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On the existence of exact conditions in the theory of electrical double layers

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It has long been thought that the total potential drop V across an isolated electrical double layer must be a monotonically increasing function of the surface charge density σ (i.e., $\partial V/\partial\sigma > 0$). This result has been "established" by thermodynamic arguments of Landau and Lifshitz [*Electrodynamics of Continuous Media* (Pergamon, Oxford, 1960)] and by a more recent statistical mechanical method of Blum *et al.* [J. Chem. Phys. **72**, 1902 (1981)]. Here we describe statistical mechanical analyses for both constant and fluctuating charge models. It is shown that the derivation of Blum *et al.* is in error and that correct statistical mechanical treatments do not determine the sign of $\partial V/\partial\sigma$. However, some rigorous bounds for related quantities are found. We also point out a mathematical problem in the method of Landau and Lifshitz which appears to invalidate their argument. We conclude that at present there is no rigorous proof that $\partial V/\partial\sigma$ must be positive and that the existence of negative values cannot be ruled out.

I. INTRODUCTION

One of the few results thought to be exact in the theory of electrical double layers states that the surface potential (i.e., the electrical potential drop across the double layer) must increase monotonically with surface charge. This result seems to stem from two sources. Thermodynamic stability arguments have been given by Landau and Lifshitz[1] and a recent statistical mechanical derivation has been put forward by Blum, Lebowitz, and Henderson,[2] and by Blum and Henderson.[3] Both derivations are often cited[4,5] as rigorous results. We find that the derivation given in Refs. 2 and 3 is in fact incorrect and that it is only due to an unfortunate error in sign that the authors reach the conclusion stated above. Indeed, when the sign error is corrected, the "proof" given in Refs. 2 and 3 actually predicts that the surface potential must *decrease* rather than increase with increasing surface charge. Physically, this conclusion is obviously false and we show that the derivation given in Refs. 2 and 3 is unsound. We give a proper statistical mechanical treatment of the problem both for constant surface charge and constant surface *chemical* potential ensembles. Both analyses are consistent in that they do not lead to any rigorous result for the sign of the derivative of the electrostatic surface potential with respect to surface charge. However, we do obtain exact conditions which certain related quantities must obey.

Since the statistical mechanical approach does not lead to a rigorous bound on the derivative of the surface potential with respect to charge, we were motivated to examine closely the thermodynamic stability analysis of Landau and Lifshitz.[1] For the reasons discussed briefly below, we are unable to reproduce their result. Thus, we can find no rigorous general proof that the derivative of the surface potential with respect to charge must obey a positivity condition. For the

simple primitive model electrolytes usually considered in explicit theoretical treatments and computer simulations,[4] it is not difficult to show that the derivative will be positive if the ion distributions obey certain relatively weak conditions, but we cannot conclude that this must be true in general.

The remainder of this note is divided into four parts. The statistical mechanical theory for the constant charge and constant potential cases is discussed in Secs. II and III. A brief discussion of the Landau–Liftshitz derivation is given in Sec. IV and our conclusions are summarized in Sec. V.

II. CONSTANT SURFACE CHARGE

This is the usual case considered in electrical double layer theory,[4] including the work of Blum *et al.*[2,3] Here we discuss the problem for both planar and spherical geometries.

A. Planar capacitor

We require expressions for the potential drop across the electrical double layer and for the derivatives of the free energy with respect to surface charge. As in all Coulombic systems, subtle questions concerning electroneutrality and the order of limits arise. Therefore, for reasons of clarity, we find it convenient to consider a capacitor formed by equally and oppositely charged half-spaces. In the limit that the separation $2h$ is much larger than the screening length κ^{-1}, one can equate the difference between the surface and midplane potentials to the potential drop across the isolated double layer.

