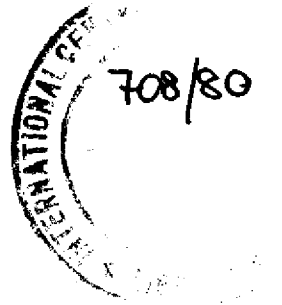


**INTERNATIONAL CENTRE FOR
THEORETICAL PHYSICS**



THEORY OF THE SURFACE DIPOLE LAYER AND OF SURFACE TENSION
IN LIQUIDS OF CHARGED PARTICLES

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THEORY OF THE SURFACE DIPOLE LAYER AND OF SURFACE TENSION

IN LIQUIDS OF CHARGED PARTICLES

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ABSTRACT

The problem of the surface density profiles and of the surface tension of a two-component liquid of charged particles in equilibrium with its vapour is examined. The exact equilibrium conditions for the profiles are given in terms of the inverse response functions of the inhomogeneous fluid, and alternative exact expressions for the surface tension are derived. The use of a density gradient expansion reduces the problem to knowledge of properties of a homogeneous charged fluid on a uniform neutralizing background, in which the total particle density and the charge density are independent variables. Additional simplifications are discussed for special cases for which a perturbative treatment of the surface charge density profile can be developed, and in particular for nearly symmetric ionic liquids and for simple liquid metals.

1. Introduction

Some attention has recently been given to the theory of the liquid-vapour interface in multicomponent neutral fluids. Of primary interest are the density profiles of the various component species across the interface, in particular the phenomenon of surface segregation and its effect on surface tension. A first principles theory has been set out by Bhatia *et al*¹ in terms of the partial direct correlation functions in the presence of a planar surface, in an extension of the fluctuation approach²⁻⁴ to the liquid-vapour interface in a one-component fluid. The use of a density gradient expansion reduces the problem to knowledge of the direct correlation functions in the bulk fluid mixture.^{5,6} Further simplifications can be introduced by perturbative schemes in special cases, such as in the model of conformal solutions for liquid binary alloys¹ when the interaction parameters of the component atoms are similar.

Surface segregation leads to a surface dipole layer in a multicomponent fluid of charged particles. Electric terms thus enter the equilibrium conditions for the surface density profiles and the expression for the surface tension of the bulk liquid in equilibrium with its bulk vapour. The surface dipole layer is also related to the net charge residing in a liquid droplet in equilibrium with its bulk vapour, as has been exhaustively discussed⁷ for electron-hole drops in semiconductors. The main aim of this paper is to develop the theory of the liquid-vapour interface in a binary fluid of charged particles in a form which exhibits explicitly the long-range electric terms and allows one to handle the residual effects of the interactions by the general methods already developed for neutral mixtures.

The formal theory of the density profiles in an inhomogeneous charged fluid is examined in detail for this purpose in section 2. The equilibrium conditions are set out in terms of the inverse response functions of the inhomogeneous fluid, thus allowing the result to be applicable to a quantum fluid as well. Section 3 considers the evaluation of the surface tension, for which several equivalent expressions are derived. The final expression achieves the desired separation into long-range Coulomb terms and neutral-mixture-like terms. It also allows us to make contact both with the fluctuation theory^{1,2} and with the Kirkwood-Buff theory⁸ of surface tension. The application of the density gradient expansion approximation is then straightforward, and is presented in section 4.

Among the possible applications of the formal results to the evaluation of surface properties of charged liquids, we give some consideration in the last sections of the paper to the classical one-component plasma on a semi-infinite background, to molten alkali halides, and to simple liquid metals. We stress in particular how perturbative treatments of the surface dipole layer can be developed under certain conditions both for molten salts and for liquid metals.

