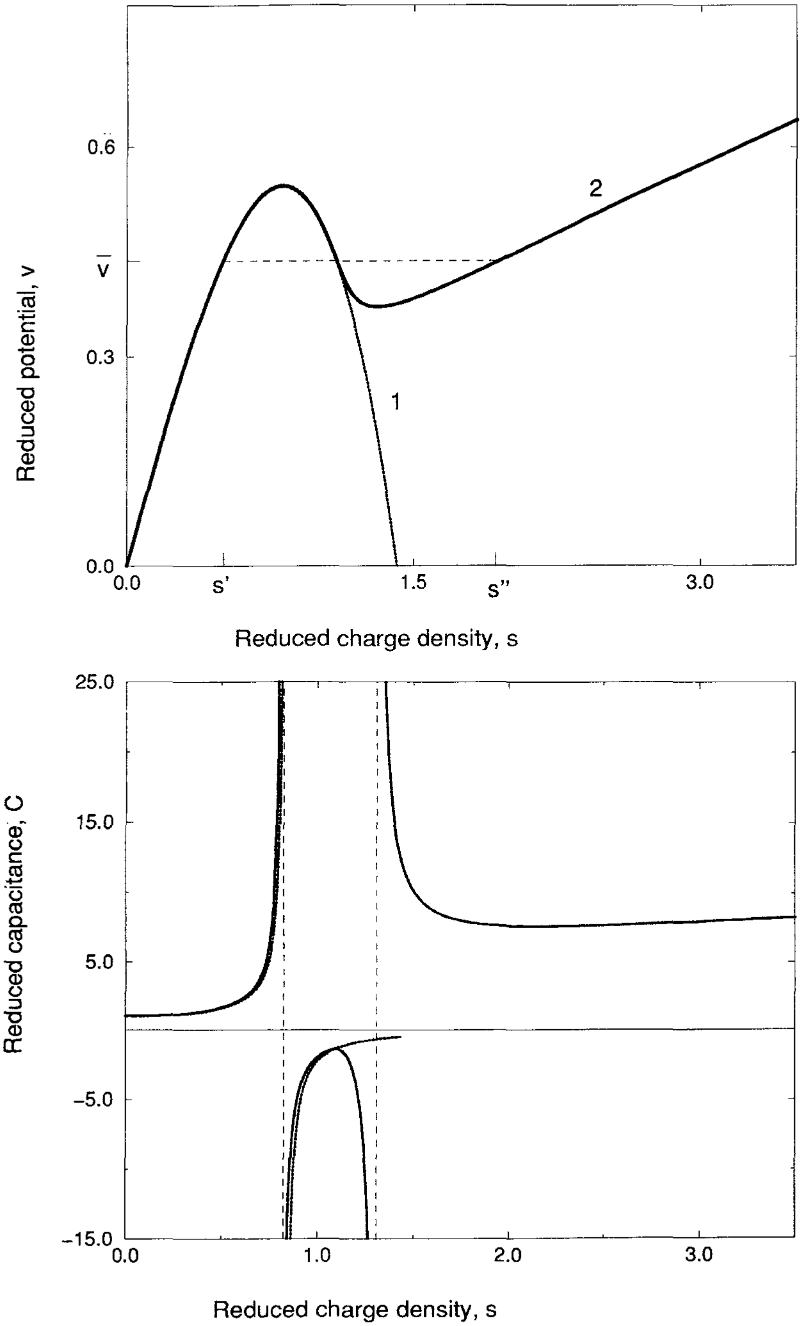

Figure 2. Comparison of reduced potential extremals, $v(s)$, and the corresponding reduced capacitance, $C(s)$, for two elastic capacitor systems under q-control as functions of the reduced surface charge density, s. Case 1 (dotted lines) corresponds to the simple EC, where no constraints oppose the tendency of the capacitor plates to attract one another, and the plate separation can approach 0. Under ϕ-control such systems are always metastable; a fluctuation can cause a transition to the unstable higher s region. Under q-control both capacitance domains are accessible. Case 2 (solid lines) illustrates the results