We consider a primitive model ($\epsilon = 1$) symmetric ($q_+ = -q_-$) electrolyte solution contained between semi-infinite half-spaces located beyond $\pm h$ with surface charges $\pm\sigma$. Then, employing Coulomb's law, the mean electrostatic potential at z (note that in our coordinate system the midplane is located at $z = 0$) is given by

$$\psi(z) = 2\pi \int_0^S dr\, r \left[\frac{\sigma}{\sqrt{r^2 + (z-h)^2}} - \frac{\sigma}{\sqrt{r^2 + (z+h)^2}} \right.$$

$$\left. + q_+ \int_{-h}^h dz' \frac{\rho_+(z') - \rho_-(z')}{\sqrt{r^2 + (z-z')^2}} \right]$$

$$= 2\pi\sigma(|h+z| - |h-z|) - 2\pi q_+$$

$$\times \int_{-h}^h [\rho_+(z') - \rho_-(z')]|z - z'|dz'. \qquad (2.1)$$

Here we have used the fact that the lateral size of the walls is much larger than the separation (i.e., $S \gg h$) and also the electroneutrality condition for the capacitor

$$q_+ \int_{-h}^h [\rho_+(z) - \rho_-(z)]dz = 0, \qquad (2.2)$$

where $\rho_\pm(z)$ are the ionic number densities. The surface potential is

$$\psi(h) = 4\pi\sigma h + 4\pi q_+ \int_0^h [\rho_+(z) - \rho_-(z)]z\, dz. \qquad (2.3)$$

Note that $\psi(0) = 0$ and that the mean potential drop across the isolated double layer is $V = \lim_{h\to\infty} \psi(h)$. This can be cast in a more familiar form by defining $\bar{\rho}_\pm(x,h) \equiv \rho_\pm(h-x)$. These measure the ionic profiles from the *positive* surface; the contact densities are $\bar{\rho}_\pm(0,h)$ as is conventional for the isolated double layer. Then one has

$$V = -4\pi q_+ \lim_{h\to\infty} \int_0^h [\bar{\rho}_+(x,h) - \bar{\rho}_-(x,h)]x\, dx$$

$$= -4\pi q_+ \int_0^\infty [\bar{\rho}_+(x) - \bar{\rho}_-(x)]x\, dx, \qquad (2.4)$$

and the electroneutrality condition for the isolated double layer is

$$q_+ \lim_{h\to\infty} \int_0^h [\bar{\rho}_+(x,h) - \bar{\rho}_-(x,h)]dx$$

$$= q_+ \int_0^\infty [\bar{\rho}_+(x) - \bar{\rho}_-(x)]dx = -\sigma. \qquad (2.5)$$

We emphasize that the potential drop across the isolated electrical double layer defined by Eq. (2.4) is in complete accord with the usual convention[4] and that at least at low coupling it will have the same sign as the surface charge.

In order to apply the methods of statistical mechanics, we require the part of the configurational Hamiltonian that depends on surface charge. Again, from Coulomb's law this is

$$H_\sigma = \sum_{i=1}^N 2\pi q_i \sigma(|h+z_i| - |h-z_i|)$$

$$= 4\pi\sigma \sum_{i=1}^N q_i z_i, \qquad (2.6)$$

where we have used the fact that since the ions are confined between the walls $|z_i| < h$. If we then consider the grand partition function Ξ and introduce the grand potential $\Omega = -\beta^{-1} \ln \Xi$, where $\beta = 1/k_B T$, it is easy to show that

$$\frac{\partial\Omega}{\partial\sigma} = \langle H_\sigma/\sigma \rangle$$

$$= 4\pi q_+ A \int_{-h}^h [\rho_+(z) - \rho_-(z)]z\, dz$$

$$= 2A[\psi(h) - 4\pi\sigma h], \qquad (2.7)$$

where A is the surface area. All partial derivatives are at constant volume, temperature, chemical potential, and surface area. In the large separation limit, we see that the derivative of the grand potential does not equal the potential drop across the isolated double layer, but contains an additional term linear in separation. The second derivative gives the fluctuation

