

The surface tension of ionic liquids A mechanical formula

by M. BAUS† and C. F. TEJERO‡

Chimie-Physique II §, C.P. 231, Université Libre de Bruxelles,
B-1050 Bruxelles, Belgium

(Received 22 June 1982; accepted 21 July 1982)

We show how both the Kirkwood-Buff and the Triezenberg-Zwanzig expressions for the surface tension of neutral fluids can be applied to charged fluids if due care is taken of the singularities introduced by the Coulomb potential. An expression previously obtained within a density functional theory is recovered and an alternative, but equivalent, mechanical expression is proposed.

1. INTRODUCTION

The statistical mechanical theory of the surface tension of planar liquid-vapour interfaces was initiated many years ago by Kirkwood and Buff [1] who based their theory on mechanical concepts such as the anisotropy of the pressure tensor within the interfacial region. More recently, Triezenberg and Zwanzig [2] developed a fluctuation theory which gave rise to a completely different expression for the surface tension. Recently, Schofield [3] succeeded in showing the equivalence of both expressions. All these expressions, as they stand, can however not be applied to the experimentally interesting case of charged fluids such as the molten salts. The problem of extending these exact results, valid for neutral fluids, to charged fluids was taken up recently by Evans and Sluckin [4, 5] and also by Senatore and Tosi [6]. These authors obtained an expression for the surface tension of charged fluids which is of the Triezenberg-Zwanzig type and which treats the average electric field, which is set up by the electric double layer characteristic of ionic interfaces, as a separate variable. It is our purpose here to derive an alternative Kirkwood-Buff like formula for the surface tension of ionic fluids and to show that it is equivalent to the result of the previous authors.

We consider a classical multicomponent electrically neutral system of point particles interacting through both short ranged pair potentials and the long ranged Coulomb potential. In § 2 we reconsider the fluctuation result obtained previously [4-6] and show how it can be obtained from the usual Triezenberg-Zwanzig (multicomponent) expression if due care is taken to remove a Coulomb singularity with the aid of the condition of electroneutrality

† Chercheur Qualifié du Fonds National Belge de la Recherche Scientifique.

‡ Permanent address: Dpto. de Termología, Facultad de Física, Universidad Complutense, Madrid 3, Spain.

§ Association Euratom-Etat Belge.

of the *bulk* phases. In this way, we are able to perform the transition from the three-dimensional Coulomb potential characteristic of the interparticle interactions ($\sim 1/r$) to the one-dimensional Coulomb potential ($\sim r$) characteristic of the electrostatic interactions between the charged sheets building up the electric double layer, without running into divergence problems. In § 3 we derive an expression for the surface tension of ionic fluids based on the rescaling of the partition function, a method first used within this context by Buff [7] for neutral fluids. In § 4 we show how the thermodynamic result of § 3 can be reinterpreted in terms of the mechanical stress tensor theory of Kirkwood and Buff provided the Maxwell stresses produced by the double layer are added not to the total stresses but only to the 'truncated stresses' where the Coulomb forces are averaged with the total correlation functions instead of the full pair distribution functions. The equivalence of the different expressions for the surface tension of ionic fluids is shown in § 5 following Schofield's steps [3] in reverse order and avoiding the singular contributions. Our conclusions are then gathered in the final § 6.

2. THE FLUCTUATION THEORY

2.1. The response functions

We consider a classical fluid composed of N_α particles of species α in equilibrium at a temperature T corresponding to a two-phase region. The two phases will be spatially separated by putting the fluid in external potentials, $V_\alpha(\mathbf{r})$, which couple to the microscopic number densities $\hat{\rho}_\alpha(\mathbf{r})$:

$$\hat{\rho}_\alpha(\mathbf{r}) = \sum_{j=1}^{N_\alpha} \delta(\mathbf{r} - \mathbf{r}_j) \quad (2.1)$$

via the interaction energy δH :

$$\beta \delta H = - \sum_\alpha \int d\mathbf{r} \hat{\rho}_\alpha(\mathbf{r}) U_\alpha(\mathbf{r}) \quad (2.2)$$

where $\beta = (k_B T)^{-1}$, while for later convenience we have introduced the alternative notation $U_\alpha(\mathbf{r}) = -\beta V_\alpha(\mathbf{r})$. From linear response theory we know that a small change in these external potentials ($U_\alpha(\mathbf{r}) \rightarrow U_\alpha(\mathbf{r}) + \delta U_\alpha(\mathbf{r})$) induces a small change $\delta \rho_\alpha(\mathbf{r})$ in the average density $\rho_\alpha(\mathbf{r}) = \langle \hat{\rho}_\alpha(\mathbf{r}) \rangle$ according to

$$\delta \rho_\alpha(\mathbf{r}) = \sum_{\alpha'} \int d\mathbf{r}' G_{\alpha\alpha'}(\mathbf{r}, \mathbf{r}') \delta U_{\alpha'}(\mathbf{r}') \quad (2.3)$$

or inversely

$$\delta U_\alpha(\mathbf{r}) = \sum_{\alpha'} \int d\mathbf{r}' K_{\alpha\alpha'}(\mathbf{r}, \mathbf{r}') \delta \rho_{\alpha'}(\mathbf{r}'), \quad (2.4)$$

where $G_{\alpha\alpha'}$ and $K_{\alpha\alpha'}$ are inverses obeying

$$\sum_{\alpha_1} \int d\mathbf{r}_1 G_{\alpha\alpha_1}(\mathbf{r}, \mathbf{r}_1) K_{\alpha_1\alpha'}(\mathbf{r}_1, \mathbf{r}') = \delta_{\alpha\alpha'} \delta(\mathbf{r} - \mathbf{r}'). \quad (2.5)$$

As is well known, the response function $G_{\alpha\alpha'}(\mathbf{r}, \mathbf{r}')$ of (2.3) is the equilibrium correlation function of the density fluctuations $\delta \hat{\rho}_\alpha(\mathbf{r})$ in the unperturbed fluid ($\delta U_\alpha(\mathbf{r}) = 0$), i.e.

$$G_{\alpha\alpha'}(\mathbf{r}, \mathbf{r}') = \langle \delta \hat{\rho}_\alpha(\mathbf{r}) \delta \hat{\rho}_{\alpha'}(\mathbf{r}') \rangle; \quad \delta \hat{\rho}_\alpha(\mathbf{r}) = \hat{\rho}_\alpha(\mathbf{r}) - \langle \hat{\rho}_\alpha(\mathbf{r}) \rangle, \quad (2.6)$$

where from (2.6) on all averages ($\langle \dots \rangle$) are taken over the unperturbed system ($\delta U_\alpha(\mathbf{r})=0$). It is also customary to rewrite (2.6) in terms of the pair density $\rho_{\alpha\alpha}(\mathbf{r}, \mathbf{r}')$:

$$\rho_{\alpha\alpha}(\mathbf{r}, \mathbf{r}') = \langle \hat{\rho}_\alpha(\mathbf{r}) \hat{\rho}_\alpha(\mathbf{r}') \rangle - \delta_{\alpha\alpha} \delta(\mathbf{r} - \mathbf{r}') \langle \hat{\rho}_\alpha(\mathbf{r}) \rangle \quad (2.7)$$

or the truncated pair density $\rho_{\alpha\alpha}^T(\mathbf{r}, \mathbf{r}')$:

$$\rho_{\alpha\alpha}^T(\mathbf{r}, \mathbf{r}') = \rho_{\alpha\alpha}(\mathbf{r}, \mathbf{r}') - \rho_\alpha(\mathbf{r}) \rho_\alpha(\mathbf{r}'), \quad (2.8)$$

where $\rho_\alpha(\mathbf{r}) = \langle \hat{\rho}_\alpha(\mathbf{r}) \rangle$ is the (average) density of species α , as

$$G_{\alpha\alpha}(\mathbf{r}, \mathbf{r}') = \rho_{\alpha\alpha}^T(\mathbf{r}, \mathbf{r}') + \delta_{\alpha\alpha} \delta(\mathbf{r} - \mathbf{r}') \rho_\alpha(\mathbf{r}). \quad (2.9)$$