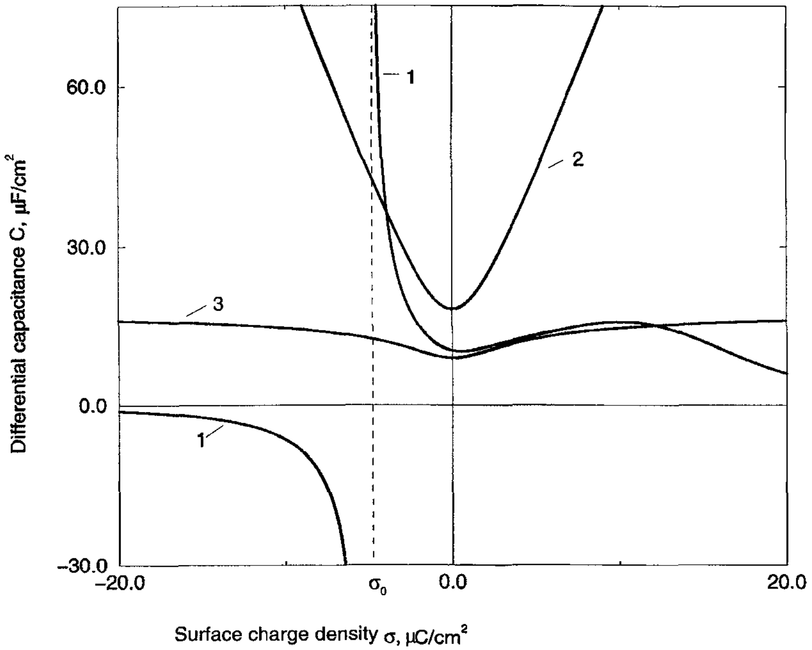

Figure 3. Plots of differential capacitance, C, as functions of surface charge density σ. Curve 1 presents typical data for Au/AgCl contact (Partenskii and Kharkats 1988) illustrating the appearance of a region of negative C; it accounts for the influence of electronic relaxation phenomena. Curve 2 describes the behaviour of the diffuse layer; the capacitance is positive everywhere. Curve 3 is analogous to curve 1, except that relaxation is not included; the interface is described in terms of a classical ideal conductor (see text) and capacitance is again positive everywhere.

anomalies in C_H can overwhelm the GC diffuse layer contribution, leading to anomalies in the total capacitance in a reasonable range of charge.

For this purpose the metal/solid electrolyte model (Partenskii and Vorobjev 1984) has been reconsidered (Partenskii *et al.* 1986, Kim *et al.* 1988, Partenskii and Kharkats 1988). The most general approach to the description of the diffuse layer was used in the last of these papers and implies the possibility of field-induced phase transition in superionic crystals (Gurevich and Kharkats 1977).

The general result of these calculations is that in spite of the 'buffering' role of the diffuse layer, in all models considered electron relaxation and related effects caused the appearance of the vertical asymptote in $C(\sigma)$ in the range $-25 < \sigma < 0$ μC cm^{-2} which is readily achieved. A typical curve calculated for Au/AgCl contact is presented as curve 1 in figure 3. For comparison the result for the same model of C_{dif} (curve 2) is presented. Curve 3 shows the total double layer capacitance if C_H is described in the classical 'ideal conductor' model, for which electron relaxation is neglected. Non-classical phenomena give rise to the negative C_H domains which can overwhelm the diffuse GC-type contribution.

---

of a similar model in which short-range interplate repulsion opposes the capacitative collapse. Here behaviour is vastly different. Increasing v under ϕ-control induces a phase transition, indicated by the Maxwell construction connecting $v(s')$ and $v(s'')$. Under q-control the states between s' and s'' are accessible and negative C is realizable. Capacitance diverges at the extremals of v and is negative in the intra-extremal domain.

4. Observability of $C < 0$, surface instabilities and phase transitions

We address now the very intriguing question of whether and under what conditions $C < 0$ can be detected in isolated and open systems. As we saw in §2, this question is closely related to the stability of interfaces. Here we investigate this relation further.

4.1. *Capacitance anomalies and phase transitions under* q-*control*

As mentioned in §2, in most theoretical studies of the double layer the interfaces are considered uniform in the yz plane on a multi-atomic scale. We have seen from §§3.2 and 3.3 that very different models treated under σ-control lead to domains where $C < 0$. Electromechanical analogues such as the elastic capacitor prove that an isolated system with $C < 0$ can be stable.

The plates of the relaxing capacitor in the electromechanical models are rigid. This forbids lateral variation of the gap width, $x(r_s)$, ($r_s = [y; z]$) and a corresponding local variation of the charge density, $\sigma(r_s)$ (needed to maintain the conductive plates as equipotentials).† For such models σ- and q-controls are equivalent. The 'plates' of the interfacial capacitor, however, are not rigid. A typical example is the ionic distribution in an electrolyte (§3.2) or the flexible boundaries of lipid bilayers in studies of electroporation (Crowley 1973, Chizmadzhev 1992, Freeman *et al.* 1994). Thus, a complete stability analysis requires checking for the possibility of 'symmetry breaking', a spontaneous appearance of structure in the yz plane and corresponding lateral variation of σ. If this can occur then the σ-control description is no longer applicable and a general q-control treatment is required. We investigate this using a modified electromechanical model.

4.1.1. *Stability of relaxing capacitors switched in parallel*

Consider two elastic capacitors in parallel with surface areas S_1 and S_2, equal elastic constants (per unit area) and equal initial gaps $z_1(0) = z_2(0) = 1$ (dimensionless units, equation (54), are used). The energy of this system (per unit area) is

$$w = \frac{p_1}{2}(z_1-1)^2 + \frac{p_2}{2}(z_2-1)^2 + \frac{p_1}{2}s_1^2 z_1 + \frac{p_2}{2}s_2^2 z_2$$

with $p_{1,2} = S_{1,2}/(S_1+S_2)$. In an isolated system the total charge is fixed. Introducing the average charge density s we get the neutrality condition

$$p_1 s_1 + p_2 s_2 = s.$$

The equivalence of the potentials gives

$$s_1 z_1 = s_2 z_2.$$

With these conditions taken into consideration the energy can be represented as a function of only two variables, z_1 and z_2

$$w = \frac{p_1}{2}(z_1-1)^2 + \frac{p_2}{2}(z_2-1)^2 + \frac{s^2}{2}\frac{z_1 z_2}{p_2 z_1 + p_1 z_2}. \tag{58}$$

---

† If a more realistic model is used (§3.2.2) then local variation of the electronic density, $n_e(x, r_s)$, is possible and can cause some local variation of the effective gap l of the surface capacitor. A corresponding contribution to the energy functional $E[n_e]$ will describe the 'cost' of such fluctuations. This effect can be important if l is comparable to atomic distances.

