2-17-1983

On Surface Properties of the One-component Plasma

M-L Rosinberg
I'Universite Pierre et Marie Curie

J-P Badiali
I'Universite Pierre et Marie Curie

Jerry Goodisman
Syracuse University

On surface properties of the one-component plasma

1983 J. Phys. C: Solid State Phys. 16 4487

(http://iopscience.iop.org/0022-3719/16/22/021)

J. Phys. C: Solid State Phys., **16** (1983) 4487–4503. Printed in Great Britain

On surface properties of the one-component plasma

M-L Rosinberg†, J-P Badiali† and J Goodisman‡

† Groupe de Recherche no 4 du CNRS, Physique des Liquides et Electrochimie, Associé à l'Université Pierre et Marie Curie, 4 place Jussieu, 75230 Paris Cedex 05, France

‡ Department of Chemistry, Syracuse University, Syracuse, New York 13210, USA

Received 20 October 1982, in final form 17 February 1983

Abstract. We consider a plasma of point ions in the presence of a non-uniform neutralising background. This background, the source of an external field, may have some of its parameters (density, form of surface profile, etc) modified, as long as the total charge is maintained. By considering such modifications in the context of the density-functional formalism for the ions, we prove sum rules giving the first and second moments of the ion density $\rho(z)$ in terms of other properties (bulk pressure and temperature derivative of surface tension).

The Poisson–Boltzmann functional is considered in detail. We show that the first and second moment conditions on $\rho(z)$ are verified. We calculate $\rho(z)$ exactly for this system, and also perform variational calculations: comparison shows the importance of respecting the asymptotic behaviour of $\rho(z)$. Variational calculations have been performed, using the density-functional formalism in the square-gradient approximation, for systems with plasma parameter Γ from 1 to 10. For $\Gamma > 3$, important oscillations appear in the profile, as shown by recent Monte Carlo calculations. The profiles calculated variationally also show increasing oscillations, but are not in good agreement with the Monte Carlo results. The surface energies are poor even for $\Gamma = 1$ showing the inadequacy of the square-gradient expansion for this system.

1. Introduction

There has been a growing interest in the past few years in the surface properties of Coulombic systems such as molten salts, electrolyte solutions and liquid metals. The one-component plasma (OCP) is a simple and useful prototype of such Coulombic systems, whose bulk properties are now well established over a wide domain of temperature and concentration. The density profile and other surface properties, such as surface energy and surface tension, have recently received great attention (Ballone *et al* 1981a, Evans and Hasegawa 1981, Jancovici 1982, Badiali and Rosinberg 1982) and Monte Carlo computations are now available (Badiali *et al* 1983). In the case where the OCP is in contact with an impenetrable wall, comparison has been made with predictions of analytical methods such as the mean spherical approximation and the hypernetted chain equation (Badiali *et al* 1983). In this paper we calculate, for small values of the plasma parameter, the density profile, the surface tension, and the surface energy of the OCP in a non-uniform background. This is done using the free-energy density functional formalism (FDFF). In § 2 we give several general thermodynamic relations for systems of this type which can be derived quite simply in the FDFF. They follow from the fact that

certain parameters of the background can be modified arbitrarily. Two of these are the classical analogues of the sum rules derived by Vannimenus and Budd (1974) for the jellium model of a metal surface: one is for the surface potential and the other for the rate of change of surface tension with bulk density.

These theorems are valid for any functional of the free-energy and this is illustrated in § 3 by the behaviour of the exact solution of the Poisson–Boltzmann equation for the semi-infinite OCP. In § 4, we consider variational calculations in the FDFF; instead of solving the equation for the profile directly, one may seek an approximate solution in the form of a parametrised trial function. We discuss the implications of our theorems for such an approach. The variational calculations are done by minimisation of the free-energy density functional in the square-gradient approximation. We calculate the surface density profile, the surface tension and the surface energy. Comparison with Monte Carlo results and concluding remarks are given in § 5.

2. General theorems

We consiser a classical fluid of point ions with charge Ze and bulk density ρ_b at temperature T, embedded in a non-uniform neutralising background of density $n(z)$ such that $n(z) \to n_b$ (bulk density, $n_b = Z\rho_b$) for $z \to -\infty$ and $n(z) \to 0$ for $z \to +\infty$. This system is characterised by the plasma coupling parameter $\Gamma = (Ze)^2/akT$ where k is the Boltzmann constant and $a = (4\pi\rho_b/3)^{-1/3}$ is the ion sphere radius. Following the pioneering work of Hohenberg and Kohn (1964) and Mermin (1965) one can show that the free energy of the system can be obtained from the functional

$$\Omega[\rho] = G[\rho] + \frac{e}{2}\int d\boldsymbol{r}\, \varphi(\boldsymbol{r})(Z\rho(\boldsymbol{r}) - n(\boldsymbol{r})) - \mu \int d\boldsymbol{r}\, \rho(\boldsymbol{r}) \tag{1}$$

where a separation has been made (Evans and Sluckin 1980) between Coulombic and non-Coulombic contributions to the free energy. $\varphi(\boldsymbol{r})$ is the electrostatic potential related to $\rho(\boldsymbol{r})$ and $n(\boldsymbol{r})$ by the Poisson equation. The functional $G[\rho]$ is a unique functional of $\rho(\boldsymbol{r})$ and μ is the position-independent chemical potential of the particles. The minimum of $\Omega[\rho]$ is the grand potential of the system and the equilibrium density satisfies the Euler–Lagrange equation (Evans and Hasegawa 1981)

$$\mu = \delta G[\rho]/\delta\rho(\boldsymbol{r}) + Ze\varphi(\boldsymbol{r}). \tag{2}$$

We now consider general theorems which are consequences of this approach. Since this model is quite similar to the uniform background model in the inhomogeneous electron-gas theory, some of these will be analogous to the sum rules derived in this case by Vannimenus and Budd (1974). However, one here considers changes in the free energy of ions instead of changes in the internal energy of electrons.

Consider an infinitesimal modification $\delta n(\boldsymbol{r})$ of the background profile such that the total number N of particles is unchanged. The modification $\delta n(\boldsymbol{r})$ will cause a change in ionic density $\delta\rho(\boldsymbol{r})$ and possibly a shift in the chemical potential $\delta\mu$. To first order, the change in the grand potential is

$$\delta\Omega = \int \frac{\delta G}{\delta\rho}\,\delta\rho(\boldsymbol{r})\, d\boldsymbol{r} + e\int d\boldsymbol{r}\, \varphi(\boldsymbol{r})[Z\delta\rho(\boldsymbol{r}) - \delta n(\boldsymbol{r})] - N\delta\mu \tag{3}$$

where N is the total number of ions, $N = \int \rho(\boldsymbol{r})\, d\boldsymbol{r}$.

Using the equilibrium condition (2) and the fact that $\int \delta\rho(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r} = 0$ we get

$$\delta\Omega = -e\int \mathrm{d}\boldsymbol{r}\,\varphi(\boldsymbol{r})\delta n(\boldsymbol{r}) - N\delta\mu. \tag{4}$$

In addition, at the minimum of $\Omega[\rho]$ one has

$$\Omega = F_0 + \gamma\tilde{A} - \mu N \tag{5}$$

where F_0 is the free energy for the homogeneous N-particle system, $\tilde{A}$ is the surface area, and γ the surface tension. For any change holding $\tilde{A}$ and N constant, we have

$$\delta\Omega = \delta F_0 + \tilde{A}\delta\gamma - N\delta\mu. \tag{6}$$

One can now compare this expression for $\delta\Omega$ with the expression of the form (4) to deduce interesting relations.