Introducing, finally, the total correlation function $h_{\alpha\alpha}(\mathbf{r}, \mathbf{r}')$

$$\rho_{\alpha\alpha}^T(\mathbf{r}, \mathbf{r}') = \rho_\alpha(\mathbf{r}) \rho_\alpha(\mathbf{r}') h_{\alpha\alpha}(\mathbf{r}, \mathbf{r}') \quad (2.10)$$

and the direct correlation function $c_{\alpha\alpha}(\mathbf{r}, \mathbf{r}')$ via the Ornstein-Zernike equation

$$h_{\alpha\alpha}(\mathbf{r}, \mathbf{r}') = c_{\alpha\alpha}(\mathbf{r}, \mathbf{r}') + \sum_{\alpha_1} \int d\mathbf{r}_1 h_{\alpha\alpha_1}(\mathbf{r}, \mathbf{r}_1) \rho_{\alpha_1}(\mathbf{r}_1) c_{\alpha_1\alpha}(\mathbf{r}_1, \mathbf{r}'), \quad (2.11)$$

(2.5) implies then that the inverse response function $K_{\alpha\alpha}(\mathbf{r}, \mathbf{r}')$ can be written as

$$K_{\alpha\alpha}(\mathbf{r}, \mathbf{r}') = \frac{\delta_{\alpha\alpha} \delta(\mathbf{r} - \mathbf{r}')}{\rho_\alpha(\mathbf{r})} - c_{\alpha\alpha}(\mathbf{r}, \mathbf{r}'). \quad (2.12)$$

2.2. The surface tension of a planar interface

If the interparticle potential is translationally invariant, an arbitrary translation ($\mathbf{r} \rightarrow \mathbf{r} + \mathbf{a}$) of the external potentials ($U_\alpha(\mathbf{r}) \rightarrow U_\alpha(\mathbf{r} + \mathbf{a})$) will shift the density profiles by the same amount ($\rho_\alpha(\mathbf{r}) \rightarrow \rho_\alpha(\mathbf{r} + \mathbf{a})$). Taking hence $\delta U_\alpha(\mathbf{r}) = U_\alpha(\mathbf{r} + \mathbf{a}) - U_\alpha(\mathbf{r}) = \mathbf{a} \cdot \nabla U_\alpha(\mathbf{r}) + O(\mathbf{a}^2)$ the linear response equations (2.3) and (2.4) reduce to the profile equations

$$\nabla \rho_\alpha(\mathbf{r}) = \sum_{\alpha'} \int d\mathbf{r}' G_{\alpha\alpha'}(\mathbf{r}, \mathbf{r}') \nabla' U_{\alpha'}(\mathbf{r}'), \quad (2.13)$$

$$\nabla U_\alpha(\mathbf{r}) = \sum_{\alpha'} \int d\mathbf{r}' K_{\alpha\alpha'}(\mathbf{r}, \mathbf{r}') \nabla' \rho_{\alpha'}(\mathbf{r}'), \quad (2.14)$$

first obtained by Lovett, Mou and Buff [8] and Wertheim [9]. In what follows we shall consider only planar interfaces in which case it is convenient to use cylindrical coordinates $\mathbf{r} = (\mathbf{x}, z)$ and a two-dimensional Fourier transform with respect to $\mathbf{x} = (x, y)$ the cartesian coordinates along the interface:

$$f(\mathbf{x}, z) = \frac{1}{(2\pi)^2} \int d\mathbf{q} \exp(i\mathbf{q} \cdot \mathbf{x}) f(\mathbf{q}, z), \quad (2.15)$$

$$f(\mathbf{q}, z) = \int d\mathbf{x} \exp(-i\mathbf{q} \cdot \mathbf{x}) f(\mathbf{x}, z) \quad (2.16)$$

while the z -axis is taken along the normal to the planar interface. In the case of a planar interface we can write $\rho_\alpha(\mathbf{r}) \equiv \rho_\alpha(z)$, $U_\alpha(\mathbf{r}) \equiv U_\alpha(z)$, $G_{\alpha\alpha}(\mathbf{r}, \mathbf{r}') \equiv G_{\alpha\alpha}(|\mathbf{x} - \mathbf{x}'|; z, z')$, $K_{\alpha\alpha}(\mathbf{r}, \mathbf{r}') \equiv K_{\alpha\alpha}(|\mathbf{x} - \mathbf{x}'|; z, z')$, i.e. the system has no translational symmetry along the z -axis but keeps its rotational symmetry

around the z -axis. With these assumptions the profile equations (2.13) and (2.14) reduce to

$$\rho'_\alpha(z) = \sum_{\alpha'} \int dz' G_{\alpha\alpha'}(q=0; z, z') U'_{\alpha'}(z'), \quad (2.17)$$

$$U'_\alpha(z) = \sum_{\alpha'} \int dz' K_{\alpha\alpha'}(q=0; z, z') \rho'_{\alpha'}(z'), \quad (2.18)$$

where $\rho'_\alpha(z) \equiv \nabla_z \rho_\alpha(z)$, $U'_\alpha(z) \equiv \nabla_z U_\alpha(z)$ while it follows from (2.16) that $f(q=0) = \int d\mathbf{x} f(\mathbf{x})$. Finally, we also write the small- q expansion of $K_{\alpha\alpha'}(q; z, z')$ as:

$$K_{\alpha\alpha'}(q; z, z') = K_{\alpha\alpha'}^{(0)}(z, z') + q^2 K_{\alpha\alpha'}^{(2)}(z, z') + O(q^4); \quad q = |\mathbf{q}| \quad (2.19)$$

with

$$K_{\alpha\alpha'}^{(0)}(z, z') = \int d\mathbf{x} K_{\alpha\alpha'}(|\mathbf{x}|; z, z'), \quad (2.20)$$

$$K_{\alpha\alpha'}^{(2)}(z, z') = -\frac{1}{4} \int d\mathbf{x} |\mathbf{x}|^2 K_{\alpha\alpha'}(|\mathbf{x}|; z, z'), \quad (2.21)$$

$$= \frac{1}{4} \int d\mathbf{x} |\mathbf{x}|^2 c_{\alpha\alpha'}(|\mathbf{x}|; z, z'), \quad (2.22)$$

where we have used the rotational invariance of $K_{\alpha\alpha'}(|\mathbf{x}|; z, z')$ and (2.12).

The surface tension σ of the planar interface can now be defined by

$$\beta\sigma = \sum_{\alpha, \alpha'} \int dz \int dz' \rho'_\alpha(z) K_{\alpha\alpha'}^{(2)}(z, z') \rho'_{\alpha'}(z') \quad (2.23)$$

a result first obtained by Triezenberg and Zwanzig [2] (for the multicomponent generalization cf. [10]) by computing the change in free energy due to a particular change in the equilibrium density profiles.

2.3. The electric double layer

The above treatment can be generalized to the case where some of the particle species are charged in which case surface segregation of these charges leads to the formation at the interface of an electric double layer. This was originally done by Evans and Sluckin [4, 5] and also by Senatore and Tosi [6], using a density functional theory in which the electric potential set up by the double layer is explicitly isolated from the remaining contributions. We shall show now that in fact this is not necessary and that the same general expression holds both for charged and neutral particle fluids *provided* the singularities introduced by the Coulomb potential are properly eliminated. Let us first introduce the truncated inverse response function, $\bar{K}_{\alpha\alpha'}$, defined by

$$K_{\alpha\alpha'}(q; z, z') = \bar{K}_{\alpha\alpha'}(q; z, z') + \beta e_\alpha e_{\alpha'} V(q; z, z') \quad (2.24)$$

where e_α is the charge of the particles of species α , which for certain species may vanish but is restricted by the condition of overall electroneutrality:

$$\sum_\alpha e_\alpha N_\alpha = 0 \quad (2.25)$$

while $V(q; z, z')$ is the two-dimensional Fourier transform of the three-dimensional Coulomb potential $V(|\mathbf{r} - \mathbf{r}'|) = 1/|\mathbf{r} - \mathbf{r}'|$, i.e.

$$V(q; z) = \int d\mathbf{x} \exp(-i\mathbf{q} \cdot \mathbf{x}) \frac{1}{(|\mathbf{x}|^2 + z^2)^{1/2}} = \frac{2\pi}{q} \exp(-q|z|). \quad (2.26)$$