In the uniform case (where the system relaxes as a whole) the solution is known (55)

$$z_1 = z_2 = 1 - \frac{s^2}{2}. \tag{59}$$

Pursuing our main goal we now study the stability of the uniform solution. The corresponding stability conditions are

$$w''_{z_1z_1} > 0 \tag{60}$$

$$w''_{z_1z_1} w''_{z_2z_2} - [w''_{z_1z_2}]^2 > 0 \tag{61}$$

Using (58) and (59) we find that the uniform solution is stable only if

$$|s| < s_0 \equiv \left(\frac{2}{3}\right)^{1/2}. \tag{62}$$

Comparing with (55) we find that the stability range corresponds to the region where $C > 0$. The critical point s_0 ($C(s_0) = \infty$) corresponds to the absolute loss of stability. Somewhere before the critical point ($s \lesssim s_0$) the system becomes metastable and can undergo a transition to a new state due to a finite fluctuation (Hill 1956).

We now see that while C becomes negative for a rigid EC in the stable domain, it is absolutely impossible if the mechanically uncoupled capacitors are switched in parallel. Reality is somewhere in between. The non-uniform redistribution of charges exacts an energy penalty similar to the magnetic non-uniformity energy determining the shape of magnetic domains (Landau and Lifshitz 1960), or the surface energy contribution in the theory of nucleation (Burton 1977). We can mimic this in our model by introducing an additional mechanical coupling between the two capacitors, with

$$w_{coupl} = 0{\cdot}5\alpha(z_1 - z_2)^2. \tag{63}$$

The stability condition is now

$$s^2 < \frac{2}{3}\left(1 + \frac{2\alpha}{\alpha + 3p_1 p_2}\right). \tag{64}$$

For $\alpha = \infty$ the system is stable for $s < 2^{1/2}$ and, correspondingly, for all $z > 0$. This is equivalent to the rigid-plate capacitor considered in §3.2. For any finite α the absolute loss of stability occurs for $s > s_0$. In other words, the negative branch becomes observable; the width of this domain grows with increasing the effective lateral 'rigidity' of the plate.

The stability condition (62) corresponding to the limit of 'soft' interface agrees with the results of the thermodynamic analysis of Nikitas (1991b) where a non-uniform contribution due to the boundary between two phases was not considered (see equations (31)–(36) of that paper). On the other hand, the conclusion previously derived (Feldman *et al.* 1986a, Partenskii *et al.* 1987, Partenskii and Jordan 1993) that C can unconditionally become negative in an isolated system is only correct under σ-control. In other words, it is only applicable to 'rigid-plate' systems and does not cover the general situation. In reality the domain $C < 0$ can exist and its width is determined by the 'lateral flexibility' of the interface which can be described by interfacial tension, mechanical coupling, energy of non-homogeneity, etc.

Figure 4 depicts a representative charging plot $v(s)$ of mechanically coupled elastic capacitors in parallel. The first vertical step corresponds to a transition from a uniform to a non-uniform phase, when z_1 and z_2 become different. The second step is the