2. Equations for density profiles

We consider a fluid composed of two species of charged particles, with charges $Z_i e$ and spacial density distributions $\rho_i(\underline{r})$ ($i = 1, 2$). Overall electrical neutrality is imposed through

$$\sum_i Z_i \int d\underline{r} \rho_i(\underline{r}) = 0. \quad (2.1)$$

In practice, we shall be interested in a two-phase fluid with a planar liquid-vapour interface perpendicular to the x-axis, and we shall impose that the charge density vanishes far away from the interface as one moves either into the bulk liquid ($x \rightarrow -\infty$) or into the bulk vapour ($x \rightarrow +\infty$). The charge density is thus localized in the surface region, in the form of a surface dipole layer.

The density profiles at equilibrium can be related to the density response functions of the inhomogeneous fluid through the argument of Lovett *et al*⁴ as extended to multicomponent systems by Bhatia *et al*¹. One considers the fluid under a set of dimensionless one-body potentials $u_i(\underline{r})$ per particle of species i ,

$$u_i(\underline{r}) = \beta [\mu_i - U_i(\underline{r})], \quad (2.2)$$

where $U_i(\underline{r})$ is the external potential for species i , while μ_i is its chemical potential. The $u_i(\underline{r})$ are functionals of the particle densities $\rho_i(\underline{r})$, and use of translational invariance yields

$$\nabla u_i(\underline{r}) = \sum_j \int d\underline{r}' \frac{\delta u_i(\underline{r})}{\delta \rho_j(\underline{r}')} \nabla \rho_j(\underline{r}'). \quad (2.3)$$

The equilibrium conditions for $\rho_i(\underline{r})$ in the unperturbed inhomogeneous fluid follow when the external potentials are reduced to zero, i.e.

$$\sum_i \int d\underline{r}' \frac{\delta u_i(\underline{r})}{\delta \rho_j(\underline{r}')} \Big|_{U \rightarrow 0} \nabla \rho_j(\underline{r}') = 0. \quad (2.4)$$

The functional derivative entering this equation is recognized at once as an element of the inverse of the density response matrix $\chi_{ij}(\underline{r}, \underline{r}') \equiv \delta \rho_i(\underline{r}) / \delta U_j(\underline{r}') \Big|_{U \rightarrow 0}$ of the inhomogeneous fluid. Namely,

$$\frac{\delta u_i(\underline{r})}{\delta \rho_j(\underline{r}')} \Big|_{U \rightarrow 0} = -\beta \chi_{ij}^{-1}(\underline{r}, \underline{r}'), \quad (2.5)$$

leading in the classical limit to the well known expression

$$\left. \frac{\delta u_i(\underline{r})}{\delta \rho_i(\underline{r}')}\right|_{U \rightarrow 0} = \frac{\delta_{ij} \delta(\underline{r}-\underline{r}')}{\rho_i(\underline{r})} - \chi_{ij}(\underline{r}, \underline{r}') \quad (2.6)$$

in terms of the Ornstein-Zernike direct correlation functions $c_{ij}(\underline{r}, \underline{r}')$ in the inhomogeneous fluid.

An alternative derivation of the above equilibrium equations can be given by noticing that the chemical potentials are related to the Helmholtz free energy F , a functional of the particle densities $\rho_i(\underline{r})$, by

$$\mu_i = \frac{\delta F}{\delta \rho_i(\underline{r})} \quad (2.7)$$

The functional derivative in this equation changes, under a uniform translation by a small amount \underline{d} , by the amount

$$\Delta \left(\frac{\delta F}{\delta \rho_i(\underline{r})} \right) = \sum_j \int d\underline{r}' \frac{\delta^2 F}{\delta \rho_i(\underline{r}) \delta \rho_j(\underline{r}')} \underline{d} \cdot \nabla \rho_j(\underline{r}'), \quad (2.8)$$

which must vanish at equilibrium. The second functional derivative of F , on the other hand, describes the change of free energy under a small perturbation of the particle densities from equilibrium and thus is an element of the inverse density response matrix of the unperturbed inhomogeneous fluid,

$$\frac{\delta^2 F}{\delta \rho_i(\underline{r}) \delta \rho_j(\underline{r}')} = - \chi_{ij}^{-1}(\underline{r}, \underline{r}') \quad (2.9)$$