Alternatively, $V(q; z)$ can also be obtained as the solution of Poisson's equation

$$(\nabla_z^2 - q^2)V(q; z) = -4\pi\delta(z) \quad (2.27)$$

which vanishes when $|z| \rightarrow \infty$. Equation (2.24) is a convenient way of writing $K_{\alpha\alpha}$, if we accept (without proof) that in this way the most singular part of $K_{\alpha\alpha}$ has been explicitly displayed so that $\bar{K}_{\alpha\alpha}$ can be assumed to have the same properties as for uncharged particles, e.g.

$$\bar{K}_{\alpha\alpha}(q; z, z') = \bar{K}_{\alpha\alpha}^{(0)}(z, z') + q^2 \bar{K}_{\alpha\alpha}^{(2)}(z, z') + O(q^4) \quad (2.28)$$

with definitions of $\bar{K}_{\alpha\alpha}^{(0)}$ and $\bar{K}_{\alpha\alpha}^{(2)}$ similar to those of (2.20)–(2.22). The difficulty with charged systems is now clearly visible since $V(q; z - z')$ and hence according to (2.24) also $K_{\alpha\alpha}$ have no analytic expansion similar to (2.19). Instead, we have from (2.26):

$$V(q; z - z') = \frac{2\pi}{q} - 2\pi|z - z'| + \pi q|z - z'|^2 - \frac{\pi}{3}q^2|z - z'|^3 + O(q^3), \quad (2.29)$$

i.e. a non-analytic expansion in q^2 implying for instance that $K_{\alpha\alpha}^{(0)}$ does not exist, invalidating thereby the expansion of (2.19). This difficulty can be avoided if we observe that the basic equations of the fluctuation theory of the surface tension, namely (2.18) and (2.23), do in fact involve only $K_{\alpha\alpha}$ acting on $\rho'_{\alpha}(z')$ while this latter quantity does have a non-singular small- q expansion (at least when the electroneutrality properties are invoked) as we now show. Consider the quantities

$$A_{\alpha}(q; z) = \sum_{\alpha'} \int dz' K_{\alpha\alpha'}(q; z, z') \rho'_{\alpha'}(z') \quad (2.30)$$

$$\begin{aligned} A(q) &= \sum_{\alpha, \alpha'} \int dz \int dz' \rho'_{\alpha}(z) K_{\alpha\alpha'}(q; z, z') \rho'_{\alpha'}(z') \\ &= \sum_{\alpha} \int dz \rho'_{\alpha}(z) A_{\alpha}(q; z). \end{aligned} \quad (2.31)$$

Using (2.24) into (2.30) we obtain

$$\begin{aligned} A_{\alpha}(q; z) &= \sum_{\alpha'} \int dz' \bar{K}_{\alpha\alpha'}(q; z, z') \rho'_{\alpha'}(z') + \beta e_{\alpha} \int dz' V(q; z - z') \rho'_{\alpha'}(z') \\ &= \bar{A}_{\alpha}(q; z) + A_{\alpha}^{(e)}(q; z) \end{aligned} \quad (2.32)$$

and similarly from (2.31)

$$\left. \begin{aligned} A(q) &= \bar{A}(q) + A^{(e)}(q); \\ A^{(e)}(q) &= \beta \int dz \int dz' \rho'_{\alpha}(z) V(q; z - z') \rho'_{\alpha}(z') \end{aligned} \right\} \quad (2.33)$$

where $\bar{A}_{\alpha}(q; z)$ and $\bar{A}(q)$ are similar to $A_{\alpha}(q; z)$ and $A(q)$ of (2.30) and (2.31) but involve now only the truncated functions $\bar{K}_{\alpha\alpha}$, instead of $K_{\alpha\alpha}$. In (2.32) and (2.33) we have also introduced the (average) charge density, $\rho_e(z)$, of the interfacial double layer

$$\rho_e(z) = \sum_{\alpha} e_{\alpha} \rho_{\alpha}(z) \quad (2.34)$$

with $\rho'_{\alpha}(z) = \nabla_z \rho_{\alpha}(z)$. Associated with this charge density there will be an electric potential $\phi(z)$ defined by the following Poisson equation

$$\nabla_z^2 \phi(z) = -4\pi \rho_e(z). \quad (2.35)$$

Notice that (2.35) is effectively what remains of the three-dimensional Poisson equation within the present symmetry: except for the factor 4π (which reminds us that the system is three-dimensional) it is a one-dimensional Poisson equation. We shall assume that $\rho_e(z)$ describes indeed a double layer, i.e. that $\rho_e(z)$ is non-vanishing only at the interface ($z \simeq 0$) but vanishes in the bulk phases:

$$\rho_e(z = \pm \infty) = 0, \quad (2.36)$$

while the system also satisfies overall electroneutrality

$$\int dz \rho_e(z) = 0. \quad (2.37)$$

The solution $\phi(z)$ of (2.35) which remains finite for $z=0$ can then be written

$$\phi(z) = -2\pi \int dz' |z - z'| \rho_e(z'), \quad (2.38)$$

where the Green's function, $-2\pi|z - z'|$, appearing in (2.38) is seen to be precisely the q -independent term in the expansion of (2.29). We now proceed by showing that because of (2.36) and (2.37) the small- q expansions of (2.30)–(2.33) are in fact analytic whereas one of the integrands (cf. (2.29)) is not. In view of (2.28) and (2.29) we can write the small- q expansion of (2.32) as

$$\bar{A}_\alpha(q; z) = \bar{A}_\alpha^{(0)}(z) + q^2 \bar{A}_\alpha^{(2)}(z) + O(q^4), \quad (2.39)$$

$$\begin{aligned} A_\alpha^{(e)}(q; z) &= \beta e_\alpha \int dz' V(q; z - z') \rho'_e(z') \\ &= \frac{2\pi e_\alpha \beta}{q} \int dz' \rho'_e(z') - 2\pi e_\alpha \beta \int dz' |z - z'| \rho'_e(z') + O(q), \end{aligned} \quad (2.40)$$

where because of (2.36) the $1/q$ term of (2.40) vanishes identically whereas we integrate by parts the remaining term (which is allowed provided $\rho_e(z)$ vanishes faster than $1/|z|$ when $|z| \rightarrow \infty$) and obtain using (2.38)

$$A_\alpha^{(e)}(q; z) = \beta e_\alpha \phi'(z) + O(q). \quad (2.41)$$

Returning to the profile equation (2.18) we see that we can write it in terms of $K_{\alpha\alpha}$ or alternatively in terms of $\bar{K}_{\alpha\alpha}$ and ϕ as done by the previous authors [5, 6]. Indeed comparing (2.18) with (2.30) and using the result of (2.41) we find

$$U'_\alpha(z) = \lim_{q \rightarrow 0} \sum_{\alpha'} \int dz' K_{\alpha\alpha'}(q; z, z') \rho'_{\alpha'}(z'), \quad (2.42)$$

$$= \beta e_\alpha \phi'(z) + \sum_{\alpha'} \int dz' \bar{K}_{\alpha\alpha'}(q=0; z, z') \rho'_{\alpha'}(z'), \quad (2.43)$$

where in (2.42) the z' integral has to be performed *before* the small- q limit is taken whereas (2.43) is the result obtained by previous authors [5]. Consider now $A(q)$ of (2.31); from (2.33) we have

$$\begin{aligned} \bar{A}(q) &= \bar{A}^{(0)} + q^2 \bar{A}^{(2)}, \\ A^{(e)}(q) &= \beta \int dz \int dz' \rho'_e(z) V(q; z - z') \rho'_e(z') = \frac{2\pi\beta}{q} \left(\int dz \rho'_e(z) \right)^2 \\ &\quad + \beta \int dz \rho'_e(z) \phi'(z) - 2\pi\beta q \left(\int dz \rho_e(z) \right)^2 \\ &\quad + 2\pi\beta q^2 \int dz \int dz' \rho_e(z) |z - z'| \rho_e(z') + O(q^3). \end{aligned} \quad (2.44)$$

Or using (2.36) and (2.37) the q and $1/q$ terms drop out leaving the analytic expansion

$$A^{(e)}(q) = \beta \int dz \rho'_e(z) \phi'(z) - q^2 \beta \int dz \rho_e(z) \phi(z) + O(q^3). \quad (2.45)$$