Consider first the case of the semi-infinite OCP: the neutralising background of our system is a slab of density n_b extending from $z = -L$ to $z = 0$ with the faces normal to the z axis each having area A (i.e. in the limit $L \to \infty$ $n(z) = n_b\theta(-z)$ where $\theta(z)$ is the Heaviside function). The area is supposed to be large enough so all properties are uniform in the x and y directions. Following Budd and Vannimenus we consider the change $\delta\Omega$ associated with stretching the slab so that it extends from $z = -L$ to $z = \delta L$ while holding A, T and N constant. It is straightforward to show that the electrostatic term in (4) becomes

$$-e\int \mathrm{d}\boldsymbol{r}\,\varphi(\boldsymbol{r})\delta n(\boldsymbol{r}) = -AL\delta n_b\Big(e[\varphi(0) - \varphi(-L/2)] - \frac{2e}{L}\int_{-L/2}^{0}[\varphi(z) - \varphi(-L/2)]\,\mathrm{d}z\Big) \tag{7}$$

where the new background density is $n_b - \delta n_b$ such that to first order $L\delta n_b = n_b\delta L$, and $\varphi(-L/2)$ is the potential in the centre of the slab. On the other hand, equation (6) becomes (with $\tilde{A} = 2A$ since there are two surfaces)

$$\delta\Omega = -(\partial F_0/\partial\rho_b)_T\delta\rho_b - 2A(\partial\gamma/\partial\rho_b)_T\delta\rho_b - N\delta\mu$$

where $\delta\rho_b$ is $\delta n_b/Z$ and $(\partial\gamma/\partial\rho_b)_T$ is the derivative of surface tension with bulk ion density. Since

$$\rho_b(\partial F_0/\partial\rho_b)_T = NP/\rho_b$$

where P is the bulk thermodynamic pressure, we get

$$\delta\Omega = -ALZ^{-1}\delta n_b\left[\frac{P}{\rho_b} + \frac{2}{L}\left(\frac{\partial\gamma}{\partial\rho_b}\right)_T\right] - N\delta\mu \tag{8}$$

where $AL\rho_b = N$ has been used.

Then, inserting (7) in (4), and comparing the expression for $\delta\Omega$ with that of (8), we have

$$Le[\varphi(0) - \varphi(-L/2)] - 2e\int_{-L/2}^{0}[\varphi(z) - \varphi(-L/2)]\,\mathrm{d}z = Z^{-1}\left[\frac{LP}{\rho_b} + 2\left(\frac{\partial\gamma}{\partial\rho_b}\right)_T\right].$$

Each member consists of a 'volume' term (proportional to L) and a surface term, which must be separately equal, so that

$$P = \rho_b Ze[\varphi(0) - \varphi(-\infty)] \tag{9a}$$

$$\left(\frac{\partial\gamma}{\partial\rho_b}\right)_T = -Ze\int_{-\infty}^{0}[\varphi(z)-\varphi(-\infty)]\,dz \tag{9b}$$

where it has been assumed that $\varphi(-L/2)$ tends toward its asymptotic value $\varphi(-\infty)$ faster than $1/L$. Equation (9*a*) has been already given by Ballone *et al* (1981b) and provides an exact relation between the potential difference $[\varphi(0)-\varphi(-\infty)]$, which is a surface property, and the bulk quantity P. This relation can also easily be derived by a direct integration of the first equation of the BGY hierachy. As noted by Ballone *et al* (1981a) the total potential drop for this system, $[\varphi(\infty)-\varphi(-\infty)]$, is divergent because of the z^{-2} asymptotic behaviour of $\rho(z)$ in the absence of a finite background density for $z>0$ (the density ρ_v of the vapour phase is strictly 0 in our system; in a real system, where ρ_v is small but not vanishing, the total potential drop of course remains finite).

On the other hand, equation (9*b*) is a new result and can also be written, after insertion of the Poisson equation and partial integration, as

$$\left(\frac{\partial\gamma}{\partial\rho_b}\right)_T = 2\pi(Ze)^2\int_{-\infty}^{0}z^2[\rho(z)-\rho_b]\,dz. \tag{10}$$

This equation, at least theoretically, provides a way of calculating the surface tension directly from the density profile $\rho(z)$. It relates the change of γ with bulk density to the second moment of the ionic distribution. By comparison, equation (9*a*) is a condition on the first moment since integration of the Poisson equation gives

$$\varphi(0)-\varphi(-\infty) = 4\pi(Ze)\int_{-\infty}^{0}z[\rho(z)-\rho_b]\,dz. \tag{11}$$

Note that the relations (9) are valid when $n(z)$ is a step function. However, from (4) and (6), similar results can be derived when the background profile has a more general shape.

In addition to (10), there exists a relation between $(\partial\gamma/\partial\rho_b)_T$ and γ itself. One can show easily by scaling arguments that the surface tension can be written

$$\gamma = a\rho_b kTf(\Gamma,\tilde{\alpha}) \tag{12a}$$

where $\tilde{\alpha}=\alpha a$, with α representing the parameters $\alpha_1\ldots\alpha_m$ specifying the background profile. For a step profile one has simply

$$\gamma = a\rho_b kTf(\Gamma) \tag{12b}$$

so that, using the definition of Γ, one finds by direct differentiation

$$\gamma = \rho_b(\partial\gamma/\partial\rho_b)_T + \tfrac{1}{3}T(\partial\gamma/\partial T)_{\rho_b} \tag{13a}$$

Consider now the case of an arbitrary background profile $n(z)$ depending on a parameter α: (13*a*) no longer holds, but, differentiating (12*a*) with α constant, we find

$$\gamma-\rho_b\left(\frac{\partial\gamma}{\partial\rho_b}\right)_T-\frac{T}{3}\left(\frac{\partial\gamma}{\partial T}\right)_{\rho_b} = \frac{\gamma}{3}\left(\frac{\partial\ln f}{\partial\ln\tilde{\alpha}}\right)_\Gamma. \tag{13b}$$

Let us consider the effect on the surface tension of a change of the parameter α, keeping $\tilde{A}$ and N constant. According to (6) and (4)

$$\frac{\partial F_0}{\partial\alpha}+\tilde{A}\frac{\partial\gamma}{\partial\alpha}-\frac{\partial\mu}{\partial\alpha}N = -e\int d\boldsymbol{r}\,\varphi(\boldsymbol{r})\frac{\partial n(\boldsymbol{r})}{\partial\alpha}-\frac{\partial\mu}{\partial\alpha}N.$$

If the parameter α affects $n(z)$ only in the region of the surface, F_0 and μ are unchanged, so that

$$\frac{\partial \gamma}{\partial \alpha} = -e \int \frac{\partial n(z)}{\partial \alpha} \varphi(z)\, \mathrm{d}z. \tag{14}$$

The effect of a non-Coulombic interaction between the ions and the background can also be considered. Suppose that we have in the RHS of (1) the extra term

$$\int \mathrm{d}\boldsymbol{r}\, \mathrm{d}\boldsymbol{r}'\, \rho(\boldsymbol{r})\, n(\boldsymbol{r}')\, U(\boldsymbol{r}, \boldsymbol{r}', \lambda)$$

where λ represents a set of parameters $\{\lambda_1 \ldots \lambda_n\}$. If λ is modified, the condition of minimisation of Ω and (6) gives (n is unchanged)

$$\frac{\partial F_0}{\partial \lambda} + \bar{A} \frac{\partial \gamma}{\partial \lambda} = \int \mathrm{d}\boldsymbol{r}_1\, \mathrm{d}\boldsymbol{r}_2 \rho(\boldsymbol{r}_1) n(\boldsymbol{r}_2) \frac{\delta U(\boldsymbol{r}_1 \boldsymbol{r}_2; \lambda)}{\partial \lambda}.$$