$$\frac{\partial^2\Omega}{\partial\sigma^2} = -\beta\langle(H_\sigma/\sigma - \langle H_\sigma/\sigma\rangle)^2\rangle \leqslant 0, \qquad (2.8)$$

and combining Eqs. (2.7) and (2.8), one obtains the condition

$$\frac{\partial\psi(h)}{\partial\sigma} - 4\pi h \leqslant 0. \qquad (2.9)$$

It can be shown that if one adds to the Hamiltonian any arbitrary term independent of the ion configuration (e.g., the direct interaction between the plates), Eqs. (2.7) and (2.8) may alter, but Eq. (2.9) remains unchanged. Thus Eq. (2.9) is an exact result for a capacitor with plates at arbitrary separation. However, it is clearly not a very strong statement about the isolated double layer since in that case $h \to \infty$.

Let us now compare our results with those of Blum *et al.*[2] (similar remarks also apply to Ref. 3). First, our expression for the potential drop across the isolated double layer [Eq. (2.4)] is of opposite sign to Eq. (33) of Ref. 3 and to the quantity V of Ref. 2 [note that the "multiplicative coefficient" that relates Eqs. (3) and (5) of Ref. 2 includes a factor of -1]. The quantity that those authors call the potential drop is negative for positive surface charge in the low coupling limit and as such is opposite to the usual convention. Thus, although Eq. (5) of Ref. 2 follows from their analysis, it actually predicts that the conventional potential drop *decreases* with increasing surface charge. Comparing Eq. (5) of Ref. 2 to our Eq. (2.9), we see that they are missing the dominant term $-4\pi h$. We have been able to trace the origin of this discrepancy. The model treated in Ref. 2 is identical to the capacitor treated here, except that the oppositely charged plate is consigned to infinity at an early stage in their analysis. This causes no problems with the use of the canonical ensemble (since electroneutrality is preserved in the capacitor when the surface charge is varied at constant ion number), nor with the Hamiltonian [Eq. (2) of Ref. 2], which is identical to our Eq. (2.6) when the coordinates are matched (i.e., $x = h - z$). However, the identification of the integral in Eq. (3) of Ref. 2 with the surface potential of the isolated double layer is erroneous because it actually includes the ionic profile due to the second plate (at infinity). This is most easily seen and corrected by placing that plate at $2h$ and splitting the resultant integral into two regions. A simple change of variable and symmetry arguments then give a result identical to our Eq. (2.7). In summary, the errors in the work of Blum *et al.*[2,3] stem from the

use of an unconventional sign for the surface potential and from the identification of the first moment of the total ionic profile of both plates of the capacitor with the potential drop of an isolated double layer.

B. Charged macrosphere

Let us now consider a spherical "macroion" of charge $Q = 4\pi R^2 \sigma$ immersed in a primitive model electrolyte. We shall derive bounds valid for arbitrary radii and shall also consider the large radius limit $R \to \infty$ at fixed surface charge density σ. The electrostatic potential about the macroion is

$$\psi(r) = \frac{Q}{r} + \frac{4\pi q_+}{r} \int_R^r [\rho_+(s) - \rho_-(s)]s^2 ds$$
$$+ 4\pi q_+ \int_r^\infty [\rho_+(s) - \rho_-(s)]s\, ds, \qquad (2.10)$$

where the ionic densities are expressed as functions of the distance from the center of the macroion. Note that this potential vanishes at infinity and that the surface potential is

$$\psi(R) = \frac{Q}{R} + 4\pi q_+ \int_R^\infty [\rho_+(s) - \rho_-(s)]s\, ds$$
$$\equiv \frac{Q}{R} + \psi_i(R), \qquad (2.11)$$

where ψ_i denotes the ionic contribution. The electroneutrality condition is

$$Q = -4\pi q_+ \int_R^\infty [\rho_+(s) - \rho_-(s)]s^2 ds. \qquad (2.12)$$

Again we express the grand potential in terms of the charge and configuration-dependent Hamiltonian

$$H_Q = Q \sum_{i=1}^N q_i r_i^{-1}, \qquad (2.13)$$

where r_i is the separation between the ion and macroion centers, and differentiate (at fixed temperature, volume, chemical potential, and radius) to obtain

$$\frac{\partial \Omega}{\partial Q} = \langle H_Q / Q \rangle$$
$$= 4\pi q_+ \int_R^\infty [\rho_+(s) - \rho_-(s)]s\, ds$$
$$= \psi_i(R). \qquad (2.14)$$