Notice that because of (2.35) and (2.36) and (2.37) we also have

$$\int dz \rho_e(z) \phi(z) = \frac{1}{4\pi} \int dz (\phi'(z))^2. \quad (2.46)$$

Finally, combining the results we find for the small- q expansion of $A(q)$:

$$A(q) = \sum_x \int dz \rho'_x(z) U'_x(z) + q^2 \beta \sigma + O(q^3), \quad (2.47)$$

$$\beta \sigma = \sum_{x,x'} \int dz \int dz' \rho'_x(z) K_{xx'}(z, z') \rho'_{x'}(z') - \beta \int dz \rho_e(z) \phi(z), \quad (2.48)$$

$$= \lim_{q \rightarrow 0} \frac{1}{q^2} \left[\sum_{x,x'} \int dz \int dz' \rho'_x(z) K_{xx'}(q; z, z') \rho'_{x'}(z') - \sum_x \int dz \rho'_x(z) U'_x(z) \right], \quad (2.49)$$

where (2.47) shows that $A(q)$ is analytic (at least to $O(q^3)$) even while $K_{xx'}(q; z, z')$ is not; (2.48) is the expression of the surface tension σ obtained by the previous authors [5, 6] while (2.49) is an expression for σ in terms of the complete $K_{xx'}$ valid whether the particles are charged or neutral.

To close this section we should like to point out that some of the *intermediate* steps in the previous treatments did contain ill defined expressions like $\int d\mathbf{r}' \rho_e(z')/|\mathbf{r}-\mathbf{r}'| = \phi(z)$ (cf. (3) of [4] and (3.2) of [6]) and $\int d\mathbf{x} x^2/(x^2+z^2)^{1/2}$ ((A 6) of [6]) which do not show up here. A proper transition from the three-dimensional Coulomb potential, $1/|\mathbf{r}-\mathbf{r}'|$, relevant to the particles to the one-dimensional Coulomb potential, $-2\pi|z-z'|$, relevant to the double layer is possible only when the small- q singularities of $V(q; z-z')$ (2.29) are properly removed by using the electroneutrality conditions (2.36) and (2.37).

3. THE THERMODYNAMIC THEORY

A different approach to the computation of the surface tension σ proceeds through the thermodynamic definition, i.e. by taking the derivative of the Helmholtz free energy $F = F(\beta, N_x, \Omega, A)$ with respect to the interfacial area A :

$$\sigma = \left[\frac{\partial F}{\partial A} \right]_{\beta, \Omega, N_x} \quad (3.1)$$

at constant temperature (β), volume (Ω) and number of particles (N_x). Writing F in terms of the canonical partition function Z as $\beta F = -\ln Z$ one can compute the derivative with respect to A by using the scaling method used by Bogoliubov, Born and Green for the computation of the pressure and adapted to the present case by Buff [7]. Omitting the irrelevant dependence on β and N_x we write $Z(L_x, L_y, L_z) = Z(\Omega, A_0, A)$ where L_x, L_y, L_z are the lengths of the edges of the rectangular vessel containing the two-phase system, $\Omega = L_x L_y L_z$ its volume, $A_0 = L_x L_z$ and $A = L_x L_y$ the area of two perpendicular cross sections, A being equal to the interfacial area. Let $Z_\lambda(L_x, L_y, L_z) = Z(\lambda L_x, L_y, \lambda^{-1} L_z) =$

$Z(\Omega, A_0, \lambda A)$, then $\partial_\lambda Z_\lambda = [\partial Z_\lambda / \partial(\lambda A)] [\partial(\lambda A) / \partial \lambda]$ while $[\partial Z_\lambda / \partial(\lambda A)]_{\lambda=1} = \partial Z / \partial A$ and hence $\partial Z / \partial A = (1/A) [\partial_\lambda Z_\lambda]_{\lambda=1}$ or from (3.1):

$$\sigma = -\frac{1}{\beta A} [\partial_\lambda \ln Z_\lambda]_{\lambda=1}. \quad (3.2)$$

Equation (3.2) can be rewritten after a change of variables ($x'_j = \lambda x_j$, $y'_j = y_j$, $z'_j = \lambda^{-1} z_j$) inside Z_λ as

$$\begin{aligned} \sigma &= \frac{1}{A} \langle [\partial_\lambda H(\{\lambda x_j, y_j, \lambda^{-1} z_j\})]_{\lambda=1} \rangle \\ &= \frac{1}{A} \left\langle \sum_x \sum_{j=1}^{N_x} \left(x_j \frac{\partial}{\partial x_j} - z_j \frac{\partial}{\partial z_j} \right) H \right\rangle, \end{aligned} \quad (3.3)$$

where $H = H(\{\mathbf{r}_j\})$ denotes the hamiltonian of the N particles of positions $\mathbf{r}_j = (x_j, y_j, z_j)$ and $\langle \dots \rangle$ the corresponding canonical ensemble average at temperature β^{-1} . Equation (3.3) can also be written in terms of the pair density of (2.7) and the central pair potentials $V_{ij}(|\mathbf{r}_i - \mathbf{r}_j|)$ (notice that $(x \nabla_x + x' \nabla_{x'}) V(|\mathbf{r} - \mathbf{r}'|) = (x - x') \nabla_{x-x'} V(|\mathbf{r} - \mathbf{r}'|)$) as

$$\begin{aligned} \sigma &= \frac{1}{2A} \sum_{x, x'} \int d\mathbf{r} \int d\mathbf{r}' \rho_{\alpha\alpha}(\mathbf{r}, \mathbf{r}') [(x - x') \nabla_{x-x'} - (z - z') \nabla_{z-z'}] \\ &\quad \times [V_{\alpha\alpha}(|\mathbf{r} - \mathbf{r}'|) + e_\alpha e_\alpha V(|\mathbf{r} - \mathbf{r}'|)], \end{aligned} \quad (3.4)$$

where we have separated the short-ranged potentials, $V_{\alpha\alpha}$, from the Coulomb potential $V(|\mathbf{r}|) = 1/|\mathbf{r}|$. Before taking the thermodynamic limit ($N, \Omega, A \rightarrow \infty$) we rewrite (3.4) with the aid of (2.8) as follows:

$$\begin{aligned} \sigma &= \frac{1}{2A} \sum_{x, x'} \int d\mathbf{r} \int d\mathbf{r}' \rho_{\alpha\alpha}(\mathbf{r}, \mathbf{r}') [(x - x') \nabla_{x-x'} - (z - z') \nabla_{z-z'}] V_{\alpha\alpha}(|\mathbf{r} - \mathbf{r}'|) \\ &\quad + \frac{1}{2A} \int d\mathbf{r} \int d\mathbf{r}' \rho_{ee}^T(\mathbf{r}, \mathbf{r}') [(x - x') \nabla_{x-x'} - (z - z') \nabla_{z-z'}] V(|\mathbf{r} - \mathbf{r}'|) \\ &\quad + \frac{1}{2A} \int d\mathbf{r} \int d\mathbf{r}' \rho_e(\mathbf{r}) \rho_e(\mathbf{r}') [(x - x') \nabla_{x-x'} - (z - z') \nabla_{z-z'}] V(|\mathbf{r} - \mathbf{r}'|), \end{aligned} \quad (3.5)$$

where $\rho_{ee}^T(\mathbf{r}, \mathbf{r}') = \rho_{ee}(\mathbf{r}, \mathbf{r}') - \rho_e(\mathbf{r}) \rho_e(\mathbf{r}')$ is the truncated pair charge density, $\rho_{ee}(\mathbf{r}, \mathbf{r}') = \sum_{x, x'} e_\alpha e_\alpha \rho_{\alpha\alpha}(\mathbf{r}, \mathbf{r}')$ the pair charge density and $\rho_e(\mathbf{r}) = \sum_x e_\alpha \rho_\alpha(\mathbf{r})$ the singlet charge density. Consider now the three terms in the right hand side of (3.5) separately. In the first term, $\rho_{\alpha\alpha}(\mathbf{r}, \mathbf{r}')$ is long ranged since asymptotically it tends to $\rho_\alpha(\mathbf{r}) \rho_\alpha(\mathbf{r}')$ when $|\mathbf{r} - \mathbf{r}'| \rightarrow \infty$ but the potential $V_{\alpha\alpha}(|\mathbf{r} - \mathbf{r}'|)$ can be assumed to be sufficiently short ranged to make the integrand well behaved in the infinite volume limit. In this case its thermodynamic limit can be taken without danger and results, for a system with a planar interface with cylindrical symmetry for which $\rho_{\alpha\alpha}(\mathbf{r}, \mathbf{r}') = \rho_{\alpha\alpha}(|\mathbf{x} - \mathbf{x}'|; z, z')$, in a contribution of the form