For example, if λ is the radius of the Ashcroft pseudopotential, $U = Ze^2 r^{-1}\, \theta(\lambda - r)$, $\partial F_0 / \partial \lambda$ is easily calculated and one finds

$$\frac{\partial \gamma}{\partial \lambda} = (Ze)^2 \int \mathrm{d}z\, \mathrm{d}\boldsymbol{r}' [n(z)\rho(z') - n_b \rho_b \theta(-z')]\, |\boldsymbol{r} - \boldsymbol{r}'|^{-1} \delta(|\boldsymbol{r} - \boldsymbol{r}'| - \lambda).$$

Finally, the effect of a non-Coulombic external potential can be investigated; it adds to Ω a term

$$\int \mathrm{d}\boldsymbol{r}\, \rho(\boldsymbol{r}) V_{\mathrm{ext}}(\boldsymbol{r}; \lambda_1 \ldots \lambda_n).$$

If the parameters λ_i can be varied, e.g. to change the 'softness' of a wall, we have

$$\frac{\partial \gamma}{\partial \lambda_i} = \int \mathrm{d}\boldsymbol{r}\, \rho(\boldsymbol{r}) \frac{\partial V_{\mathrm{ext}}(\boldsymbol{r}; \lambda_1 \ldots \lambda_n)}{\partial \lambda_i}. \tag{15}$$

The relations (9) and (13)–(15) are exact regardless of the form of the functional, so do not provide a test of its validity. Note that P and $(\partial \gamma / \partial \rho_b)_T$ are supposed to be calculated with the same functional as the moments of the profile in (9) and (10). To test the functional, one requires an alternative route to the quantities considered, such as a calculation of $(\partial \gamma / \partial \rho_b)_T$ from the Hamiltonian of the system that the functional is supposed to describe. It may also be noted that the theorems require for their proof an arbitrarily modifiable external field. For a metal, where both electrons and ions can rearrange simultaneously, such theorems do not exist. Indeed, in this case, one has to consider a functional which depends both on $\rho(z)$ and $n(z)$ (Evans and Hasegawa 1981). Ω must be a minimum with respect to these two profiles, hence $\delta\Omega = 0$. Equation (3) no longer holds and the theorems cannot be derived.

In the remainder of this work we are principally concerned with the relations (9) and (13). We shall use them as a test of a correct minimisation of the functional Ω.

3. The local approximation and the Poisson–Boltzmann equation

The local approximation consists of taking $G[\rho]$ in equation (1) to be given by

$$G[\rho] = \int g(\rho(\boldsymbol{r}))\, \mathrm{d}\boldsymbol{r} \tag{16}$$

where $g(\rho(\boldsymbol{r}))$ depends on $\rho(\boldsymbol{r})$ and represents the free-energy density of a homogeneous

OCP of density $\rho(\boldsymbol{r})$. The surface tension may be defined as the surface excess free energy $(\Omega - \Omega_b)/A$, i.e.

$$\gamma = \int [g(\rho) - g(\rho_b)\theta(-z)]\, dz + \frac{e}{2}\int (Z\rho - n)\varphi(z)\, dz. \tag{17}$$

After integration by parts and use of the Euler–Lagrange equation (2) we get

$$\gamma = e\int \varphi(z) z \frac{dn}{dz} dz - e\int (Z\rho - n)\varphi(z)\, dz. \tag{18}$$

Thus γ can be calculated without explicit reference to the nature of $g(\rho)$; $\rho(z)$ is, however, determined from (2), in which g plays a role. When $n(z)$ is a step, the first integral in (18) vanishes.

The simplest local approximation, which should be valid for low densities, is obtained when one supposes that $g(\rho(\boldsymbol{r}))$ in (16) is given by the free energy of a non-interacting gas. Then one gets (Sluckin 1981, Ballone *et al* 1981a) immediately from (2)

$$\rho(z) = \rho_b \exp[-(Ze/kT)\varphi(z)] \tag{19}$$

where the origin of the potential is at $z = -\infty$. Equation (19), together with the Poisson equation, yields the Poisson–Boltzmann equation which, if $n(z)$ is a step, is

$$\frac{d}{dz}\left(\frac{\rho'(z)}{\rho(z)}\right) = \kappa^2\left(\frac{\rho(z)}{\rho_b} - \theta(-z)\right) \tag{20}$$

where $\rho'(z) = d\rho(z)/dz$, and $\kappa = (4\pi\rho_b Z^2 e^2/kT)^{1/2}$ is the reciprocal Debye–Huckel length.

In terms of the reduced length $u = \kappa z$ and $\tilde{\rho}(u) = \rho(u)/\rho_b$, (20) simply reads

$$\frac{d}{du}\left(\frac{\tilde{\rho}'(u)}{\tilde{\rho}(u)}\right) = \tilde{\rho}(u) - \theta(-u). \tag{21}$$

For $u > 0$ this equation can be solved analytically (Ballone *et al* 1981a) to give

$$\tilde{\rho}(u) = 2/[u + (2/\tilde{\rho}(0))^{1/2}]^2. \tag{22}$$

The value of $\tilde{\rho}(0)$ can readily be obtained after some simple manipulations. From (21) we have

$$\int_{-\infty}^{u} \frac{\tilde{\rho}'(\nu)}{\tilde{\rho}(\nu)}\frac{d}{d\nu}\left(\frac{\tilde{\rho}'(\nu)}{\tilde{\rho}(\nu)}\right) d\nu = \frac{1}{2}\left(\frac{\tilde{\rho}'(u)}{\tilde{\rho}(u)}\right)^2 = \begin{cases} \tilde{\rho}(u) - 1 - \ln\tilde{\rho}(u) & u < 0 \\ \tilde{\rho}(u) - 1 - \ln\tilde{\rho}(0) & u > 0 \end{cases} \tag{23}$$

so that

$$\tfrac{1}{2}(\tilde{\rho}'(0)/\tilde{\rho}(0))^2 = \tilde{\rho}(0) - 1 - \ln\tilde{\rho}(0). \tag{24}$$

Using (22) to evaluate $\tilde{\rho}'(0)$, since $\tilde{\rho}$ and $\tilde{\rho}'$ are continuous at $u = 0$, we get the exact result

$$\tilde{\rho}(0) = 1/e \qquad (e = 2.718\ldots). \tag{25}$$

With this value it is clear that equation (9*a*) is satisfied since in the Poisson–Boltzmann theory $P = \rho_b kT$ and from equation (19) $\varphi(0) = -(kT/Ze)\ln[\rho(0)/\rho_b] = (kT/Ze)\ln e$. In fact, (9*a*) could have been used to find $\rho(0)$.