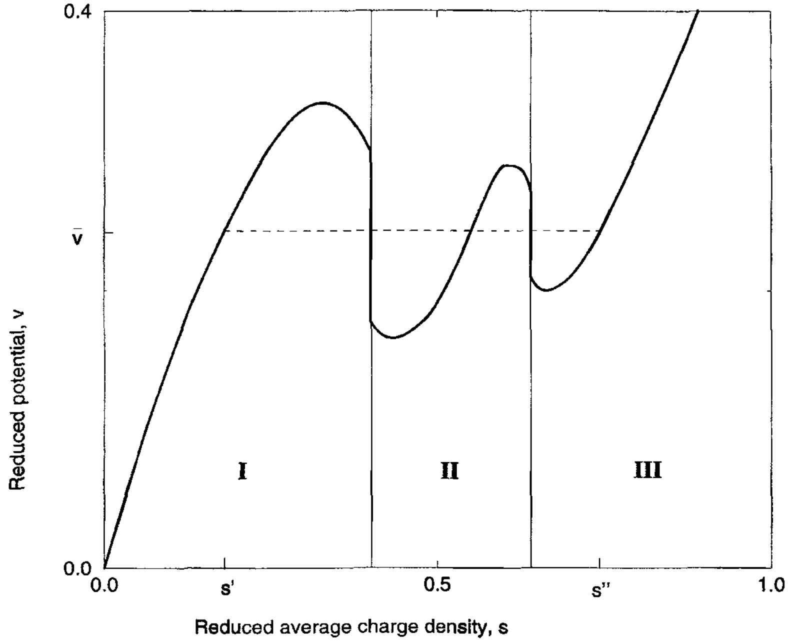

Figure 4. A representative plot of the reduced potential, v, as a function of the average charge density, s, for mechanically coupled elastic capacitors in parallel. There are two regions of negative C (where $\mathrm{d}v/\mathrm{d}s < 0$). The discontinuities in v under q-control represent (at the I–II boundary) a transition to the non-uniform system, where the capacitors have different charge densities, and (at the II–III boundary) a transition back to a uniform system (this latter branch corresponds to the region $s > s''$, illustrated in curve 2 of figure 2). The horizontal dashed line represents the Maxwell path describing the phase transition under ϕ-control. In general it may consist of two (or more) parallel paths describing sequential transitions. The $C(\phi)$ curves will exhibit a corresponding number of sharp peaks.

transition to a uniform phase with $z_1 = z_2$, both defined by the second stable branch of the EC due to the short-range repulsion between the plates, as in figure 2.

To imitate the possible role of surface non-homogeneity we considered the model described by (58) and (63) but with $z_2 = z_0 = \text{const}$. Thus, the second capacitor imitates a rigid domain in the double layer or membrane, while the first remains 'flexible'. If the ratio p_2/p_1 is large enough, the rigid domain plays the role of potentiostat for the flexible one. In this sense q-control becomes equivalent to ϕ-control with all possible consequences, including the fact that the $C < 0$ domain becomes inaccessible.

The instabilities discussed in this section are fairly universal. They appear because near s_0 each fragment of the double layer is unstable with respect to charging. Trying to obtain charge in the absence of an external source (potentiostat), different fragments of the plane begin to cooperate in order to redistribute charge in an optimal way. The 'gains' of the charge acceptors should compensate for the 'losses' of the donors and the additional contributions from the non-uniform distribution of double layer components (i.e. metal electrons, ions, water dipoles). This condition determines the structure of the resulting non-uniform phase.

Thus it is only important that C becomes negative. As seen from the discussion in §§3.2 and 3.3, this may be a typical property of the double layer when electronic and ionic relaxation are considered. Even the simplest GC system should undergo this transition due to the 'electronic plate' (x_e) displacement causing C_H to become negative for large enough negative polarization (§3.2.2). It does not require any specific interactions between the particles in the adsorbate submonolayers, special site-occupation restrictions etc. This lack of sensitivity to any particular interaction and its origin in the combined effect of the compact and diffuse parts of the double layer makes the critical behaviour we are considering different from the variety of phase transitions occurring in surface water layers, submonolayers of ionic or molecular adsorbates, in the surface atomic plane of the electrode (see, for example Blum and Huckaby (1991), Huckaby and Blum (1991), Benderskii *et al.* (1994), Kornyshev and Vilfan (1995) and references therein). In real cases the loss of stability can lead to the appearance of a non-uniform phase similar to the waves of concentration in alloys (Khachaturyan 1974) or stratification into dense and rarified phases in plasma (March and Tosi 1984). Stability is typically lost for a certain range of wave numbers $\vec{k}$. It is significant that both dense and diffuse parts of the double layer should be involved in the transformation. These phenomena make it very important to conduct the studies of double layer critical properties under q-control.

4.2. *Interrelation between properties of isolated and open systems*

In 'normal' systems the extremal $\phi(\sigma)$ is a monotonic function, $C > 0$ and the two types of electrical control lead to the same results. Differences appear if the isolated system possesses a negative capacitance branch (which may include points where $C = -0$, the vertical steps of fig. 4). What happens if such a system is subject to ϕ-control? Here we describe the most general features of a system under ϕ-control; further details can be found in the literature (Feldman *et al.* 1986b, Nikitas 1992a, 1994, Partenskii and Jordan 1993, Stafiej 1993).

The results depend on the shape of the extremal $\phi^Q(\sigma)$. If it has $\cap$-type shape describing, for example, an elastic capacitor without a 'block' between the plates (figure 2) then the system is absolutely unstable under ϕ-control. When a second stable branch ($C > 0$) exists (a simple example is the EC with 'blocker', figure 2) then the system can experience a potential-induced surface phase transition. Its features are:

1. Divergence of capacitance $C(\phi \to \bar{\phi}) \sim (\phi - \bar{\phi})^r$. Here r is the critical index (equal to 0·5 for an elastic capacitor (Feldman *et al.* 1986b)), $\bar{\phi}$ is the critical potential which can be determined, for instance, using the Maxwell rule ('equal-area theorem') (Nikitas 1993, Partenskii and Jordan 1993).
2. Hysteresis—the shape of $C(\phi)$ differs for forward and backward potential variation and can depend on the rate of potential change in the vicinity of the critical point (Feldman *et al.* 1986a, 1986b, Partenskii and Kharkats 1988).
3. Strong low-frequency dispersion of ac impedance in the vicinity of the critical point (Feldman *et al.* 1986b).