$$\frac{1}{2} \sum_{x, x'} \int dz \int dz' \int d\mathbf{R} \rho_{\alpha\alpha}(|\mathbf{R}|; z, z') f_{\alpha\alpha}(|\mathbf{R}|; |z - z'|), \quad (3.6)$$

with $\mathbf{R} = \mathbf{x} - \mathbf{x}'$ and

$$[(\mathbf{x} - \mathbf{x}') \nabla_{\mathbf{x} - \mathbf{x}'} - (z - z') \nabla_{z - z'}] V_{\alpha\alpha}(|\mathbf{r} - \mathbf{r}'|) = \frac{(\mathbf{x} - \mathbf{x}')^2 - (z - z')^2}{|\mathbf{r} - \mathbf{r}'|} V'_{\alpha\alpha}(|\mathbf{r} - \mathbf{r}'|), \quad (3.7)$$

$$f_{\alpha\alpha}(|\mathbf{R}|; |z - z'|) = \frac{1}{2} \frac{R^2 - 2(z - z')^2}{|\mathbf{r} - \mathbf{r}'|} V'_{\alpha\alpha}(|\mathbf{r} - \mathbf{r}'|), \quad (3.8)$$

where $V'_{\alpha\alpha}(|\mathbf{r}|) = (d/d|\mathbf{r}|)V_{\alpha\alpha}(|\mathbf{r}|)$ and $|\mathbf{r} - \mathbf{r}'|^2 = R^2 + (z - z')^2$. In the second term of (3.5) the Coulomb potential $V(|\mathbf{r} - \mathbf{r}'|)$ is long ranged but $\rho_{ee}^T(\mathbf{r}, \mathbf{r}')$ can be assumed to be sufficiently short ranged leading in the thermodynamic limit to a contribution to σ of the form

$$\frac{1}{2} \int dz \int dz' \int d\mathbf{R} \rho_{ee}^T(|\mathbf{R}|; z, z') f(|\mathbf{R}|; |z - z'|), \quad (3.9)$$

where the definition of $f(|\mathbf{R}|; |z - z'|)$ is similar to that of (3.8) with $V_{\alpha\alpha}(|\mathbf{r} - \mathbf{r}'|)$ replaced by the Coulomb potential $V(|\mathbf{r} - \mathbf{r}'|)$. For the third term of (3.5) we use, at finite volume, the Fourier series representation of (2.26):

$$V(|\mathbf{r} - \mathbf{r}'|) = \frac{1}{A} \sum_{\mathbf{q}} \exp[i\mathbf{q} \cdot (\mathbf{x} - \mathbf{x}')] \frac{2\pi}{q} \exp(-q|z - z'|) \quad (3.10)$$

and obtain in the infinite volume limit ($\hat{\mathbf{q}} = \mathbf{q}/|\mathbf{q}|$)

$$\begin{aligned} & \frac{1}{2} \int dz \int dz' \rho_e(z) \rho_e(z') \int d\mathbf{R} \int \frac{d\mathbf{q}}{(2\pi)^2} \exp[i\mathbf{q} \cdot \mathbf{R} - q|z - z'|] (2\pi|z - z'| + i\pi\hat{\mathbf{q}} \cdot \mathbf{R}) \\ &= \frac{1}{2} \int dz \int dz' \rho_e(z) \rho_e(z') \int d\mathbf{q} \exp[-q|z - z'|] \left(2\pi|z - z'| + \pi\hat{\mathbf{q}} \cdot \frac{\partial}{\partial \mathbf{q}} \right) \delta(\mathbf{q}) \\ &= \frac{1}{2} \int dz \int dz' \rho_e(z) \rho_e(z') (2\pi|z - z'| + 2\pi|z - z'|) \\ &= - \int dz \rho_e(z) \phi(z), \end{aligned} \quad (3.11)$$

where we have used (2.38). Finally, gathering all results we obtain the following expression for the surface tension:

$$\begin{aligned} \sigma &= \frac{1}{4} \sum_{\alpha, \alpha'} \int dz \int dz' \int d^2(\mathbf{x} - \mathbf{x}') \rho_{\alpha\alpha}(|\mathbf{x} - \mathbf{x}'|; z, z') \\ & \quad \times \frac{|\mathbf{x} - \mathbf{x}'|^2 - 2|z - z'|^2}{|\mathbf{r} - \mathbf{r}'|} V'_{\alpha\alpha}(|\mathbf{r} - \mathbf{r}'|) \\ & \quad + \frac{1}{4} \int dz \int dz' \int d^2(\mathbf{x} - \mathbf{x}') \rho_{ee}^T(|\mathbf{x} - \mathbf{x}'|; z, z') \\ & \quad \times \frac{|\mathbf{x} - \mathbf{x}'|^2 - 2|z - z'|^2}{|\mathbf{r} - \mathbf{r}'|} V'(|\mathbf{r} - \mathbf{r}'|) - \frac{1}{4\pi} \int dz (\phi'(z))^2, \end{aligned} \quad (3.12)$$

where we have used (2.46) and put $|\mathbf{r} - \mathbf{r}'| = (|\mathbf{x} - \mathbf{x}'|^2 + |z - z'|^2)^{1/2}$. This is an alternative expression for the surface tension of charged fluids in terms of the singlet and pair distribution functions and the pair potentials.

4. THE MECHANICAL THEORY

A third approach to the surface tension due originally to Kirkwood and Buff [1] proceeds from the surface excess value of the tangential pressure.

For a planar interface normal to the z -axis this leads to the following definition of σ :

$$\sigma = \int dz (\sigma_{zz}(z) - \sigma_{xx}(z)), \quad (4.1)$$

where the normal pressure, σ_{zz} , will be a constant for a system in hydrostatic equilibrium while the tangential pressure, σ_{xx} , will be a function of z only for a planar interface, while cylindrical symmetry will imply moreover that $\sigma_{xx} = \sigma_{yy}$. The cartesian elements, σ_{ij} , of the local pressure tensor, $\sigma(\mathbf{r})$, can be defined in general from the mechanical equation of motion

$$\langle \hat{\mathbf{g}}(\mathbf{r}) \rangle + \nabla \cdot \sigma(\mathbf{r}) = \mathbf{F}(\mathbf{r}), \quad (4.2)$$

where $\langle \hat{\mathbf{g}}(\mathbf{r}) \rangle = \left\langle \sum_j \mathbf{P}_j \delta(\mathbf{r} - \mathbf{r}_j) \right\rangle$ is the average local momentum density and $\mathbf{F}(\mathbf{r})$ is the average external force density. The explicit computation of (4.2) yields (see for example [11])

$$\sigma(\mathbf{r}) = \sigma^K(\mathbf{r}) + \sigma'(\mathbf{r}), \quad (4.3)$$

$$\sigma^K(\mathbf{r}) = \mathbf{1} \sum_{\alpha} \rho_{\alpha}(\mathbf{r}) / \beta, \quad (4.4)$$

$$\nabla \cdot \sigma'(\mathbf{r}) = \sum_{\alpha, \alpha'} \int d\mathbf{r}' \rho_{\alpha\alpha'}(\mathbf{r}, \mathbf{r}') \nabla [V_{\alpha\alpha'}(|\mathbf{r} - \mathbf{r}'|) + e_{\alpha} e_{\alpha'} V(|\mathbf{r} - \mathbf{r}'|)], \quad (4.5)$$

where σ^K is the kinetic and σ' the potential contribution to the pressure tensor σ . In (4.5) we have again separated the interactions into short-ranged potentials $V_{\alpha\alpha'}$ and the Coulomb potential V . Proceeding as in (3.4) and (3.5) we obtain:

$$\begin{aligned} \nabla \cdot \sigma'(\mathbf{r}) = & \sum_{\alpha, \alpha'} \int d\mathbf{r}' \rho_{\alpha\alpha'}(\mathbf{r}, \mathbf{r}') \nabla V_{\alpha\alpha'}(|\mathbf{r} - \mathbf{r}'|) \\ & + \int d\mathbf{r}' \rho_{ee}^T(\mathbf{r}, \mathbf{r}') \nabla V(|\mathbf{r} - \mathbf{r}'|) \\ & + \rho_e(\mathbf{r}) \int d\mathbf{r}' \rho_e(\mathbf{r}') \nabla V(|\mathbf{r} - \mathbf{r}'|). \end{aligned} \quad (4.6)$$