The second derivative is

$$\frac{\partial^2 \Omega}{\partial Q^2} = -\beta \langle (H_Q/Q - \langle H_Q/Q \rangle)^2 \rangle \leqslant 0 \qquad (2.15)$$

and, accordingly, one has the exact result

$$\frac{\partial \psi_i(R)}{\partial Q} \leqslant 0. \qquad (2.16)$$

We remark that an analogous result holds for the planar case [cf. Eqs (2.9) and (2.1)]. Directly differentiating Eq. (2.11), one obtains

$$\frac{\partial \psi(R)}{\partial Q} = \frac{1}{R} + \frac{\partial \psi_i(R)}{\partial Q}, \qquad (2.17)$$

or in terms of σ,

$$\frac{\partial \psi(R)}{\partial \sigma} = 4\pi R + \frac{\partial \psi_i(R)}{\partial \sigma}. \qquad (2.18)$$

Equations (2.16) and (2.18) immediately yield the exact condition

$$\frac{\partial \psi(R)}{\partial \sigma} - 4\pi R \leqslant 0, \qquad (2.19)$$

which resembles Eq. (2.9) and clearly does not determine the sign of the derivative of the surface potential.

It is also of interest to consider the limiting expressions obtained as $R \to \infty$. In this limit, we would expect the density profiles measured from the surface $\bar{\rho}_\pm(x) \equiv \rho_\pm(s)$ ($x \equiv s - R$) to approach those of the isolated planar double layer. The electroneutrality condition given by Eq. (2.12) then becomes

$$Q = -4\pi q_+ \int_0^\infty [\bar{\rho}_+(x) - \bar{\rho}_-(x)](R+x)^2 dx \qquad (2.20)$$

and the ionic contribution to the potential is

$$\psi_i(R) = 4\pi q_+ \int_0^\infty [\bar{\rho}_+(x) - \bar{\rho}_-(x)](R+x)dx$$
$$= \frac{-Q}{R} - 4\pi q_+ \int_0^\infty [\bar{\rho}_+(x) - \bar{\rho}_-(x)]x\, dx$$
$$+ \mathcal{O}(R^{-1}). \qquad (2.21)$$

The second line follows from the electroneutrality condition and the fact that the screening length of the double layer is finite, meaning that the integrals are dominated by regions $x \ll R$. Insertion of Eq. (2.21) into Eq. (2.11) yields an expression for the surface potential in the planar limit and we note that the result is identical to Eq. (2.4) for the capacitor at infinite separation.

Although there is no general bound on the derivative of the macroion surface potential with respect to surface charge, one can deduce bounds valid if certain conditions are met. For example, at least in the low coupling regime, we would expect monotonic ion profiles that satisfy the conditions

$$Q[\rho_+(s) - \rho_-(s)] \leqslant 0, \quad R \leqslant s \leqslant \infty, \qquad (2.22a)$$
$$[\rho'_+(s) - \rho'_-(s)] \leqslant 0, \quad R \leqslant s \leqslant \infty, \qquad (2.22b)$$

where the prime denotes differentiation with respect to Q. From the definition of $\psi_i(R)$ [cf. Eq. (2.11)] and Eq. (2.22a), it follows that

$$Q\psi_i(R) \leqslant 0 \qquad (2.23)$$

and the electroneutrality condition [Eq. (2.12)] yields

$$Q^2 \geqslant -4\pi Q q_+ \int_R^\infty [\rho_+(s) - \rho_-(s)]Rs\, ds$$
$$= -RQ\psi_i(R). \qquad (2.24)$$