(see also eqn. (A.1)). From the above equations there follows at equilibrium

$$\nabla_i \frac{\delta F}{\delta \rho_i(\underline{r})} = - \sum_j \int d\underline{r}' \chi_{ij}^{-1}(\underline{r}, \underline{r}') \nabla \rho_j(\underline{r}') = 0, \quad (2.10)$$

which is eqn. (2.4).

It is convenient in the case of a charged fluid to focus at once on collective density variables which are the total particle density $\rho_N(\underline{r})$,

$$\rho_N(\underline{r}) = \rho_1(\underline{r}) + \rho_2(\underline{r}), \quad (2.11)$$

and the charge density $\rho_Q(\underline{r})$,

$$\rho_Q(\underline{r}) = Z_1 \rho_1(\underline{r}) + Z_2 \rho_2(\underline{r}), \quad (2.12)$$

measured in units of the elementary charge e . The dimensionless potentials for these variables are

$$\begin{aligned} \mu_N(\underline{r}) &= [Z_1 \mu_1(\underline{r}) - Z_2 \mu_2(\underline{r})] / (Z_1 - Z_2) \\ &\equiv \beta [\mu_N - U_N(\underline{r})] \end{aligned} \quad (2.13)$$

and

$$\begin{aligned} \mu_Q(\underline{r}) &= [\mu_1(\underline{r}) - \mu_2(\underline{r})] / (Z_1 - Z_2) \\ &\equiv \beta [\mu_Q - U_Q(\underline{r})], \end{aligned} \quad (2.14)$$

where we have introduced the appropriate chemical potentials as

$$\mu_N = (Z_1 \mu_1 - Z_2 \mu_2) / (Z_1 - Z_2) \quad (2.15)$$

and

$$\mu_Q = (\mu_1 - \mu_2) / (Z_1 - Z_2). \quad (2.16)$$

We can now bring out the long range effects of the Coulomb interactions by introducing a new dimensionless potential $\tilde{u}_Q(\underline{r})$ which is defined as

$$\tilde{u}_Q(\underline{r}) = \beta [\mu_Q - U_Q(\underline{r}) - V_Q(\underline{r})]. \quad (2.17)$$

Here, $V_Q(\underline{r})$ is the internal potential due to the charge polarization $\delta \rho_Q(\underline{r})$ induced by the external potentials,

$$V_Q(\underline{r}) = e^2 \int d\underline{r}' \delta \rho_Q(\underline{r}') / |\underline{r} - \underline{r}'|. \quad (2.18)$$

Therefore,

$$\frac{\delta \mu_Q(\underline{r})}{\delta \rho_Q(\underline{r}')} = \frac{\delta \tilde{u}_Q(\underline{r})}{\delta \rho_Q(\underline{r}')} + \frac{\beta e^2}{|\underline{r} - \underline{r}'|}. \quad (2.19)$$

Equations (2.4) can then be written

$$\int d\mathbf{r}' [X_{NN}^{-1}(\mathbf{r}, \mathbf{r}') \nabla \rho_N(\mathbf{r}') + X_{NQ}^{-1}(\mathbf{r}, \mathbf{r}') \nabla \rho_Q(\mathbf{r}')] = 0 \quad (2.20)$$

and

$$\int d\mathbf{r}' [X_{QN}^{-1}(\mathbf{r}, \mathbf{r}') \nabla \rho_N(\mathbf{r}') + \tilde{X}_{QQ}^{-1}(\mathbf{r}, \mathbf{r}') \nabla \rho_Q(\mathbf{r}')] = \int d\mathbf{r}' \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \nabla \rho_Q(\mathbf{r}'), \quad (2.21)$$