Introducing the average electric field, $\mathbf{E}(\mathbf{r})$, and average potential, $\phi(\mathbf{r})$, through

$$\mathbf{E}(\mathbf{r}) = -\nabla\phi(\mathbf{r}) = -\nabla \int d\mathbf{r}' \rho_e(\mathbf{r}') V(|\mathbf{r} - \mathbf{r}'|) \quad (4.7)$$

we can split σ' of (4.6) into a truncated part σ^T and the electric or Maxwell pressure tensor (i.e. minus the Maxwell stress tensor) σ^M according to:

$$\begin{aligned} \nabla \cdot \sigma^T(\mathbf{r}) = & \sum_{\alpha, \alpha'} \int d\mathbf{r}' \rho_{\alpha\alpha'}(\mathbf{r}, \mathbf{r}') \nabla V_{\alpha\alpha'}(|\mathbf{r} - \mathbf{r}'|) \\ & + \int d\mathbf{r}' \rho_{ee}^T(\mathbf{r}, \mathbf{r}') \nabla V(|\mathbf{r} - \mathbf{r}'|), \end{aligned} \quad (4.8)$$

$$\nabla \cdot \sigma^M(\mathbf{r}) = -\rho_e(\mathbf{r}) \mathbf{E}(\mathbf{r}). \quad (4.9)$$

Notice that since $\sigma = \sigma^K + \sigma^T + \sigma^M$, the Maxwell tensor has to be added not to the total pressure tensor but only to its truncated part. There remains now to 'solve' (4.8) and (4.9) for σ^T and σ^M . From (4.7) we obtain $\nabla \cdot \mathbf{E} = 4\pi\rho_e$, using this result we eliminate ρ_e from (4.9) and obtain the usual Maxwell pressure tensor.

$$\sigma^M(\mathbf{r}) = -\frac{1}{4\pi} [\mathbf{E}(\mathbf{r})\mathbf{E}(\mathbf{r}) - \frac{1}{2}\mathbf{E}(\mathbf{r}) \cdot \mathbf{E}(\mathbf{r})\mathbf{1}] \quad (4.10)$$

provided $\nabla \times \mathbf{E} = 0$, which in view of (4.7) is trivially satisfied. To obtain σ^T we rewrite as usual (4.8) as

$$\nabla \cdot \sigma^T(\mathbf{r}) = \frac{1}{2} \sum_{\alpha, \alpha'} \int d\mathbf{r}' [\rho_{\alpha\alpha'}(\mathbf{r} - \mathbf{r}', \mathbf{r}) - \rho_{\alpha\alpha'}(\mathbf{r}, \mathbf{r} + \mathbf{r}')] \nabla' V_{\alpha\alpha'}(|\mathbf{r}'|) \\ + \frac{1}{2} \int d\mathbf{r}' [\rho_{ee^T}(\mathbf{r} - \mathbf{r}', \mathbf{r}) - \rho_{ee^T}(\mathbf{r}, \mathbf{r} + \mathbf{r}')] \nabla' V(|\mathbf{r}'|) \quad (4.11)$$

and hence

$$\sigma^T(\mathbf{r}) = -\frac{1}{2} \sum_{\alpha, \alpha'} \int d\mathbf{r}' \bar{\rho}_{\alpha\alpha'}(\mathbf{r}, \mathbf{r} + \mathbf{r}') \mathbf{r}' \nabla' V_{\alpha\alpha'}(|\mathbf{r}'|) \\ - \frac{1}{2} \int d\mathbf{r}' \bar{\rho}_{ee^T}(\mathbf{r}, \mathbf{r} + \mathbf{r}') \mathbf{r}' \nabla' V(|\mathbf{r}'|), \quad (4.12)$$

where

$$\bar{\rho}_{\alpha\alpha'}(\mathbf{r}, \mathbf{r} + \mathbf{r}') = \int_0^1 d\lambda \rho_{\alpha\alpha'}(\mathbf{r} - \lambda\mathbf{r}', \mathbf{r} + (1-\lambda)\mathbf{r}') \quad (4.13)$$

and similarly for $\bar{\rho}_{ee^T}(\mathbf{r}, \mathbf{r} + \mathbf{r}')$. Returning now to (4.1) we obtain finally

$$\sigma = \frac{1}{2} \sum_{\alpha, \alpha'} \int dz \int d\mathbf{r}' \bar{\rho}_{\alpha\alpha'}(\mathbf{r}, \mathbf{r} + \mathbf{r}') [x' \nabla'_x - z' \nabla'_z] V_{\alpha\alpha'}(|\mathbf{r}'|) \\ + \frac{1}{2} \int dz \int d\mathbf{r}' \bar{\rho}_{ee^T}(\mathbf{r}, \mathbf{r} + \mathbf{r}') [x' \nabla'_x - z' \nabla'_z] V(|\mathbf{r}'|) \\ - \frac{1}{4\pi} \int dz (\nabla_z \phi(z))^2, \quad (4.14)$$

where we take into account that within the present symmetry $\phi = \phi(z)$ while

$$\rho_{\alpha\alpha'}(\mathbf{r}, \mathbf{r}') = \rho_{\alpha\alpha'}(|\mathbf{x} - \mathbf{x}'|; z, z'), \quad (4.15)$$

$$\bar{\rho}_{\alpha\alpha'}(\mathbf{r}, \mathbf{r} + \mathbf{r}') = \int_0^1 d\lambda \rho_{\alpha\alpha'}(|\mathbf{x}'|; z - \lambda z', z + (1-\lambda)z') \\ = \bar{\rho}_{\alpha\alpha'}(|\mathbf{x}'|; z, z'). \quad (4.16)$$

The expression (4.14) can also be written as

$$\sigma = \int dz (\sigma_{zz}^T(z) - \sigma_{xx}^T(z)) + \int dz (\sigma_{zz}^M(z) - \sigma_{xx}^M(z)), \quad (4.17)$$

which resembles Frenkel's formula [12] except that σ_{ij}^T are not the elements of the total pressure tensor but only of its truncated part (cf. (4.12)).

5. THE EQUIVALENCE PROBLEM

We have investigated three different approaches to the definition of the surface tension of planar interfaces and shown how each of them could be extended to the case of charged fluids. There now remains to show that these three approaches also yield equivalent results. We shall consider the three approaches two by two.

The mechanical result of (4.14) will be equivalent to the thermodynamic result of (3.12) if we can show that the following relation holds together with a similar relation for ρ_{ee^T} :

$$\int dz \int dz' \int d\mathbf{x}' \int_0^1 d\lambda \rho_{\alpha\alpha'}(|\mathbf{x}'|; z - \lambda z', z' + z - \lambda z') [x' \nabla'_x - z' \nabla'_z] V_{\alpha\alpha'}(|\mathbf{r}'|) \\ = \int dz \int dz' \int d\mathbf{x}' \rho_{\alpha\alpha'}(|\mathbf{x}'|; z, z' + z) [x' \nabla'_x - z' \nabla'_z] V_{\alpha\alpha'}(|\mathbf{r}'|), \quad (5.1)$$

where as usual $\mathbf{r}' = (\mathbf{x}', z') = (x', y', z')$. If in the left hand side of (5.1) we change the order of the integrations and change the z -variable to $z - \lambda z'$ we end

up with the right hand side of (5.1) provided this latter integral exists, i.e. provided the integrand $\int d\mathbf{x}' \rho_{\alpha\alpha'}(|\mathbf{x}'|; z, z'+z) \dots$, is a decreasing function of z while $\rho_{\alpha\alpha'}(|\mathbf{x}'|; z, z'+z)$ itself obviously is not. Assuming this to be the case the thermodynamic and mechanical theories will be equivalent.