Let us now consider the verification of equation (9*b*). Within the Poisson–Boltzmann

approximation, the surface tension for a step background profile is simply

$$\gamma = -\frac{1}{4\pi}\int_{-\infty}^{+\infty} \mathrm{d}z \left(\frac{\mathrm{d}\varphi}{\mathrm{d}z}\right)^2 \tag{26}$$

which can be written, with the help of equation (19), as

$$\gamma = -\frac{\kappa}{4\pi}\left(\frac{kT}{Ze}\right)^2 \int_{-\infty}^{+\infty} \mathrm{d}u \left(\frac{\tilde{\rho}'(u)}{\tilde{\rho}(u)}\right)^2. \tag{27}$$

By integrating equation (23) we get

$$\frac{1}{2}\int_{-\infty}^{\infty}\left(\frac{\tilde{\rho}'(\nu)}{\tilde{\rho}(\nu)}\right)^2 \mathrm{d}\nu = \int_{-\infty}^{0}[\tilde{\rho}(\nu)-1]\,\mathrm{d}\nu - \int_{-\infty}^{0}\ln\tilde{\rho}(\nu)\,\mathrm{d}\nu + \int_{0}^{\infty}\tilde{\rho}(\nu)\,\mathrm{d}\nu$$

$$= -\int_{-\infty}^{0}\ln\tilde{\rho}(\nu)\,\mathrm{d}\nu \tag{28}$$

where we have used equation (25) and the overall electroneutrality condition. Hence

$$\gamma = \frac{\kappa}{2\pi}\left(\frac{kT}{Ze}\right)^2 \int_{-\infty}^{0}\ln\tilde{\rho}(u)\,\mathrm{d}u = \frac{2\rho_b akT}{(3\Gamma)^{1/2}}\int_{-\infty}^{0}\ln\tilde{\rho}(u)\,\mathrm{d}u. \tag{29}$$

Therefore we get, using the definition of κ,

$$\left(\frac{\partial\gamma}{\partial\rho_b}\right)_T = \frac{1}{4\pi}\left(\frac{kT}{Ze}\right)^2\frac{\kappa}{\rho}\int_{-\infty}^{0}\ln\tilde{\rho}(u)\,\mathrm{d}u = \frac{kT}{\kappa}\int_{-\infty}^{0}\left(-\frac{Ze}{kT}\varphi(u)\right)\mathrm{d}u \tag{30}$$

which clearly satisfies equation (9*b*).

For $z < 0$, the profile can be obtained only numerically. A method for generating it is given in Appendix 1. By inserting our solution into (29) we get γ (compare Ballone *et al* (1981a)) in the form of (12*b*):

$$\frac{\gamma}{a\rho_b kT} = -2.164\,(3\Gamma)^{-1/2}. \tag{31}$$

The excess surface energy U_s is given by the thermodynamic relation

$$U_s = \gamma - T(\partial\gamma/\partial T)_V = \gamma - T(\partial\gamma/\partial T)_{\rho_b} = -2\gamma + 3\rho_b(\partial\gamma/\partial\rho_b)_T. \tag{32}$$

The use of $(\partial\gamma/\partial T)_{\rho_b}$ instead of $(\partial\gamma/\partial T)_V$ is discussed after (36). Equation (13*a*) has been used in deriving the second part of equation (32). It follows from the form (12*b*) with f proportional to $\Gamma^{-1/2}$ that (Ballone *et al* 1981a).

$$U_s = -\tfrac{1}{2}\gamma \tag{33}$$

which can be also obtained by the direct definition of the surface energy.

More generally equation (9*a*) can be used in order to get the exact value of $\tilde{\rho}(0)$ in the local approximation, for any free energy density $g(\rho)$. According to equation (2) we have

$$\mu = \frac{\mathrm{d}g[\rho(z)]}{\mathrm{d}\rho} + Ze\varphi(z)$$

and hence, using (9*a*),

$$(\mathrm{d}g/\mathrm{d}\rho)_{z=0} = \mu - Ze\varphi(0) = \mu - P/\rho_b. \tag{34}$$

For the homogeneous sytem, $z \to -\infty$

$$\mu = \left(\frac{dg}{d\rho}\right)_{z=-\infty} \qquad \text{and} \qquad \frac{P}{\rho_b kT} = \rho_b \frac{d}{d\rho}\left(\frac{g(\rho)}{\rho kT}\right)_{z=-\infty}.$$

Inserting these formulas into (34) we find

$$(dg/d\rho)_{z=0} = g(\rho_b)/\rho_b. \tag{35}$$

If g is known for the homogeneous system as a function of ρ or Γ, both sides of the equation are calculable. Then one inserts the bulk density in the expression $g(\rho)/\rho$ and finds the density for which $dg/d\rho$ is equal to it. This is the value of $\rho(z)$ for $z = 0$.

For example, when $1 \leqslant \Gamma \leqslant 160$, Slattery *et al* (1980) have given an expression which fits very well the Monte Carlo results for the free-energy density of the bulk OCP

$$g(\rho)/\rho kT = -0.89752\,\Gamma + 3.78176\,\Gamma^{1/4} - 0.71816\,\Gamma^{1/4} + 2.19951 \ln \Gamma - 3.30108. \tag{36a}$$

In the weak-coupling limit $0.1 \leqslant \Gamma \leqslant 1$ we have derived

$$g(\rho)/\rho kT = -0.64986 - 0.33676\,\Gamma - 0.19797\,\Gamma^2 + 0.04929\,\Gamma^3 + 3.012285 \ln \Gamma \tag{36b}$$

by numerical integration for the internal energy (for $0.1 \leqslant \Gamma \leqslant 0.6$ we have used the HNC results and for $0.6 \leqslant \Gamma \leqslant 1$ the Monte Carlo results). With the use of equations (36) in equation (35) we find, for a given value of $\Gamma_b = \Gamma(z \to -\infty)$, $\Gamma(z = 0)$ and hence $\tilde{\rho}(0)$. Results are shown in table 1. The decrease of $\tilde{\rho}(0)$ with Γ, corresponding to a displacement of the ion profile into the jellium and implying oscillations for $z < 0$, is to be noted.

Table 1. Exact values of $\tilde{\rho}(0)$ for OCP profile with no gradients.

Γ	$\tilde{\rho}(0)$
$\ll 1$	0.368
1	0.354
2	0.329
3	0.276

As noted after equation (32), the thermodynamic formula for U_s in terms of γ requires the temperature derivative of γ with V constant, whereas we have taken the derivative at constant ρ_b. To justify this, we note that we consider a system of N positive ions in a volume V ($N \to \infty$, $V \to \infty$, but N/V finite) and in the presence of a neutralising background whose rigidity is maintained by some external constraint. When the temperature T varies the background is not affected and hence the bulk value n_b remains unchanged. Since electrostatic considerations require that $\rho_b = Zn_b$, ρ_b is also constant. It may be noted that in the recent Monte Carlo computations (Badiali *et al* 1983) the thermodynamic limit of the finite physical system is supposed to be taken as follows: Consider N ions in a spherical volume $V = 4\pi R^3/3$, at the centre of which is a sphere of radius R_0 containing neutralising charge at density n_b, so $4\pi R_0^3 n_b/3 = ZN$. Then, as V and N become infinite, the ratio R_0/R is to be held constant. With the constancy of N/V this implies the constancy of ZN/R_0^3 and hence n_b. On the other hand, if the profile of the neutralising background is not a step, ambiguities arise.

In the local approximation it is easy to verify that $\gamma - T(\partial\gamma/\partial T)_{\rho_b}$ correctly gives U_s since the surface tension is given by (17). Now $g(\rho)$, the free-energy density of the homogeneous system of density ρ, is related to the energy density of such a system $u(\rho)$ by

$$u(\rho) = g(\rho) - T(\partial g(\rho)/\partial T). \tag{37}$$

Therefore

$$\gamma - T(\partial\gamma/\partial T)_{\rho_b} = \int [u(\rho) - u(\rho_b)\,\theta(-z)]\,\mathrm{d}z + \frac{e}{2}\int (Z\rho - n)\,\varphi(z)\,\mathrm{d}z$$

which is clearly U_s. Although there is a T dependence through ρ, terms in $(\partial\rho/\partial T)(\delta\Omega/\delta\rho)$ vanish because the minimisation process makes $\delta\Omega/\delta\rho$ vanish.