Equations (2.24) and (2.11) immediately imply that

$$Q\psi(R) \geqslant 0, \qquad (2.25)$$

or that the surface potential and charge must have the same sign. Differentiating Eq. (2.12) and using the condition (2.22b), we obtain

$$1 = -4\pi q_+ \int_R^\infty [\rho'_+ (s) - \rho'_- (s)] s^2 ds$$

$$\geqslant -4\pi q_+ \int_R^\infty [\rho'_+ (s) - \rho'_- (s)] Rs\, ds$$

$$= -R\psi'_i(R), \qquad (2.26)$$

which together with Eq. (2.17) yields the bound

$$\frac{\partial \psi(R)}{\partial Q} \geqslant 0. \qquad (2.27)$$

We emphasize that this result is rigorous only when the assumptions (2.22) hold. However, from the form of the integral in Eq. (2.26), one can see that unless the short-range part of the ion profiles deviate very strongly from monotonicity, it is unlikely that the inequalities will be violated. This probably (in the absence of an exact theorem) explains why no disagreement with the planar limit of Eq. (2.27) has ever been found in computer simulations employing primitive model electrolytes.[4] It is possible, though, that even for primitive models Eq. (2.26) and consequently Eq. (2.27) could be violated at couplings strong enough to induce large charge oscillations.

III. CONSTANT SURFACE CHEMICAL POTENTIAL CASE

Here we consider the surface charge to be a fluctuating quantity and introduce a $(\mu_e, \mu, A, \mathscr{V}, T)$ ensemble, where μ_e is the chemical potential associated with adding a particle of charge e to a surface of area A. Also, μ is the chemical potential of the bulk electrolyte, T is the temperature, and $\mathscr{V}$ is the volume of the sample.

The partition function for this ensemble is of the form

$$\Xi(\mu_e, \mu, A, \mathscr{V}, T)$$
$$= \sum_{N_e} e^{\beta\mu_e N_e} \sum_N e^{\beta\mu N} \sum_K \exp[-\beta E_K(N_e, N, A, \mathscr{V})], \qquad (3.1)$$

where E_K represents the total internal energy including the interactions among all particles in the system. Of course, in the classical case, the sum on K can be written as an integral over phase space. From Eq. (3.1) it follows immediately that

$$\langle N_e \rangle = -\frac{\partial \Omega}{\partial \mu_e}, \qquad (3.2a)$$

$$\frac{\partial \langle N_e \rangle}{\partial \mu_e} = -\frac{\partial^2 \Omega}{\partial \mu_e^2} = \beta \langle (N_e - \langle N_e \rangle)^2 \rangle \geqslant 0, \qquad (3.2b)$$

where Ω is again the grand potential and all partial derivatives are taken holding μ, A, $\mathscr{V}$, and T fixed. If we let $\langle \sigma \rangle$ denote the average charge density on the surface, then $e\langle N_e \rangle = \langle \sigma \rangle A$ and it is clear that

$$\frac{1}{e} \frac{\partial \langle \sigma \rangle}{\partial \mu_e} \geqslant 0. \qquad (3.2c)$$

Now if the mean electrostatic potential of the surface is V, we can write the chemical potential μ_e in the general form

$$\mu_e = Ve + \mu_e^{\text{other}}, \qquad (3.3a)$$

where Ve is an electrostatic part and μ_e^{other} contains all other contributions. If we regard the charged particles on the surface as an interacting two-dimensional classical system, then μ_e^{other} can be divided into ideal plus excess contributions such that

$$\mu_e^{\text{other}} = \beta^{-1} \ln \Lambda^2 \frac{\langle N_e \rangle}{A} + \mu_e^{\text{ex}}, \qquad (3.3b)$$