The proof that the thermodynamic result (3.12) is also equivalent to the fluctuation theory result (2.48) and (2.49) is clearly a much more difficult matter. This was first done for the uncharged case in a remarkable paper by Schofield [3]. Its extension to the charged case undertaken here is seen to require only that due care be taken of the Coulomb singularities, a problem already encountered in § 2. We find it slightly easier to take Schofield's steps in reverse order and to start from the formula (2.49) which we write in view of (2.30) as

$$\beta\sigma = \lim_{q \rightarrow 0} \frac{1}{q^2} \sum_{\alpha} \int dz \rho'_{\alpha}(z) [A_{\alpha}(q; z) - A_{\alpha}(q=0; z)] \quad (5.2)$$

since we have already shown in (2.40) that $A_{\alpha}(q; z)$ is well behaved at $q=0$. In the present symmetry (2.5) becomes:

$$\sum_{\alpha_1} \int dz_1 G_{\alpha\alpha_1}(q; z, z_1) K_{\alpha_1\alpha}(q; z_1, z') = \delta_{\alpha\alpha} \delta(z - z'). \quad (5.3)$$

Multiplying by $\rho'_{\alpha}(z')$ and summing over α' and z' we obtain from (5.3):

$$\sum_{\alpha_1} \int dz_1 G_{\alpha\alpha_1}(q; z, z_1) A_{\alpha_1}(q; z_1) = \rho'_{\alpha}(z). \quad (5.4)$$

Since $A_{\alpha_1}(q=0, z_1)$ is finite and non-zero (in non-zero external fields) (5.4) tells us that $G_{\alpha\alpha_1}(q=0; z, z_1)$ is finite (this will be shown explicitly elsewhere [13] in relation to the long range correlations [9] developed by $G_{\alpha\alpha_1}$ along the electric double layer) and we can subtract the equation

$$\sum_{\alpha_1} \int dz_1 G_{\alpha\alpha_1}(q=0; z, z_1) A_{\alpha_1}(q=0, z_1) = \rho'_{\alpha}(z) \quad (5.5)$$

from (5.4) to yield

$$\begin{aligned} & \sum_{\alpha_1} \int dz_1 G_{\alpha\alpha_1}(q=0; z, z_1) [A_{\alpha_1}(q; z_1) - A_{\alpha_1}(q=0, z_1)] \\ &= - \sum_{\alpha_1} \int dz_1 [G_{\alpha\alpha_1}(q; z, z_1) - G_{\alpha\alpha_1}(q=0; z, z_1)] A_{\alpha_1}(q=0; z_1) \\ & \quad - \sum_{\alpha_1} \int dz_1 [G_{\alpha\alpha_1}(q; z, z_1) - G_{\alpha\alpha_1}(q=0; z, z_1)] [A_{\alpha_1}(q; z_1) \\ & \quad \quad \quad - A_{\alpha_1}(q=0, z_1)]. \end{aligned} \quad (5.6)$$

Multiplying (5.6) by $U'_{\alpha}(z)$, summing over α and z , we obtain in view of (2.17), (2.42) and (5.2)

$$\beta\sigma = - \lim_{q \rightarrow 0} \frac{1}{q^2} \sum_{\alpha, \alpha'} \int dz \int dz' U'_{\alpha}(z) [G_{\alpha\alpha'}(q; z, z') - G_{\alpha\alpha'}(q=0; z, z')] U'_{\alpha'}(z'), \quad (5.7)$$

where moreover we take into account that the second term in the right hand side of (5.6) is $O(q^3)$ [13]. Using now (2.6) and (2.16) we can rewrite (5.7) as

$$\beta\sigma = - \lim_{q \rightarrow 0} \frac{1}{q^2} \int dz \int dz' \int d(\mathbf{x} - \mathbf{x}') (\exp[-i\mathbf{q} \cdot (\mathbf{x} - \mathbf{x}')] - 1) \times \left\langle \left(\sum_{\alpha} U'_{\alpha}(z) \delta \hat{\rho}_{\alpha}(\mathbf{x}, z) \right) \left(\sum_{\alpha'} U'_{\alpha'}(z') \delta \hat{\rho}_{\alpha'}(\mathbf{x}', z') \right) \right\rangle. \quad (5.8)$$

We then eliminate the external field from (5.8) with the aid of the microscopic equation of motion :

$$\dot{g}_i(\mathbf{x}, z) + \sum_j \nabla_j \delta \hat{\sigma}_{ji}(\mathbf{x}, z) = \delta_{iz} \frac{1}{\beta} \sum_{\alpha} U'_{\alpha}(z) \delta \hat{\rho}_{\alpha}(\mathbf{x}, z), \quad (5.9)$$

where we have subtracted the equation for $\langle \dot{g}_i(\mathbf{x}, z) \rangle$ ($=0$ for a system in equilibrium) and put $\delta \hat{\rho}_{\alpha} = \hat{\rho}_{\alpha} - \rho_{\alpha}$ and $\delta \hat{\sigma}_{ij} = \hat{\sigma}_{ij} - \sigma_{ij}$. Separating ∇_j into the gradients normal (∇_z) and along (∇_{x_j}) the interface we obtain, neglecting surface terms in z and z'

$$\beta \sigma = - \lim_{q \rightarrow 0} \frac{\beta^2}{q^2} \int dz \int dz' \int d(\mathbf{x} - \mathbf{x}') (\exp[-i\mathbf{q}(\mathbf{x} - \mathbf{x}')] - 1) \\ \times \left\langle \left(\dot{g}_z(\mathbf{x}, z) + \sum_j \nabla_{x_j} \delta \hat{\sigma}_{jz}(\mathbf{x}, z) \right) \right. \\ \left. \times \left(\dot{g}_z(\mathbf{x}', z') + \sum_{j'} \nabla_{x_{j'}} \delta \hat{\sigma}_{j'z'}(\mathbf{x}', z') \right) \right\rangle. \quad (5.10)$$

Taking the limit and using the isotropy parallel to the interface we obtain ($\hat{\mathbf{q}} = \mathbf{q}/|\mathbf{q}|$)

$$\sigma = \frac{\beta}{2} \int dz \int dz' \int d(\mathbf{x} - \mathbf{x}') (\hat{\mathbf{q}} \cdot (\mathbf{x} - \mathbf{x}'))^2 \left\{ \langle \dot{g}_z(\mathbf{x}, z) \dot{g}_z(\mathbf{x}', z') \rangle \right. \\ \left. + \sum_{j, j'} \nabla_{x_j} \nabla_{x_{j'}} \langle \delta \hat{\sigma}_{jz}(\mathbf{x}, z) \delta \hat{\sigma}_{j'z'}(\mathbf{x}', z') \rangle \right\}, \quad (5.11)$$

whereas up to surface terms (which we assume to vanish) (5.11) can be rewritten as

$$\sigma = \frac{\beta}{2} \int dz \int dz' \int d(\mathbf{x} - \mathbf{x}') (\hat{\mathbf{q}} \cdot (\mathbf{x} - \mathbf{x}'))^2 \left\{ \langle \dot{g}_z(\mathbf{x}, z) \dot{g}_z(\mathbf{x}', z') \rangle \right. \\ \left. + \frac{(z - z')^2}{2} \sum_{j, j'} \nabla_{x_j} \nabla_{x_{j'}} \langle \dot{g}_j(\mathbf{x}, z) \dot{g}_{j'}(\mathbf{x}', z') \rangle \right\} \quad (5.12)$$

Integrating by parts we obtain

$$\sigma = \frac{\beta}{2} \int dz \int dz' \int d(\mathbf{x} - \mathbf{x}') \{ (\hat{\mathbf{q}} \cdot (\mathbf{x} - \mathbf{x}'))^2 \langle \dot{g}_z(\mathbf{x}, z) \dot{g}_z(\mathbf{x}', z') \rangle \\ - (z - z')^2 \langle \hat{\mathbf{q}} \cdot \dot{\mathbf{g}}(\mathbf{x}, z) \hat{\mathbf{q}} \cdot \dot{\mathbf{g}}(\mathbf{x}', z') \rangle \}. \quad (5.13)$$