4. The square-gradient approximation

The simplest improvement to the local approximation is to add a square-gradient term to the expression for $G[\rho]$:

$$G[\rho] = \int \mathrm{d}\boldsymbol{r}\,[g(\rho(r)) + g_2(\rho(r))\,(\nabla\rho(r))^2]. \tag{38}$$

In the limit where the ionic density varies slowly and exhibits only small departure from the bulk value ρ, it can be shown (Evans 1979) that the quantity $g_2(\rho(r))$ is determined by the second moment of the direct correlation function $c(r)$ of the homogeneous OCP. More precisely

$$g_2(\rho) = -\tfrac{1}{2}kT\,\alpha(\rho)$$

where $\alpha(\rho)$ is the coefficient of q^2 in the expansion of the non-Coulombic part of $c(q)$, the Fourier transform of $c(r)$. Following the scheme used by Evans and Sluckin (1981) to calculate $c(q)$ it can be shown that

$$\rho\alpha(\rho) = \frac{-\Gamma a^2}{264}\,\kappa_0^4(\Gamma) \tag{39}$$

where $\kappa_0(\Gamma)$ is a dimensionless parameter determined by fitting the isothermal compressibility of the OCP. Using the fits of (36) we have

$$\begin{aligned} \kappa_0^2(\Gamma) &= -0.0246 + 0.89802\,\Gamma + 1.31982\,\Gamma^2 - 0.59154\,\Gamma^3 && 0.1 \leqslant \Gamma \leqslant 1 \\ \kappa_0^2(\Gamma) &= 2.3934 - 2.0484\,\Gamma^{-3/4} - 0.32916\,\Gamma^{-5/4} + (1.6008/\Gamma) && 1 \leqslant \Gamma \leqslant 160. \end{aligned} \tag{40}$$

Although the fits (36*b*) and (40) are strictly valid for $\Gamma > 0.1$ we shall use them even for $\Gamma < 0.1$, since we can verify from (38) that the region of very small Γ (when $\rho(z) \ll \rho_b$) does not give any significant contribution to the free energy when $\Gamma_b \geqslant 1$.

The truncated gradient approximation is now fully specified and the problem is to solve the non-linear differential Euler–Lagrange equation (2). This is a difficult task and one usually prefers to assume some parametrised form for the profile and choose the parameters to minimise the surface excess free energy per unit area $(\Omega - \Omega_b)/A$.

We first considered a three-parameter class of trial functions

$$\tilde{\rho}(z) = \begin{cases} 1 - [\alpha/(\beta+\alpha)]\exp[\alpha(z-z_0)]\cos\gamma(z-z_0) & z \leqslant z_0 \\ [\alpha/(\beta+\alpha)]\exp[-\beta(z-z_0)] & z > z_0 \end{cases} \tag{41}$$

with

$$z_0 = \frac{\alpha}{\beta}\frac{\beta^2 - \alpha^2 - \gamma^2}{(\alpha+\beta)(\alpha^2+\gamma^2)}.$$

With this value of z_0, the profile satisfies the overall electroneutrality condition. To test the variational method, we first consider the Poisson–Boltzmann limiting case where $\Omega[\rho]$ is the functional corresponding to the equation (19). In figure 1 we compare the exact solution of this equation with the profile obtained by minimisation for an arbitrary

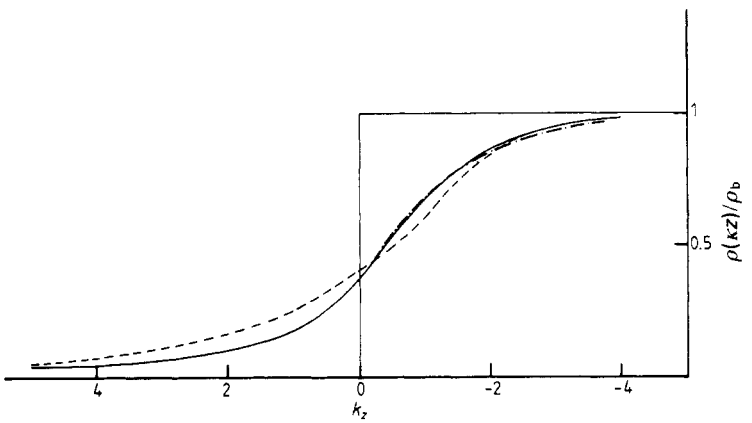

Figure 1. Density profile in the Poisson–Boltzmann approximation: Full curve, exact solution (integration of equation (21)); broken curve, variational function (41); chain curve, variational function, imposing exact solution for $z > 0$.

value of Γ. The agreement with the exact profile seems qualitatively correct even for $z > 0$ but we get for the reduced surface tension $\gamma/a\rho_b kT$ the value $-1.76\,(3\Gamma)^{-1/2}$ instead of the exact value $-2.164\,(3\Gamma)^{-1/2}$ (cf equation (31)). Of course, (41) does not behave like the exact solution for $z \to +\infty$. One can impose the correct behaviour by taking (cf equations (22) and (25)) $\tilde{\rho}(z) = 2(\kappa z + (2e)^{1/2})^{-2}$ for $z > 0$ and the first part of (41) for $z \leqslant 0$, demanding that $\tilde{\rho}$ be continuous, have continuous slope, and satisfy electroneutrality; the remaining free parameter is chosen variationally. The profile obtained is much better (figure 1) and $\gamma/a\rho_b kT = -2.157\,(3\Gamma)^{-1/2}$. This shows the importance, at least for small Γ, of taking into account the z^{-2} asymptotic behaviour. We then consider the second class of functions:

$$\tilde{\rho}(z) = \begin{cases} 1 - A\exp[\alpha(z - z_0)]\cos\gamma(z - z_0) & z \leqslant z_0 \\ 2/3\beta(z + B)^2 & z > z_0 \end{cases} \tag{42}$$

where A, B and z_0 are calculated as functions of α, β and γ in order to satisfy continuity of $\tilde{\rho}$ and $\tilde{\rho}'$ at $z = z_0$ and the electroneutrality condition, so (42) is, like (41), a three-parameter trial function. The optimised value of β may be compared with the exact asymptotic value Γ (since $\kappa^2 = 3\Gamma$ if we take the ion radius as a length unit).

For instance, for $\Gamma = 1$, (still for the Poisson–Boltzmann case) we find after minimisation the parameter values (in units of a): $\alpha = 1.347$, $\gamma = 0.255$, $\beta = 1.006$, $B = 1.365$ and $z_0 = -0.151$. The value of $\tilde{\rho}$ at $z = 0$ is 0.3555, to be compared with the theoretical value of $1/e = 0.3679$. The surface tension in units of $a\rho_b kT$ is -1.250, to be compared

with $-2.16/\sqrt{3} = -1.249$, from solution of the differential equation. This indicates that the trial functions (42) should be adequate for the present kind of problem. We may note that the moment integrals $\int_{-\infty}^{0}[\tilde{\rho}(u)-1]u^j\,du$ for $j = 1$ and 2 are 0.3275 and -0.4527 instead of the theoretical values (cf Appendix 1) of $\frac{1}{3}$ and -0.4165, reflecting their sensitivity to the behaviour of $\tilde{\rho}(u)$ for large negative u.