where Λ is the usual thermal de Broglie wavelength. In general, the excess chemical potential will depend on the specific interactions among all particles. Employing Eqs. (3.2) and (3.3), we obtain the exact conditions

$$\frac{\partial \mu_e^{\text{ex}}}{\partial \langle N_e \rangle} + \frac{1}{\beta \langle N_e \rangle} + e \frac{\partial V}{\partial \langle N_e \rangle} \geqslant 0, \qquad (3.4a)$$

or equivalently

$$\frac{1}{e} \frac{\partial \mu_e^{\text{ex}}}{\partial \langle \sigma \rangle} + \frac{1}{\beta e \langle \sigma \rangle} + \frac{\partial V}{\partial \langle \sigma \rangle} \geqslant 0. \qquad (3.4b)$$

As for the constant charge ensemble considered above, it is obvious that these results do not determine the sign of $\partial V/\partial \langle \sigma \rangle$.

In constant charge double layer theory (cf. Sec. II), it is usual to consider that the charge density is spread uniformly over the surface and remains undistorted by the presence of mobile ions in the double layer. In order to generate comparable conditions here, we must choose μ_e^{other} such that the charged particles on the surface form a two-dimensional fluid and allow the electrolyte to see only a uniform surface charge density rather than individual particles. For this model, it is clear that the relationship between $\langle \sigma \rangle$ and V will be independent of the interactions among the particles on the surface. Choosing an ideal gas (i.e., $\mu_e^{\text{ex}} = 0$), we obtain the condition

$$\beta e \langle \sigma \rangle \frac{\partial V}{\partial \langle \sigma \rangle} \geqslant -1. \qquad (3.5)$$

This bound is obviously satisfied if $\partial V/\partial \langle \sigma \rangle$ is positive. For the ideal gas model, it is also apparent that if $\partial V/\partial \langle \sigma \rangle$ is negative, then stable systems can always be found by simply decreasing the charge and increasing the density of the surface particles while keeping $\langle \sigma \rangle$ fixed.

IV. QUESTIONS CONCERNING THE METHOD OF LANDAU AND LIFSHITZ

As mentioned above, Landau and Lifshitz[1] used thermodynamic stability arguments in order to conclude that the derivative of the surface potential with respect to surface charge must be positive. We are unable to understand their proof and the following is a brief discussion of our problem. In order to reduce confusion, in this section we will employ the notation of Landau and Lifshitz and attempt to follow their arguments as closely as we can. Also, we shall only consider the mathematical steps that follow from their axioms and we shall not address broader questions concerning the validity of their particular stability approach.

Landau and Lifshitz consider two oppositely charged conductors characterized by electrostatic potentials ϕ_1 and ϕ_2, and total surfaces charges e_1 and e_2. They then introduce (cf. Secs. 10 and 24 of Ref. 1) two thermodynamic potentials

$\tilde{g}_s$ and g_s (the subscript s indicates that only surface parts are included) which at fixed temperature and pressure are related by [cf. Eq. (24.6) of Ref. 1]

$$\tilde{g}_s - g_s = -e\phi, \tag{4.1}$$

where $\phi = \phi_1 - \phi_2$ is the total potential difference between oppositely charged plates (in the notation used above $\phi \equiv 2V$) and $e_1 = -e_2 = e$. According to Landau and Lifshitz, at equilibrium $\tilde{g}_s$ must be a minimum with respect to charge at fixed potential and g_s must be a minimum with respect to potential at fixed charge. Mathematically, this implies that

$$\left(\frac{\partial \tilde{g}_s}{\partial e}\right)_\phi = 0 \quad \text{(equilibrium)}, \tag{4.2a}$$

$$\left(\frac{\partial^2 \tilde{g}_s}{\partial e^2}\right)_\phi \geqslant 0 \quad \text{(equilibrium)}, \tag{4.2b}$$