Finally, using the multicomponent generalization of the sum rule derived by Jhon *et al.* [14]

$$\beta \langle \dot{g}_i(\mathbf{r}) \dot{g}_j(\mathbf{r}') \rangle = - \sum_{\alpha, \alpha'} \rho_{\alpha\alpha'}(\mathbf{r}, \mathbf{r}') \nabla_i \nabla_j (V_{\alpha\alpha'}(|\mathbf{r} - \mathbf{r}'|) + e_{\alpha} e_{\alpha'} V(|\mathbf{r} - \mathbf{r}'|)) \\ + \text{local terms}, \quad (5.14)$$

where the 'local terms' contain delta functions leading to vanishing contributions to (5.13), the latter reduces to

$$\sigma = \frac{1}{2A} \int d\mathbf{r} \int d\mathbf{r}' \sum_{\alpha, \alpha'} \rho_{\alpha\alpha'}(\mathbf{r}, \mathbf{r}') \{ (z - z')^2 (\hat{\mathbf{q}} \cdot \nabla)^2 \\ - (\hat{\mathbf{q}} \cdot (\mathbf{x} - \mathbf{x}'))^2 \nabla_z^2 \} (V_{\alpha\alpha'}(|\mathbf{r} - \mathbf{r}'|) + e_{\alpha} e_{\alpha'} V(|\mathbf{r} - \mathbf{r}'|)) \\ = \frac{1}{2A} \int d\mathbf{r} \int d\mathbf{r}' \sum_{\alpha, \alpha'} \rho_{\alpha\alpha'}(\mathbf{r}, \mathbf{r}') \{ (z - z') \nabla_{z-z'} \\ - (\mathbf{x} - \mathbf{x}') \cdot \hat{\mathbf{q}} \hat{\mathbf{q}} \cdot \nabla_{\mathbf{x}-\mathbf{x}'} \} (V_{\alpha\alpha'}(|\mathbf{r} - \mathbf{r}'|) + e_{\alpha} e_{\alpha'} V(|\mathbf{r} - \mathbf{r}'|)), \quad (5.15)$$

where the last step follows from the central character of the potentials. Equation (5.15) is identical to (3.4) which, as shown in § 3, can be further reduced to (3.12). And hence, provided the above assumptions are verified, the fluctuation theory and the thermodynamic theory will yield the same result.

6. CONCLUSIONS

We have derived a number of exact expressions for the surface tension of planar interfaces of fluids consisting of mixtures of charged and uncharged particles interacting through short ranged pair potentials and, for the charged species, the long ranged Coulomb potential. All difficulties due to the Coulomb potential could be avoided provided the system satisfies overall electroneutrality (2.37) as well as electroneutrality of the bulk phases (2.36). Charge segregation in the interfacial region, where an electric double layer can be built up, is however allowed. We have shown that the general expressions obtained for the surface tension σ within the fluctuation theory (2.49)

$$\sigma = \frac{1}{\beta} \lim_{q \rightarrow 0} \frac{1}{q^2} \left[\sum_{\alpha, \alpha'} \int dz \int dz' \rho'_{\alpha}(z) K_{\alpha\alpha'}(q; z, z') \rho'_{\alpha'}(z') - \sum_{\alpha} \int dz \rho'_{\alpha}(z) U'_{\alpha}(z) \right], \quad (6.1)$$

within the thermodynamic theory (3.1)–(3.3)

$$\sigma = \left[\frac{\partial F}{\partial A} \right]_{\rho, \Omega, N_{\alpha}} = \frac{1}{A} \left\langle \sum_{\alpha} \sum_{j=1}^{N_{\alpha}} \left(x_j \frac{\partial}{\partial x_j} - z_j \frac{\partial}{\partial z_j} \right) H \right\rangle \quad (6.2)$$

and within the mechanical theory (4.1)

$$\sigma = \int dz (\sigma_{zz}(z) - \sigma_{xx}(z)) \quad (6.3)$$

remain applicable to charged fluids and yield, respectively, the following results. The fluctuation theory leads to an expression (2.48)

$$\sigma = \frac{1}{\beta} \sum_{\alpha, \alpha'} \int dz \int dz' \rho'_{\alpha}(z) \bar{K}_{\alpha\alpha'}^{(2)}(z, z') \rho'_{\alpha'}(z') + 2\pi \int dz \int dz' \rho_e(z) |z - z'| \rho_e(z') \quad (6.4)$$

defining σ in terms of the density profiles $\rho_{\alpha}(z)$ (the charge density $\rho_e(z) = \sum_{\alpha} e_{\alpha} \rho_{\alpha}(z)$) and the second moment of the truncated inverse response functions (or direct correlation functions) $\bar{K}_{\alpha\alpha'}^{(2)}$. Taking into account the relation (2.38) between the charge density and the electric potential of the double layer (6.4) is equivalent to the result of the previous authors [4, 6]. The thermodynamic theory leads to the result (3.12)

$$\begin{aligned} \sigma = & \frac{1}{4} \sum_{\alpha, \alpha'} \int dz \int dz' \int d^2(\mathbf{x} - \mathbf{x}') \rho_{\alpha\alpha'}(|\mathbf{x} - \mathbf{x}'|; z, z') \frac{|\mathbf{x} - \mathbf{x}'|^2 - 2|z - z'|^2}{|\mathbf{r} - \mathbf{r}'|} \\ & \times V'_{\alpha\alpha'}(|\mathbf{r} - \mathbf{r}'|) + \frac{1}{4} \int dz \int dz' \int d^2(\mathbf{x} - \mathbf{x}') \rho_{ee}^T(|\mathbf{x} - \mathbf{x}'|; z, z') \\ & \times \frac{|\mathbf{x} - \mathbf{x}'|^2 - 2|z - z'|^2}{|\mathbf{r} - \mathbf{r}'|} V'(|\mathbf{r} - \mathbf{r}'|) \\ & + 2\pi \int dz \int dz' \rho_e(z) |z - z'| \rho_e(z') \quad (6.5) \end{aligned}$$

expressing σ in terms of the interaction potentials ($V_{\alpha\alpha'}$ and V), the pair distributions $\rho_{\alpha\alpha'}$, the truncated pair charge density ρ_{ee}^T and the charge density ρ_e . To our knowledge (6.5) is proposed here for the first time. The mechanical theory leads to an expression for σ (4.17)

$$\sigma = \int dz (\sigma_{zz}^T(z) - \sigma_{xx}^T(z)) + \int dz (\sigma_{zz}^M(z) - \sigma_{xx}^M(z)) \quad (6.6)$$

in terms of the elements of the Maxwell pressure tensor (σ_{ij}^M) and of the *truncated* pressure tensor (σ_{ij}^T). Finally, all three expressions, (6.4)–(6.6), have been shown, under relatively mild conditions, to be equivalent.

REFERENCES

- [1] KIRKWOOD, J. G., and BUFF, F. P., 1949, *J. chem. Phys.*, **17**, 338.
- [2] TRIEZENBERG, D. G., and ZWANZIG, R., 1972, *Phys. Rev. Lett.*, **28**, 1183.
- [3] SCHOFIELD, P., 1979, *Chem. Phys. Lett.*, **62**, 413.
- [4] EVANS, R., and SLUCKIN, T. J., 1980, *J. Phys. C*, **13**, L77.
- [5] EVANS, R., and SLUCKIN, T. J., 1980, *Molec. Phys.*, **40**, 413.
- [6] SENATORE, G., and TOSI, M. P., 1980, *Nuovo Cim.*, **56 B**, 109.
- [7] BUFF, F. P., 1955, *J. chem. Phys.*, **23**, 419.
- [8] LOVETT, R., MOU, C. Y., and BUFF, F. P., 1976, *J. chem. Phys.*, **65**, 570.
- [9] WERTHEIM, M. S., 1976, *J. chem. Phys.*, **65**, 2377.
- [10] BHATIA, A. B., MARCH, N. H., and TOSI, M. P., 1980, *Physics Chem. Liq.*, **9**, 229.
- [11] BAUS, M., 1982, *J. chem. Phys.*, **76**, 2003.
- [12] FRENKEL, J., 1946, *Kinetic Theory of Liquids* (Dover Publications), p. 362.
- [13] BAUS, M., *Molec. Phys.* (to be published).
- [14] JHON, H. S., DESAI, R. C., and DAHLER, J. S., 1978, *Chem. Phys. Lett.*, **56**, 151.