with the definitions

$$X_{NN}^{-1}(\mathbf{r}, \mathbf{r}') = (Z_1 - Z_2)^{-2} [Z_1^2 X_{11}^{-1}(\mathbf{r}, \mathbf{r}') + Z_2^2 X_{22}^{-1}(\mathbf{r}, \mathbf{r}') - Z_1 Z_2 X_{12}^{-1}(\mathbf{r}, \mathbf{r}') - Z_1 Z_2 X_{21}^{-1}(\mathbf{r}, \mathbf{r}')], \quad (2.22)$$

$$X_{NQ}^{-1}(\mathbf{r}, \mathbf{r}') = (Z_1 - Z_2)^{-2} [-Z_2 X_{11}^{-1}(\mathbf{r}, \mathbf{r}') - Z_1 X_{22}^{-1}(\mathbf{r}, \mathbf{r}') + Z_2 X_{12}^{-1}(\mathbf{r}, \mathbf{r}') + Z_1 X_{21}^{-1}(\mathbf{r}, \mathbf{r}')], \quad (2.23)$$

$$X_{QN}^{-1}(\mathbf{r}, \mathbf{r}') = (Z_1 - Z_2)^{-2} [-Z_2 X_{11}^{-1}(\mathbf{r}, \mathbf{r}') - Z_1 X_{22}^{-1}(\mathbf{r}, \mathbf{r}') + Z_1 X_{12}^{-1}(\mathbf{r}, \mathbf{r}') + Z_2 X_{21}^{-1}(\mathbf{r}, \mathbf{r}')], \quad (2.24)$$

$$X_{QQ}^{-1}(\mathbf{r}, \mathbf{r}') = (Z_1 - Z_2)^{-2} [X_{11}^{-1}(\mathbf{r}, \mathbf{r}') + X_{22}^{-1}(\mathbf{r}, \mathbf{r}') - X_{12}^{-1}(\mathbf{r}, \mathbf{r}') - X_{21}^{-1}(\mathbf{r}, \mathbf{r}')], \quad (2.25)$$

and

$$\tilde{X}_{QQ}^{-1}(\mathbf{r}, \mathbf{r}') = -k_B T \left. \frac{\delta \tilde{\mu}_Q(\mathbf{r}')}{\delta \rho_Q(\mathbf{r}')} \right|_{U, \mu} = X_{QQ}^{-1}(\mathbf{r}, \mathbf{r}') + \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} \quad (2.26)$$

The term on the r.h.s. of eqn. (2.21) is the negative of the macroscopic electric field $\underline{E}(\underline{r})$ created at point \underline{r} by the charge density profile in the fluid.

Equations (2.20) and (2.21) are the basic equations which determine the density profiles, the inverse response functions being those of the inhomogeneous fluid. In essence, the above procedure is equivalent to superposing onto the inhomogeneous fluid with charge density profile $\rho_Q(\underline{r})$ a background of charge density $-\rho_Q(\underline{r})$, which keeps it neutralized, and a background of charge density $\rho_Q(\underline{r})$ from which the long range Coulomb effects such as $\underline{E}(\underline{r})$ are calculated. That is, we have separated the effects of the interactions into "correlation" and "Hartree" terms. The former contain, of course, also the effects of short range interactions such as the overlap repulsion and the van der

Waals attraction in an ionic system. Since we have explicitly exhibited the long range effects in the r.h.s. of eqn. (2.21), we expect that the behaviour of $\tilde{X}_{QQ}^{-1}(\underline{r}, \underline{r}')$ will be analogous to that of the concentration-concentration inverse response function in a neutral mixture.