We now use these trial functions with the more general density functional including gradients (cf equations (1), (36) and (38)). We show in Appendix 2 that in this case too the parametrisation (42) correctly describes the asymptotic behaviour of $\rho(z)$ for $z > 0$. The surface tension may be written

$$\gamma = \frac{e}{2}\int (Z\rho - n)\,\varphi(z)\,dz + \int [g(\rho) - g(\rho_b)\,\theta(-z)]\,dz + \int g_2(\rho)(\nabla\rho)^2\,dz$$

$$= \gamma_{es} + \gamma_i + \gamma_{ij} \tag{43}$$

where γ_{es} is the electrostatic contribution, γ_i comes from the non-gradient term and γ_{ij} from the square-gradient correction. Minimised density profiles are given in figures 2 and 3, and numerical results in tables 2 and 3. We have verified that the trial functions

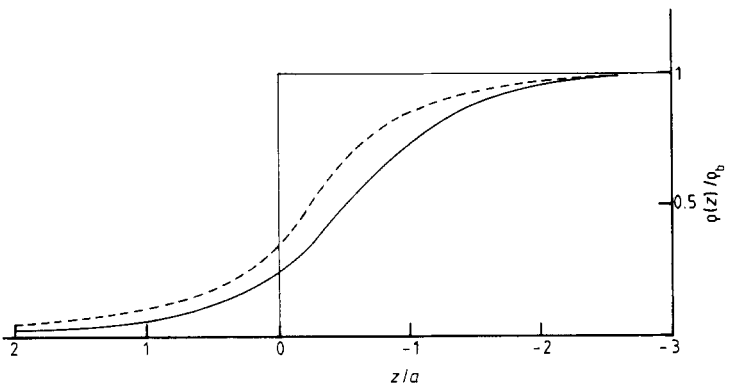

Figure 2. Density profile for $\Gamma = 1$. Full curve, Monte Carlo results (Badiali *et al* 1983); broken curve, variational function (42). $\rho(0)/\rho_b = 0.338$.

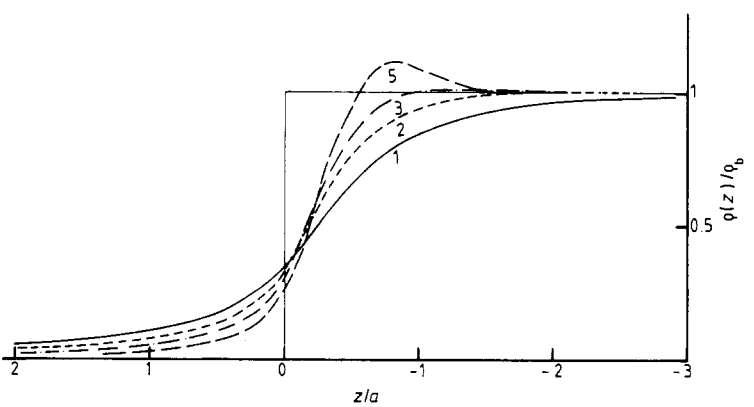

Figure 3. Density profiles obtained from variational calculation with the class of functions (42) for various values of the plasma parameter $\Gamma = 1$, $\rho(0)/\rho_b = 0.338$; $\Gamma = 2$, $\rho(0)/\rho_b = 0.321$; $\Gamma = 3$, $\rho(0)/\rho_b = 0.298$; $\Gamma = 5$, $\rho(0)/\rho_b = 0.251$.

(41) give higher values of γ (for instance, $\gamma/a\rho_b kT = -0.806$ for $\Gamma = 1$). This point shows that the class of function (42) remains better far from the Poisson–Boltzmann limiting case (this is not a general statement, as we shall see in the case $\Gamma = 10$). As expected, the square-gradient contribution γ_{ij} increases with Γ. For $\Gamma = 1$ and $\Gamma = 2$, it gives a negligible or very small contribution for the surface tension but, because $g(\rho)$ for the OCP is different from the Poisson–Boltzmann expression $kT[\rho \ln(\Lambda^3\rho) - 1]$, surface tensions are quite different from the Poisson–Boltzmann values. Similarly, U_s is quite different from $-\frac{1}{2}\gamma$ (see below for calculation of U_s). For $\Gamma = 3$, oscillations become significant in the profile and γ_{ij} is no longer negligible. For $\Gamma = 5$ the gradient term becomes 80% of the non-gradient one and twice the value of γ, as important oscillations in the profile appear. These effects can also be seen from the value of the profile at $z = 0$, in comparison with the local approximation results given in table 1.

On the other hand, when Γ increases the behaviour of $\rho(z)$ for $z > 0$ differs more and more from the Poisson–Boltzmann behaviour, as we can see from the variational parameter β which takes the values 1.097, 2.475, 4.225 and 8.209 for $\Gamma = 1, 2, 3, 5$ instead of the asymptotic value $\beta = \Gamma$ (at the same time z_0 remains in the vicinity of $z = 0$).

One can compare our surface tensions with those calculated by Ballone *et al* (1981a) who have solved the differential equation (2) in the local approximation, using for $g(\rho)$ a mean spherical approximation result. As shown in table 2, the agreement is satisfactory as long as there is no significant contribution coming from the gradient correction. This comparison tends to prove that our minimisation process is correct (at least for $\Gamma < 3$) which means that the class of trial functions (42) permits a good approximation of the exact profile.

We can also use other tests. The first one is the balance between the various contributions γ_{es}, γ_i, γ_{ij}, to the surface tension in the density functional formalism.

Starting from (43) and making explicit the relations between the different contributions to γ implied by the differential equation (2), it is possible to show (Evans and Sluckin 1980) that

$$\gamma = -e\int (Z\rho - n)\,\varphi(z)\,\mathrm{d}z + 2\int g_2(\rho)(\nabla\rho)^2\,\mathrm{d}z = 2(-\gamma_{es} + \gamma_{ij}). \tag{44}$$

Comparing with (43) we get

$$\gamma_i = \gamma_{ij} - 3\gamma_{es}. \tag{45}$$

The results of table 2 satisfy (45) quite well. We must note, however, that (45) is a necessary but not sufficient condition for a good minimisation since a single-parameter profile (for instance a single exponential form) can be easily shown to satisfy (45), although this one-parameter profile is not at all the exact solution. As indicated in § 2, the two sum rules (9) can also be used as a test of minimisation since they are valid for any approximation of $\Omega[\rho]$ as long as the true minimum is obtained. The sum rules are checked in table 3. To evaluate the left-hand side of (9*b*) we require the isothermal derivative of γ with respect to the bulk density ρ_b. The derivative $(\partial\gamma/\partial\rho_b)_T$ (or $(\partial\gamma/\partial T)_{\rho_b}$) has been calculated by changing ρ_b (or T) by a small amount, while holding constant the parameters of the profile (since $\delta\Omega/\delta\rho = 0$ for the equilibrium density profile, variations of the optimal parameters accompanying infinitesimal changes in ρ_b or T can be neglected in first order). The accuracy of the numerical differentiations can be checked by the relation (13*a*) which gives a thermodynamical link between γ, $(\partial\gamma/\partial T)_{\rho_b}$ and $(\partial\gamma/\partial\rho_b)_T$, valid whenever Ω is minimised within a given class of functions.

Table 2. Variational results for square-gradient functional.