The important question of the correspondence between the phase transitions in isolated and global systems has been raised in Partenskii and Kharkats (1988) and Nikitas (1991b). It was shown by Partenskii and Kharkats that the phase transition to the superionic state promotes the appearance of a $C < 0$ branch under q-control and, accordingly, the phase transition under ϕ-control. A similar relation between the two types of phase transition was noticed by Nikitas (1991b). Possible transition to the non-uniform phase creates some additional possibilities. In figure 4 the Maxwell path describing the transition under ϕ-control is drawn as the dashed line $s's''$. However, analysis indicates that it can be separated into two parallel paths corresponding to different values $\bar{\phi}_1$ (uniform → non-uniform) and $\bar{\phi}_2$ (non-uniform → uniform phase). Two sharp peaks on the $C(\phi)$ plots should appear in this case.

Under ϕ-control total capacitance should be positive. But what of its components, C_H and C_d? Can, for example, C_H become negative? To answer this question Nikitas (1992a, 1994) tried to show that the condition for a phase transition under ϕ-control, $C = \infty$, can be achieved only if both C_{dif} and C_H are infinite and corresponding potential drops, ϕ_H and ϕ_{dif}, remain constant during the transition. His proof is based on the relation

$$\frac{1}{C_H} + \frac{1}{C_{dif}} = \frac{1}{C_{dl}} = 0.$$

According to (12), charge fluctuations are enormous at this point. The interface can then roughly be described as fluctuating between two states with different charge density and different ionic distributions, corresponding to the two edge points of the 'Maxwell' transition path (see points s' and s'' of figures 2 and 4). Moreover, due to the presence of a fluctuating charging current the potential drop is now distributed between the double layer, the bulk of electrolyte and the external resistors.

Thus, this domain is least appropriate for dividing the double layer into two parts or reaching any conclusions on the basis of such a division. It is no surprise that this analysis leads to contradictions (Nikitas 1992a, 1994) because the GC model does not yield $C_{dif} = \infty$ for any finite σ or ϕ_d (41). Accordingly, the quality of GC or any other approximation has nothing to do with its ability to describe the system in the critical region (see discussion in Nikitas (1994)).

For the same reason we agree with Nikitas' criticism (Nikitas 1992a) of the scenario (Kim *et al.* 1989) of a ϕ-control instability arising due to compensation between a $C_H^{-1} < 0$ and a $C_{dif}^{-1} > 0$. We can only say that negative values of C_H (or C_{dif}) in an isolated system may lead to negative C_{dl} under q-control and to related phase transitions in the global system. Also, in the stable domains of a global system where capacitance can be reasonably divided into two components (including regions close enough to the critical point (Partenskii and Jordan 1993)), there are no restrictions on the sign of the C_H or C_{dif} except for those considered in §4.1.† Therefore, negative values of C_H, extracted from experimental data for total double layer capacitance (e.g. Hamelin and Stoicoviciu (1987), Hamelin *et al.* (1988)) do not contradict any general principle.

In addition to electrochemical applications the phenomena discussed are closely related to membrane instabilities and electroporation. Crowley (1973) suggested an elegant linkage between electroporation and electroelastic instability. Later on this approach was abandoned in favour of phenomenological theories describing water pore formation (see for review Chizmadzhev (1992), Freeman *et al.* (1994)). The reasons for abandoning the Crowley picture were clearly described by Chizmadzhev (1992). Crowley's model predicted significant thinning of the membrane before

---

† The attempt to derive such restrictions is described in Nikitas (1992a) (N). In our view, equations (32) and (38) of N imply that potential drops across inner and diffuse layers can be controlled autonomously, which is equivalent to separate potential control of both compact and diffuse layers. In reality only the total potential drop can be fixed externally, while its components adjust themselves accordingly. Consequently we believe that concluding that C_H and C_{dif} (using our notation) are strictly non-negative does not have solid justification. In addition, analysis of the molecular model, (45) of N, leading to a CH catastrophe under σ-control, is not consistent with the electrostatic analysis (§3.1).

breakdown (see the discussion in §3.2.2) and a significant increase in capacitance; experiment provides no evidence for such behaviour. In our view, Crowley's original idea can be made more consistent with experiment if the non-uniform nature of the membrane is taken into consideration. As we have shown in §4.1, the local loss of stability in more flexible parts of the membrane can appear without noticeable changes in the average membrane characteristics. This approach can shed some light on the early stages of pore formation. Preliminary results also indicate that coupling between the 'elastic' (related to the local compression or stretching of the membrane) degrees of freedom and current across the pore (or ion channel) can lead to self-oscillations of charge and current and transition to a chaotic regime in membrane pore (or ion channel) conductance (Partenskii *et al.* 1994). It can be expected that for these phenomena separate consideration of ϕ- and q-control will be productive.†

5. Conclusions

As we have seen (§3.1) the CH catastrophe raised the very important question of whether negative differential capacitance is allowable. This problem catalyzed a lively discussion and a large literature. Ironically, the appearance of the CH catastrophe was based on an erroneous treatment of the electrostatic field in the molecular capacitor. This result seemed to satisfy common sense.