3. Surface tension of charged fluids

The surface tension of a neutral fluid can be determined from the density profiles and the inverse response functions through a formula derived by Triezenberg and Zwanzig² in the one-component case and extended to multicomponent fluids by Bhatia et al¹. In this section we shall analyze the surface tension of a charged fluid with the aim of isolating a Hartree term and terms which can be calculated as for a neutral fluid. Since we shall make use of the equilibrium conditions and of an expression for the equilibrium pressure, which contain Hartree contributions, we shall obtain in this process various equivalent expressions for the surface tension. We shall also make contact with the theory of Kirkwood and Buff⁸, which expresses the surface tension through an integral of the deficit of tangential pressure across the surface layer. The equivalence of the Triezenberg-Zwanzig theory and the Kirkwood-Buff theory for a neutral fluid with pair interaction potentials has recently been demonstrated by Schofield⁹.

The free energy density $\psi(x)$ for a two-phase charged fluid with a planar interface perpendicular to the x-axis can be written

$$\Psi(x) = \frac{1}{2} \rho_Q(x) \phi(x) + \tilde{\Psi}(x), \quad (3.1)$$

where the first term gives the Hartree contribution and the second is the free energy density of the inhomogeneous fluid neutralized by a background of charge density $-\rho_Q(x)$, and is a functional of $\rho_N(x)$ and $\rho_Q(x)$. The electrostatic potential $\phi(x)$ generated by the charge density $\rho_Q(x)$, on account of the electrical neutrality condition (2.1), is evaluated as

$$\begin{aligned} \phi(x) &= e^2 \int dx' \rho_Q(x') / |x-x'| \\ &= \phi(\infty) + 4\pi e^2 \int_x^\infty dx' \rho_Q(x') (x-x'). \end{aligned} \quad (3.2)$$

The free energy of the fluid with surface area A is thus given by

$$F = A f_H + \int dx \tilde{\Psi}(x), \quad (3.3)$$

where

$$\begin{aligned} f_H &= \frac{1}{2} \int_{-\infty}^{\infty} dx \rho_Q(x) \phi(x) \\ &= 2\pi e^2 \int_{-\infty}^{\infty} dx \rho_Q(x) \int_x^\infty dx' \rho_Q(x') (x-x'). \end{aligned} \quad (3.4)$$

We note for future reference that eqn. (3.4) is equivalent to

$$f_H = \frac{1}{8\pi} \int_{-\infty}^{\infty} dx E^2(x) \quad (3.5)$$

where $E(x) = -e^{-1} d\phi(x)/dx$ is the electric field normal to the interface, related to $\rho_Q(x)$ by Poisson's equation.

The first term on the r.h.s. of eqn. (3.3) is already a surface term, since $\rho_Q(x)$ is nonvanishing only in the surface region. In order to achieve a complete separation of F into terms which are proportional to the volume V and to the surface area A, we must compare it with the free energy F_0 of a bulk liquid and a bulk vapour at the given temperature and chemical potentials, and densities $\rho_\ell = \rho_N(-\infty)$ and $\rho_v = \rho_N(+\infty)$ on the

coexistence curve. Since the charge density vanishes in the bulk phases (i.e. $\rho_Q(x) \rightarrow 0$ for $x \rightarrow \pm\infty$), we can unambiguously locate the Gibbs surface on the total density profile $\rho_N(x)$, as for a neutral one-component fluid¹⁰. Therefore,

$$F_0 = -PV + \mu_N N, \quad (3.6)$$

where N is the total number of particles in the fluid and P is the pressure. Hence, the surface tension is given by

$$\sigma = f_H + \int_{-\infty}^{\infty} dx [\tilde{\Psi}(x) + P - \mu_N \rho_N(x)]. \quad (3.7)$$

This derivation of an expression for σ is equivalent to that commonly followed for the electron gas¹¹, and in particular our expression (3.4) for f_H coincides with that given by Kalia and Vashishta⁷ for the electrostatic contribution to the surface tension of the electron-hole liquid in semiconductors.