Γ	$\frac{\gamma_{es}}{a\rho_b kT}$	$\frac{\gamma_i}{a\rho_b kT}$	$\frac{\gamma_{ij}}{a\rho_b kT}$	$\frac{\gamma}{a\rho_b kT}$	$\frac{1}{a\rho_b k}\left(\frac{d\gamma}{dT}\right)_{\rho_b}$	$\frac{U_s}{a\rho_b kT}$
1	0.512	−1.559	0.003	−1.044	−1.825	0.781
				(−1.04)†		(1.309)‡
2	0.285	−0.848	0.020	−0.543	−1.220	0.677
				(−0.56)†		
3	0.179	−0.502	0.047	−0.275	−0.927	0.651
				(−0.31)†		
5	0.103	−0.175	0.136	0.064	−0.632	0.696

† Results of Ballone *et al* (1981a).
‡ Monte Carlo result (Badiali *et al* 1983).

Table 3. Verification of sum-rules (9):

$$\frac{P}{\rho_b kT} = 3\Gamma\int_{-\infty}^{0}[\tilde{\rho}(u)-1]u\,du \tag{9a}$$

$$\frac{1}{akT}\left(\frac{d\gamma}{d\rho_b}\right)_T = \frac{3}{2}\Gamma\int_{-\infty}^{0}[\tilde{\rho}(u)-1]u^2\,du \qquad u = z/a. \tag{9b}$$

Γ	$\frac{P}{\rho_b kT}$	$3\Gamma\int_{-\infty}^{0}[\tilde{\rho}(u)-1]u\,du$	$\frac{3}{2}\Gamma\int_{-\infty}^{0}[\tilde{\rho}(u)-1]u^2\,du$	$\left(\frac{d\gamma}{d\rho_b}\right)_T\frac{1}{akT}$
1	0.809	0.858	−0.532	−0.443
2	0.560	0.523	−0.030	−0.070
3	0.296	0.279	0.021	0.010
5	−0.251	−0.209	0.041	0.055

From table 3 we see that, while sum rule (9*a*) is rather well satisfied, the agreement is much worse for the sum rule (9*b*). We have noted that these sum rules are related respectively to the first and second moment of the profile for $z < 0$, so (9*b*) is more sensitive to the asymptotic behaviour for $z < 0$. Because of this sensitivity, it is unfortunately not possible to calculate $(\partial\gamma/\partial\rho_b)_T$ from the Monte Carlo profile $\rho(z)$ obtained by Badiali *et al* (1983). Note that in the Poisson–Boltzmann case, the precision on the sum rule (9*b*) was only 8% while the minimised value of γ was better than 0.1%.

Unlike equation (45), sum rules (9) can be shown not to be satisfied by the minimisation of a single exponential type profile.

5. Comparison with Monte Carlo results and concluding remarks

Monte Carlo computations for the profile and the surface energy of the OCP are now available for $\Gamma = 1$, 10 and 30 (Badiali *et al* 1983). For $\Gamma = 1$ the comparison with the FDFF results (figure 2 and table 2) shows that the agreement is only qualitative for the profile and rather poor for the surface energy (note that since both profiles satisfy global electroneutrality they must cross each other at large positive z). For this value of Γ the width of the ion profile is large compared with the radius of the sphere in which Monte

Carlo computations are performed and one could have some doubts about the N dependence of the Monte Carlo results. Recent Monte Carlo computations by Levesque (private communication) with a greater number of particules ($N = 679$ instead of 329) show that within statistical errors this dependence is negligible. On the other hand, the discrepancies between Monte Carlo and density functional results are not due to inadequacies in the trial functions since the Monte Carlo profile can be satisfactorily fitted within the class (42). The problem indeed seems to be that the truncated gradient expansion itself is incorrect even for this small value of Γ. As noted by Alastuey and Levesque (1983) for the two-dimensional OCP, the non-local terms neglected in the square-gradient expansion (38) may have the same order in Γ as the first terms considered.

We have also done the minimisation work for $\Gamma = 10$ keeping the same functional and the two classes of functions (41) and (42). The class (41) appears to give the lowest minimum for the free-energy (the asymptotic tail for $z > 0$ is now making small contributions) but disagreement is important with Monte Carlo results as we can see from figure 4 and table 4. It is possible to increase the oscillations by multiplying the gradient term by an adjustable parameter:

$$G[\rho] = \int \mathrm{d}\boldsymbol{r}\,[g(\rho) + kg_2(\rho)(\nabla\rho)^2].$$

If the value of k is chosen in order to get the Monte Carlo results for the surface energy, we find $k = 0.535$. We see in figure 4 that the agreement with the Monte Carlo profile becomes satisfactory now. But if the background profile becomes of exponential form (characterised by a width λ) we observe again important deviations in the surface energies (table 4). This fact may show the inadequacy of the *ad hoc* correction, although there may be also a problem in the definition of the thermodynamic limit for the Monte Carlo computations when the background profile is not a step (Badiali *et al* 1983). Anyway the adjustable parameter k is Γ dependent.

This failure of the truncated gradient expansion, even when no oscillations are present in the profile, is of great importance since this approximation has been used in

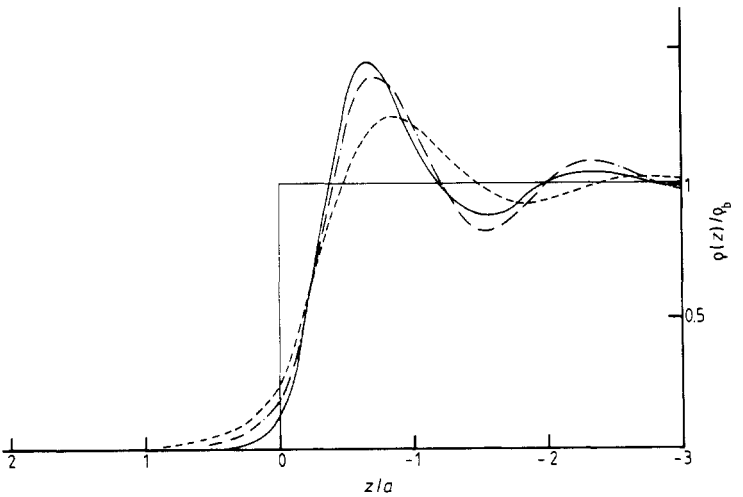

Figure 4. Density profile for $\Gamma = 10$ when the background has a step profile ($\lambda/a = 0$). Full curve, Monte Carlo results (Badiali *et al* 1983); broken curve, variational calculation; chain curve, variational calculation with corrected gradient term ($k = 0.535$).

Table 4. Values of γ_{es}, γ_t, γ_{ij}, γ and U_s in units of $a\rho kT$ for $\Gamma = 10$.

k	λ/a	γ_{es}	γ_t	γ_{ij}	γ	$\frac{1}{\alpha\rho_0 k}\left(\frac{\partial\gamma}{\partial T}\right)_{\rho_0}$	U_s	
							Our results	MC results†
1	0	0.112	0.069	0.406	0.587	−0.270	0.857	0.481†
0.535	0	0.140	−0.100	0.323	0.363	−0.118	0.481	0.481†
0.535	0.345	0.148	0.162	0.211	0.521	−0.302	0.823	2.589†
0.535	0.439	0.099	0.390	0.150	0.635	−0.481	1.120	4.644†
0.535	0.690	0.071	0.808	0.086	0.965	−0.886	1.851	7.430†

† Monte Carlo results (Badiali *et al* 1983).

other Coulombic systems such as liquid metals in order to obtain the surface tension. We see that the discrepancies between theory and experiment, which have been attributed to an oversimplified treatment of the electron–ion interaction (Evans and Hasegawa 1981, Goodisman and Rosinberg 1983), may come also from the truncated gradient expansion itself.