However, the same problem appeared in the statistical mechanical treatment of the ionic diffuse layer and in the microscopic analysis of the compact layer accounting for electronic and molecular relaxation (§3.2). All these studies implicitly assumed that the interface is uniform in the plane parallel to the electrode surface. The local charge density σ was thus considered a controlled variable. In this sense q-control (where the total charge is fixed) was substituted by σ-control. It was proved, using exactly solvable electromechanical models (also uniform in the plane), that under σ-control there are no restrictions on the sign of C.

However, the σ-control assumption is only reasonable for laterally rigid systems (e.g. metallic-plate capacitors) while the typical contacts, such as electrode–electrolyte interfaces or lipid bilayers are quite flexible and charge distributions non-uniform in the zy plane are achievable. Thus, consistent theoretical analysis must consider the stability of the uniform state in a q-controlled system.

It appears (§4.1) that in absolutely soft systems (if the effective surface tension is negligible or, as in the model considered, in the absence of mechanical coupling between the parallel capacitors) uniform relaxation becomes absolutely unstable at $\sigma = \sigma_0$ where $C^{-1}(\sigma)$ crosses the abscissa. The system makes a transition to the non-uniform state with both the charge density σ and the ionic distribution in the electrolyte varying in the electrode plane keeping the total charge q fixed. Thus, the region $C < 0$ disappears; C in the 'soft' limit is strictly positive. Real systems dwell somewhere between the 'rigid' and 'soft' limits, because non-homogeneity exacts an energetic price. That is why there can be a domain with $C < 0$ before the transition to the non-uniform state occurs. We have illustrated this using a model with mechanical coupling between two parallel elastic capacitors.

The long-standing theoretical question of whether C can become negative under σ-control (a condition applicable to a wide class of diffuse layer studies) is resolved: $C < 0$ is allowed. But one must also check the applicability of σ-control. The possibility

---

† Using isolated electrodes (see Breazeal *et al.* (1995) and references therein) may be helpful for maintaining q-control.

of a phase transformation from the $C < 0$ domain and the conditions for its appearance require more careful examination. Consistent treatment of both the electronic system of the metal and the ion–dipolar system of the electrolyte may be crucial in this analysis. The important candidates are those models which predict a negative diffuse layer contribution, $C_{\text{dif}} < 0$ (§3.2.1). Their unification with electron contributions can possibly make the appearance of critical anomalies inevitable. An important issue is the effect of intrinsic non-homogeneity (such as the roughness of the electrode surface and inclusions in membranes). As an example, these can significantly reduce or nullify the domain where $C < 0$ and restrict the area where transformation can occur.

The appearance of a $C < 0$ domain under q-control is a direct signal that instability and phase transition can occur under ϕ-control. This transition is possible even for rigid systems which can be absolutely stable under q-control. Thus it can occur between two uniform phases, although a non-uniform phase may also form. Further analysis of the interrelation between transitions in isolated and global systems is required for better understanding of critical properties and double layer anomalies at electrified interfaces covering a broad class of systems and phenomena, from phase transitions at electrochemical interfaces to membrane electroporation.

Acknowledgments

This work was supported by a grant from the National Institutes of Health, GM-28643.

References

Amokrane, S., and Badiali, J., 1993, *Modern aspects of electrochemistry*, Vol. 22, edited by B. Conway, J. Bockris and R. White (New York, London: Plenum Press), p. 1.

Attard, P., Wei, D., and Patey, G., 1992, *J. chem. Phys.*, **96**, 3767.

Badiali, J., Rosinberg, M., and Goodisman, J., 1983a, *J. electroanal. Chem.*, **143**, 73.

Badiali, J., Rosinberg, M., and Goodisman, J., 1983b, *J. electroanal. Chem.*, **150**, 25.

Badiali, J., Rosinberg, M., Vericat, F., and Blum, L., 1983c, *J. electroanal. Chem.*, **158**, 253.

Baxter, R. 1982, *Exactly Solved Models in Statistical Mechanics* (London, New York: Academic Press), Chap. 1.

Benderskii, V., Brodskii, A., Daikhin, L., and Velichko, G., 1994, *Modern Aspects of Electrochemistry*, Vol. 26, edited by B. Conway, J. Bockris and R. White (New York, London: Plenum Press), Chap. 1, p. 1.

Blum, L., 1977, *J. phys. Chem.*, **81**, 136.

Blum, L., and Huckaby, D., 1991, *J. chem. Phys.*, **94**, 6887.

Blum, L., Lebovitz, J., and Henderson, D., 1980, *J. chem Phys.*, **72**, 4249.

Bockris, J., and Reddy, A., 1972, *Modern Aspects of Electrochemistry* (New York: Plenum Press).

Borkowska, Z., and Stafiej, J., 1985, *J. electroanal. Chem.*, **182**, 253.

Breazeal, W., Flynn, K., and Gwinn, E., 1995, *Phys. Rev. E*, **52**, 1503.

Brodsky, A., Watanabe, M., and Reinhardt, W., 1991, *Electrochim. Acta*, **36**, 1695.