The expression (3.1) for the free energy density can now be used to evaluate the pressure P entering eqn. (3.7). The chemical potentials introduced in eqns. (2.15) and (2.16) are given by

$$\mu_N = A \int_{-\infty}^{\infty} dx' \frac{\delta \tilde{\Psi}(x')}{\delta \rho_N(x)} \quad (3.8)$$

and

$$\begin{aligned} \mu_Q &= \phi(x) + A \int_{-\infty}^{\infty} dx' \frac{\delta \tilde{\Psi}(x')}{\delta \rho_Q(x)} \\ &\equiv \phi(x) + \tilde{\mu}_Q(x), \end{aligned} \quad (3.9)$$

where $\tilde{\mu}_Q(x)$ represents the difference in chemical potentials between the two components in the neutralized fluid with density profiles $\rho_N(x)$ and $\rho_Q(x)$. As we noted in the preceding section in connection with eqn. (2.7), these equations are equivalent to the equilibrium conditions for the surface density profiles. We now multiply eqn. (3.8) by $d\rho_N(x)/dx$

and eqn. (3.9) by $d\rho_Q(x)/dx$, and integrate both equations over x from the vapour to x . Adding the results and subtracting the free energy density Ψ_V of the vapour, we get

$$\left\{ \mu_N \rho_N(x) + \tilde{\mu}_Q(x) \rho_Q(x) - A \int_{-\infty}^x dx' \int_{-\infty}^{\infty} dz' \left[\frac{\delta \tilde{\Psi}(x')}{\delta \rho_N(x'')} \frac{d\rho_N(x'')}{dz''} + \frac{\delta \tilde{\Psi}(x')}{\delta \rho_Q(x'')} \frac{d\rho_Q(x'')}{dz''} \right] - \Psi_V \right\} + \left\{ \rho_Q(x) \phi(x) - \int_{-\infty}^x dx' \phi(x') \frac{d\rho_Q(x')}{dx'} \right\} = \mu_N \rho_V - \Psi_V, \quad (3.10)$$

where the r.h.s. refers to the bulk vapour phase and can be identified with the pressure P . Clearly, the two curly brackets on the l.h.s. represent the pressure $\tilde{P}(x)$ of the neutralized fluid and the Hartree term in the pressure, respectively. We thus write

$$P = \tilde{P}(x) + P_H(x) \quad (3.11)$$

and it is easy to show, through the use of Poisson's equation, that

$$P_H(x) = -\frac{1}{8\pi} E^2(x). \quad (3.12)$$

In fact, $P_H(x)$ is (aside for the conventional change in sign) the normal force per unit area associated with the Maxwell stress tensor, whose components in the present geometry are

$$\begin{cases} \sigma_{xx}(x) = \frac{1}{8\pi} E^2(x) \\ \sigma_{yy}(x) = \sigma_{zz}(x) = -\frac{1}{8\pi} E^2(x) \\ \sigma_{xy} = \sigma_{yz} = \sigma_{zx} = 0 \end{cases} \quad (3.13)$$

Substitution of eqn. (3.11) into eqn. (3.7) yields, through the use of eqn. (3.5),

$$\sigma = \int_{-\infty}^{\infty} dx \left[\tilde{\Psi}(x) + \tilde{P}(x) - \mu_N \rho_N(x) \right], \quad (3.14)$$

in which the Hartree term no longer appears explicitly.

Equation (3.14) still does not reflect all the thermodynamic properties of the neutralized binary fluid, which include also the chemical potential $\tilde{\mu}_Q(x)$. The neutrality condition (2.1) allows us, however, to add a term $-\mu_Q \rho_Q(x)$ to the integrand, and use of eqn. (3.9) leads then to our final expression for the surface tension,

$$\sigma = -2f_H + \int_{-\infty}^{\infty} dx \left[\tilde{\Psi}(x) + \tilde{P}(x) - \mu_N \rho_N(x) - \tilde{\mu}_Q(x) \rho_Q(x) \right]. \quad (3.15)$$