where we indicate explicitly that the partial derivatives are taken at constant ϕ and that the relationships hold only when evaluated at equilibrium state points. It is understood that the pressure, temperature, and surface area are also held fixed. Differentiation of Eq. (4.1) with respect to e holding ϕ fixed yields

$$\left(\frac{\partial \tilde{g}_s}{\partial e}\right)_\phi - \left(\frac{\partial g_s}{\partial e}\right)_\phi = -\phi, \tag{4.3a}$$

$$\left(\frac{\partial^2 \tilde{g}_s}{\partial e^2}\right)_\phi - \left(\frac{\partial^2 g_s}{\partial e^2}\right)_\phi = 0, \tag{4.3b}$$

and these together with Eqs (4.2) give the equilibrium conditions

$$\left(\frac{\partial g_s}{\partial e}\right)_\phi = \phi \quad \text{(equilibrium)}, \tag{4.4a}$$

$$\left(\frac{\partial^2 g_s}{\partial e^2}\right)_\phi = \left(\frac{\partial^2 \tilde{g}_s}{\partial e^2}\right)_\phi \geqslant 0 \quad \text{(equilibrium)}. \tag{4.4b}$$

To complete their analysis, it appears to us that Landau and Lifshitz now simply differentiate Eq. (4.4a) without holding ϕ fixed to obtain

$$\frac{\partial}{\partial e}\left(\frac{\partial g_s}{\partial e}\right)_\phi = \frac{\partial \phi}{\partial e} \quad \text{(equilibrium)} \tag{4.5}$$

and then use Eq. (4.4b) to conclude that

$$\frac{\partial \phi}{\partial e} \geqslant 0 \quad \text{(equilibrium)}. \tag{4.6}$$

However, we cannot understand how this can be correct. The equilibrium condition given by Eq. (4.4b) only holds if the second partial derivative is first taken at constant potential and then evaluated at equilibrium values of ϕ and e. To obtain Eq. (4.5), the first derivative is taken at constant ϕ, evaluated at equilibrium, and then differentiated along the equilibrium path in the $e - \phi$ plane. Thus the left-hand side of Eq. (4.5) is not equivalent to the left-hand side of Eq. (4.4b). We are unable to show that the left-hand side of Eq.

(4.5) must be greater than or equal to zero and hence we cannot complete the Landau–Lifshitz "proof." Indeed, a more detailed mathematical treatment shows that the sign of $\partial \phi / \partial e$ (along the equilibrium path) will depend on the sign of the cross derivative $\partial^2 \tilde{g}_s / \partial \phi \partial e$, which is not determined by equilibrium conditions.

V. CONCLUSION

The principal conclusion of this paper is that we can find no valid proof that for an isolated double layer the derivative of the surface potential with respect to surface charge $\partial V / \partial \sigma$ must be positive. A bound, or more precisely the lack of one for this quantity is important both experimentally and theoretically. For example, that the hypernetted-chain (HNC) theory sometimes predicts negative values has been taken as an indication of serious qualitative problems with that approximation, whereas the present work suggests that the failure may only be quantitative. Indeed, we expect that future simulations will give negative results for systems where strong coupling produces highly structured double layers. We note further that the sign of $\partial V / \partial \sigma$ has also been controversial in the theory of dielectric capacitors.[6]

We have shown that a previous statistical mechanical proof that $\partial V / \partial \sigma$ is positive[2,3] is in error and that correct statistical mechanical analyses do not determine the sign of $\partial V / \partial \sigma$. In addition, the much earlier thermodynamic argument of Landau and Lifshitz appears to us to be mathematically unsound.

In our statistical mechanical analysis, we have considered both constant and fluctuating (i.e., fixed surface chemical potential) charge cases and some useful exact bounds are obtained. These are given by Eq. (2.9) for planar capacitors, Eq. (2.19) for charged spheres, and Eqs. (3.4) for the constant surface chemical potential ensemble. In all cases, these conditions can be satisfied by both positive and negative values of the derivative of the potential with respect to charge.

ACKNOWLEDGMENTS

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