Burton, J., 1977, *Statistical mechanics*, edited by B. Berne (New York: Plenum Press), p. 195.

Carnie, S., Chan, D., Mitchell, D. and Ninham, B., 1981, *J. chem. Phys.*, **74**, 1472.

Chizmadzhev, Y., 1992, *Electrified interfaces in physics, chemistry and biology*, edited by R. Guidelli (Dordrecht: Kluwer).

Cooper, I., and Harrison, J., 1975, *J. electroanal. Chem.* **66**, 85.

Crowley, J., 1973, *Biophys. J.*, **13**, 711.

Damaskin, B., and Frumkin, A., 1974, *Electrochim. Acta*, **19**, 173.

Dogonadze, R., and Chizmadzhev, Y., 1964, *Dokl. Akad. Nauk. USSR*, **157**, 944.

Fawcett, W., 1978, *J. phys. Chem.*, **82**, 13.

Fawcett, W., 1979, *Israel J. of Chem.*, **18**, 3.

Feldman, V., Kornyshev, A., and Partenskii, M., 1985, *Solid State Commun.*, **53**, 157.

Feldman, V., and Partenskii, M., 1991, *Electrochim. Acta*, **36**, 1703.

Feldman, V., Partenskii, M., and Kornyshev, A., 1987, *J. electroanal. Chem.*, **237**, 1.

Feldman, V., Partenskii, M., and Vorobjev, M., 1986a, *Electrochim. Acta*, **31**, 291.

Feldman, V., Partenskii, M., and Vorobjev, M., 1986b, *Prog. Surf. Science*, **23**, 3.

Freeman, S., Wang, M., and Weaver, J., 1994, *Biophys. J.*, **67**, 42.

Graham, D., 1947, *Chem. Rev.*, **41**, 441.

Grahame, D. C., 1954, *J. Am. chem. Soc.*, **76**, 4819.

Guidelli, R., 1990, *J. chem. Phys.*, **92**, 6152.

Gurevich, Y., and Kharkats, Y. I., 1977, *Sov. Phys. Dokl.*, **236**, 332.

Halley, J., Johnson, B., Price, D., and Schwalm, M., 1985, *Phys. Rev.* B, **31**, 7695.

Halley, J., and Price, D., 1987, *Phys. Rev.* B, **35**, 9095.

Hamelin, A., Doubove, L., Stoicoviciu, L., and Trassati, S., 1988, *J. electroanal. Chem.*, **244**, 133.

Hamelin, A. and Stoicoviciu, L. 1987, *J. electroanal. Chem.*, **236**, 267.

Hautman, J., Halley, J., and Rhee, Y.-J., 1989, *J. chem. Phys.*, **91**, 467.

Henderson, D., Blum, L., and Smith, W., 1979, *Chem. Phys. Lett.*, **63**, 381.

Hill, T., 1956, *Statistical Mechanics* (New York: McGraw-Hill).

Huang, K., 1963, *Statistical Mechanics* (New York: Wiley).

Huckaby, D., and Blum, L., 1991, *J. electroanal. Chem.*, **315**, 255.

Khachaturyan, A., 1974, *Theory of Phase Transformations and Structure of Solid Solvents* (Moscow: Nauka).

Kim, Z., Kornyshev, A., and Partenskii, M., 1989, *J. electroanal. Chem.*, **265**, 1.

Kim, Z., Partenskii, M., and Solovjeva, L., 1988, *Rasplavy* (*The Melts*), **2(1)**, 102 (in Russian).

Kornyshev, A., 1985, *Chemical Physics of Solvation*, Vol. C, edited by R. E. Kalman, A. Kornyshev and J. Ulstrup (Amsterdam: Elsevier Science), Chap. 6.

Kornyshev, A., 1989, *Electrochim. Acta*, **34**, 1829.

Kornyshev, A., and Vilfan, I., 1995, *Electrochim. Acta*, **40**, 109.

Kornyshev, A., and Vorotyntsev, M., 1981, *Can. J. Chem.*, **59**, 2031.

Landau, L., and Lifshitz, E., 1960, *Electrodynamics of Continuous Media* (Oxford: Pergamon Press).

Lang, N., 1973, *Solid State Physics*, Vol. 28 (New York: Academic Press) p. 225.

Lang, N., 1983, *Theory of the inhomogeneous electron gas* (New York, London: Plenum Press), p. 309.

Levine, L., Bell, G., and Smith, A., 1969, *J. phys. Chem.*, **73**, 3534.

Macdonald, J., 1954, *J. chem. Phys.*, **22**, 1857.

Macdonald, J., 1964, *J. appl. Phys.*, **35**, 3053.

Macdonald, J., 1987, *J. electroanal. Chem.*, **223**, 1.

Macdonald, J., Franceschetti, D., and Lehnen, A., 1980, *J. chem. Phys.*, **73**, 5272.

Macdonald, R., and Barlow, C., 1962, *J. chem. Phys.*, **36**, 3062.

March, N., and Tosi, M., 1984, *Coulomb liquids* (New York: Academic Press).