All the terms in the correlation contribution clearly have an analogue in a neutral mixture, and their treatment can now be developed in full analogy with that of neutral mixtures¹ as we shall see in detail in the next section through the use of a density gradient expansion. Equation (3.15) can also be rewritten in the form

$$\sigma = \int_{-\infty}^{\infty} dx \left\{ \left[\tilde{P}(x) - \sigma_{xx}(x) \right] - \left[\mu_N \rho_N(x) + \tilde{\mu}_Q(x) \rho_Q(x) - \tilde{\Psi}(x) - \sigma_{yy}(x) \right] \right\} \quad (3.16)$$

having used the expressions for the components of the Maxwell stress tensor given in eqn. (3.13). The first square bracket is the pressure P and the second is the density of the negative of the thermodynamic potential $\tilde{\Sigma}$, supplemented by a Maxwell stress term. In this form, our result can be compared¹² with the result of Kirkwood and Buff⁸,

$$\sigma = \int_{-\infty}^{\infty} dx \left[P - P_t(x) \right], \quad (3.17)$$

where $P_t(x)$ is the pressure normal to an area element in the x - y plane at height x .

Finally, we note that the correlation term in eqn. (3.15) can be expressed through the inverse response functions of the inhomogeneous fluid as in the Triezenberg-Zwanzig theory, with the only proviso that $\tilde{\chi}_{QQ}(\underline{r}, \underline{r}')$ must be used in place of the full charge-charge response function. Indeed, starting from

the expression for the surface tension of a multicomponent fluid given by Bhatia et al¹ (their eqn. (3.25)) and using eqn. (2.26), a straightforward calculation leads to

$$\sigma = -2f_H + \iint_{-\infty}^{\infty} dz_1 dz_2 \left\{ K_{NN}(z_1, z_2) \frac{d\rho_N(z_1)}{dz_1} \frac{d\rho_N(z_2)}{dz_2} + \tilde{K}_{QQ}(z_1, z_2) \frac{d\rho_Q(z_1)}{dz_1} \frac{d\rho_Q(z_2)}{dz_2} + [K_{NQ}(z_1, z_2) + K_{QN}(z_2, z_1)] \frac{d\rho_N(z_1)}{dz_1} \frac{d\rho_Q(z_2)}{dz_2} \right\}, \quad (3.18)$$

with

$$\tilde{K}_{QQ}(z_1, z_2) = -\frac{1}{2} \left. \frac{d^2}{dk^2} \tilde{\chi}_{QQ}^{-1}(k; z_1, z_2) \right|_{k=0} \quad (3.19)$$

and similar expressions for the other K's. Here, $\tilde{\chi}_{QQ}^{-1}(k; z_1, z_2)$ is the two-dimensional Fourier transform of $\tilde{\chi}_{QQ}^{-1}(R; z_1, z_2)$ with respect to the planar variable \mathbf{R} . A detailed derivation is given in the Appendix.

4. Density gradient expansion

The equilibrium conditions and the expressions for the surface tension that we have derived in the preceding sections, though formally exact, require information on the response functions of the inhomogeneous fluid. These are not at present available, and we thus turn to the use of a density gradient expansion for the free energy density, which will lead to approximate results involving only the free energy and the response functions of a bulk fluid with total density ρ_N and charge density ρ_Q , neutralized by a background of charge density $-\rho_Q$. Our use of the expansion limits the usefulness of these results to classical fluids, since its application to the kinetic energy density in the case of a quantum fluid can lead only to rough results.