Acknowledgments

The authors acknowledge with thanks D Levesque, A Alastuey and J J Weis for interesting discussions. This work was supported by a grant from the Petroleum Research Fund, administered by the American Chemical Society.

Appendix 1. Solution of the Poisson–Boltzmann equation

In reduced units, the equation to be solved is

$$\frac{\mathrm{d}}{\mathrm{d}u}\left(\frac{\tilde{\rho}'(u)}{\tilde{\rho}(u)}\right) = \tilde{\rho}(u) - 1 \qquad u \leqslant 0 \tag{A1.1}$$

with the condition $\tilde{\rho} \to 1$ for $u \to -\infty$. If we make the transformation

$$f = \ln \tilde{\rho} \qquad \text{and} \qquad u \equiv \ln x$$

equation (A1.1) becomes

$$x^2 \frac{\mathrm{d}^2 f}{\mathrm{d}x^2} + x\frac{\mathrm{d}f}{\mathrm{d}x} = \mathrm{e}^f - 1 = \sum_{j=1}^{\infty} \frac{f^j}{j!}. \tag{A1.2}$$

Now we take for f a power series

$$f = \sum_{k=1}^{\infty} a_k x^k$$

and substitute into (A1.2). The coefficient of each power of x must vanish, which gives $a_0 = 0$ and relates all the a_k ($k > 1$) to a_1. The boundary condition $\tilde{\rho}(0) = 1/\mathrm{e}$ implies $\Sigma a_k = -1$, which becomes an algebraic equation for a_1. This may be solved on truncating the series for f at any k. The convergence of this process is shown by the results of table

Table A1. Values of coefficients in $\ln \tilde{\rho} = \Sigma\, a_k\, e^{ku}$ for various truncations.

Series truncated at $k =$	a_1	a_2	a_3	a_4	a_5	$\frac{1}{e}\sum_{j=1}^{k} j a_j$	$\sum_{j=1}^{k} \frac{a_j}{j}$
1	−1					−0.36788	−1
2	−1.26795	0.26795				−0.26931	−1.13398
3	−1.15902	0.22389	−0.06487			−0.33324	−1.06870
4	−1.18991	0.23598	−0.07020	0.02413		−0.30609	−1.08929
5	−1.17960	0.23191	−0.06839	0.02331	−0.00723	−0.31780	−1.0821

A1. We give the values of the first a_j calculated from various values of k, as well as the slope at 0, calculated as

$$\left(\frac{d\tilde{\rho}}{du}\right)_{u=0} = \left(x\, e^{f}\frac{df}{dx}\right)_{x=1} = \frac{1}{e}\sum_{j=1}^{\infty} j a_j.$$

The exact value of this quantity, from the solution for $u > 0$, is $-4(2e)^{-3/2} = -0.3155$. The convergence is quite satisfactory. We can then use the solution to compute the integral needed for the dimensionless part of the surface tension γ, equations (27) and (28). Thus

$$\int_{-\infty}^{0} du \ln \tilde{\rho} = \sum_j \frac{a_j}{j}$$

becomes -1.08206 using the last line of table A1, and $\gamma = -2.1641\, a\rho_b kT\,(3\Gamma)^{-1/2}$.

Appendix 2. Asymptotic behaviour in the gradient approximation

When the square-gradient approximation (38) is used for $G[\rho]$, the Euler–Lagrange equation (2) becomes

$$\mu = \frac{dg(\rho)}{d\rho} - \frac{dg_2(\rho)}{d\rho}\left(\frac{d\rho}{dz}\right)^2 - 2g_2(\rho)\frac{d^2\rho}{dz^2} + Ze\varphi(z). \tag{A2.1}$$

Consider now the region $z \to +\infty$, i.e. $\rho(z) \to 0$. From (34*b*) we see that the leading term in $g(\rho)$ comes from $\ln \Gamma$:

$$g(\rho) \sim \rho kT \ln \rho(z)/\rho_b$$

hence

$$dg/d\rho \sim kT \ln \rho(z)/\rho_b. \tag{A2.2}$$

From (39) and (40) we get

$$g_2(\rho) = \frac{Z^2e^2}{528}\left(\frac{4\pi}{3}\right)^{-1/3}\rho(z)^{-4/3}\kappa_0^4(\Gamma) \sim A\rho(z)^{-4/3} \tag{A2.3}$$

where A is a constant. Hence

$$dg_2(\rho)/d\rho \sim -\tfrac{4}{3}A\rho(z)^{-7/3}.$$

The asymptotic equation for $\rho(z)$ is then

$$\mu = kT \ln \rho(z)/\rho_b + \tfrac{1}{3}A\rho(z)^{-7/3}(\mathrm{d}\rho/\mathrm{d}z)^2 - 2A\rho(z)^{-4/3}\mathrm{d}^2\rho/\mathrm{d}z^2 + Ze\varphi(z). \qquad \text{(A2.4)}$$

In the Poisson–Boltzmann limit, (A2.1) simply becomes

$$\mu = kT \ln \rho(z)/\rho_b + Ze\varphi(z)$$

and we know (see equation (22)) that the asymptotic behaviour of the solution is $\rho(z) \sim z^{-2}$. We argue that we have the same algebraically decay for the solution of (A2.4). Indeed when $\rho(z) \sim z^{-2}$

$$kT \ln \rho(z)/\rho_b \sim \varphi(z) \sim \ln z$$

and it is easy to check that the two gradient terms have a faster decay, in $z^{-4/3}$.

We can also look at the asymptotic behaviour of $\rho(z)$ in the bulk phase, i.e. when $z \to -\infty$. Differentiating (A2.1) twice in order to introduce the Poisson equation and linearising with respect to $h(z) = \rho(z) - \rho_b$, it is clear that we get a linear differential equation with constant coefficients. The general solution is then

$$\rho(z) \sim \text{constant}\, \mathrm{e}^{\alpha z} \cos(\gamma z + \varphi). \qquad \text{(A2.5)}$$

References

Alastuey A and Levesque D 1983 *Mol. Phys.* **47** 1349–59
Badiali J-P and Rosinberg M-L 1982 *J. Chem. Phys.* **76** 3264–70
Badiali J-P, Rosinberg M-L, Levesque D and Weis J J 1983 *J. Phys. C: Solid State Phys.* **16** 2183–95
Ballone P, Senatore G and Tosi M P 1981a *Nuovo Cim.* **65**B 293–301
—— 1981b *Lett. Nuovo Cim.* **31** 619–24
Evans R 1979 *Adv. Phys.* **28** 143–200
Evans R and Hasegawa M 1981 *J. Phys. C: Solid State Phys.* **14** 5225–46
Evans R and Sluckin T J 1980 *Mol. Phys.* **40** 413–35
—— 1981 *J. Phys. C: Solid State Phys.* **14** 3137–53
Goodisman J and Rosinberg M-L 1983 *J. Phys. C: Solid State Phys.* **16** 1143–51
Hohenberg P and Kohn W 1964 *Phys. Rev.* **136** B864–71
Jancovici B 1982 *J. Stat. Phys.* **28** 43–65
Mermin N D 1965 *Phys. Rev.* **137** A1441–3
Slattery W L, Doolen G D and Dewitt H E 1980 *Phys. Rev.* A **21** 2087–95
Sluckin T J 1981 *J. Chem. Soc. Faraday Trans II* **77** 575–86
Vannimenus J and Budd H F 1974 *Solid State Commun.* **15** 1739–43