Marshall, S., and Conway, B., 1987, *J. electroanal. Chem.*, **227**, 245.

Marshall, S., and Conway, B., 1992, *J. electroanal. Chem.*, **337**, 67.

Marshall, S., and Conway, S., 1984, *J. chem. Phys.*, **81**, 923.

McCombie, C., 1971, *Problems in thermodynamics and statistical physics*, edited by P. Landsberg (London: Pion), p. 459 (Problem 21.3).

Mott, N., and Watts-Tobin, R., 1961, *Electrochim. Acta*, **4**, 79.

Nikitas, P., 1987, *J. electroanal. Chem.*, **227**, 237.

Nikitas, P., 1991a, *J. electroanal. Chem.*, **306**, 13.

Nikitas, P., 1991b, *J. electroanal. Chem.*, **316**, 23.

Nikitas, P., 1992a, *Electrochim. Acta*, **37**, 81.

Nikitas, P., 1992b, *Electrochim. Acta*, **37**, 1919.

Nikitas, P., 1993, *Electrochim. Acta*, **38**, 1441.

Nikitas, P., 1994, *Electrochim. Acta*, **39**, 2055.

Parsons, R., 1954, *Modern Aspects of Electrochemistry*, Vol. 1, edited by J. Bockris and B. Conway (New York: Academic Press), p. 103.

Parsons, R., 1975, *J. electroanal. Chem.*, **59**, 359.

Parsons, R., 1980, *J. electroanal. Chem.*, **109**, 369.

Parsons, R., and Reeves, R., 1985, *J. electroanal. Chem.*, **123**, 141.

PARTENSKII, M., 1979, *Sov. Phys. Usp.*, **22**, 330.

PARTENSKII, M., and BLUM, L., 1990, unpublished results.

PARTENSKII, M., DORMAN, V., and JORDAN, P., 1994, *Biophys. J.*, **66**, A223.

PARTENSKII, M., and FELDMAN, V., 1989, *J. electroanal. Chem.*, **273**, 57.

PARTENSKII, M., and JORDAN, P., 1993, *J. chem. Phys.*, **99**, 2992.

PARTENSKII, M., and KHARKATS, Y., 1988, *Rasplavy* (*The Melts*), **2(6)**, 57 (in Russian).

PARTENSKII, M., and KIM, Z., 1986, *Electrodynamics and quantum phenomena at interfaces: Proceedings of the International Conference, Telavi, USSR, 1984* (Tbilisi: Mecneareba), p. 72.

PARTENSKII, M., KIM, Z., and FELDMAN, V., 1987, *Sov. Phys. J.*, **30**, 907.

PARTENSKII, M., KIM, Z., FELDMAN, V., and SOLOVJEVA, L., 1986, in 37th Meet. Intern. Soc. Electrochem. Extend. Abstr., p. 160, Vilnus, USSR. Lithv. Acad. Sci.

PARTENSKII, M., KUZEMA, V., and FELDMAN, V., 1981, *Sov. Phys. J.*, **11**, 985.

PARTENSKII, M., and VOROBJEV, M. 1984, *Sov. Phys. Dokl.*, **29**, 746.

PRICE, D., and HALLEY, J., 1983, *J. electroanal. Chem.*, **150**, 347.

PRICE, D., and Halley, J., 1995, *J. chem. Phys.*, **102**, 6603.

RALEIGH, D., 1976, *Electrode processes in solid state ionics* (Dordrecht: Reidel) p. 119.

REMEZ, I., and CHEBOTIN, V., 1984, *Electrochim. Acta*, **29**, 1389.

RICE, O., 1928, *Phys. Rev.*, **31**, 1051.

ROSINBERG, M., BLUM, L., and LEBOWITZ, J., 1985, *J. chem. Phys.*, **83**, 892.

SCHMICKLER, W., 1983, *J. electroanal. Chem.*, **149**, 15.

SCHMICKLER, W., and HENDERSON, D., 1984, *J. chem. Phys.*, **80**, 3381.

SCHMICKLER, W., and HENDERSON, D., 1986, *Progr. Surf. Science*, **22**, 323.

SCHMICKLER, W., and HENDERSON, D., 1989, *J. electroanal. Chem.*, **265**, 11.

STAFIEJ, J., 1993, *J. electroanal. Chem.*, **351**, 1.

STYLLER, M., 1995, unpublished results.

SZE, S., 1969, *Physics of Semiconductor Devices* (New York: Wiley & Sons).

THEOPHYLOU, A., 1972, *J. phys.* F, **2**, 1124.

TOPPING, J., 1927, *Proc. R. Soc. London* A., **114**, 67.

TORRIE, G., 1992, *J. chem. Phys.*, **96**, 3772.

TORRIE, G., and VALLEAU, J., 1982, *J. phys. Chem.*, **86**, 3251.

TSONG, T., and MULLER, E., 1969, *Phys. Rev.*, **181**, 530.

WATTS-TOBIN, R., 1961, *Phil. Mag.*, **6**, 133.

WEI, D., TORRIE, G., and PATEY, G., 1993, *J. chem. Phys.*, **99**, 3990.