The gradient expansion approximates^{5,1} the free energy density $\tilde{\Psi}(\mathbf{x})$ of the neutralized inhomogeneous fluid by

$$\tilde{\Psi}(\mathbf{x}) = \tilde{\Psi}(\{\rho\}) + \frac{1}{2} A_{NN}(\{\rho\}) (\rho'_N)^2 + A_{NQ}(\{\rho\}) \rho'_N \rho'_Q + \frac{1}{2} A_{QQ}(\{\rho\}) (\rho'_Q)^2, \quad (4.1)$$

where the local term $\tilde{\Psi}(\{\rho\})$ is the free energy density of a neutralized homogeneous fluid of densities $\{\rho\} = \{\rho_N(\mathbf{x}), \rho_Q(\mathbf{x})\}$, and a prime denotes differentiation with respect to \mathbf{x} . The other quantities in eqn. (4.1) are defined by

$$\begin{cases} A_{NN}(\{\rho\}) = -\frac{1}{2} \left. \frac{d^2}{dk^2} \tilde{\chi}_{NN}^{-1}(k; \{\rho\}) \right|_{k=0} \\ A_{NQ}(\{\rho\}) = -\frac{1}{2} \left. \frac{d^2}{dk^2} \tilde{\chi}_{NQ}^{-1}(k; \{\rho\}) \right|_{k=0} \\ A_{QQ}(\{\rho\}) = -\frac{1}{2} \left. \frac{d^2}{dk^2} \tilde{\chi}_{QQ}^{-1}(k; \{\rho\}) \right|_{k=0} \end{cases} \quad (4.2)$$

in terms of the Fourier transforms of the inverse density response functions in the neutralized homogeneous fluid. In a classical fluid these can be replaced by the corresponding direct correlation functions multiplied by $k_B T$ (see eqns (2.5) and (2.6)), with the only proviso that the asymptotic Coulomb value $-4\pi\beta e^2/k^2$ must be subtracted from $c_{QQ}(k; \{\rho\})$.

The chemical potentials follow from eqns (3.8) and (3.9) as

$$\mu_N = \frac{\partial \tilde{\Psi}(\{\rho\})}{\partial \rho_N(\mathbf{x})} - A_{NN} \rho_N'' - \frac{1}{2} \frac{\partial A_{NN}}{\partial \rho_N} (\rho'_N)^2 - \frac{\partial A_{NN}}{\partial \rho_Q} \rho'_N \rho'_Q - A_{NQ} \rho_Q'' + \left(\frac{1}{2} \frac{\partial A_{QQ}}{\partial \rho_N} - \frac{\partial A_{NQ}}{\partial \rho_Q} \right) (\rho'_Q)^2 \quad (4.3)$$

and

$$\mu_Q(\mathbf{x}) = \frac{\partial \tilde{\Psi}(\{\rho\})}{\partial \rho_Q(\mathbf{x})} - A_{QQ} \rho_Q'' - \frac{1}{2} \frac{\partial A_{QQ}}{\partial \rho_Q} (\rho'_Q)^2 - \frac{\partial A_{QQ}}{\partial \rho_N} \rho'_N \rho'_Q - A_{NQ} \rho_N'' + \left(\frac{1}{2} \frac{\partial A_{NN}}{\partial \rho_Q} - \frac{\partial A_{NQ}}{\partial \rho_N} \right) (\rho'_N)^2, \quad (4.4)$$

while eqn. (3.10) for the pressure yields

$$\tilde{P}(\mathbf{x}) = \mu_N \rho_N(\mathbf{x}) + \mu_Q(\mathbf{x}) \rho_Q(\mathbf{x}) - \tilde{\Psi}(\{\rho\}) + \frac{1}{2} A_{NN} (\rho'_N)^2 + A_{NQ} \rho'_N \rho'_Q + \frac{1}{2} A_{QQ} (\rho'_Q)^2. \quad (4.5)$$

All these expressions are formally equivalent to those¹ holding for a neutral mixture in the same approximation, with the charge density replacing the concentration variable. Finally, eqn. (3.15) for the surface tension yields

$$\sigma = -2f_N + \int_{-\infty}^{\infty} dz [A_{NN}(\rho'_N)^2 + 2A_{NQ} \rho'_N \rho'_Q + A_{QQ}(\rho'_Q)^2], \quad (4.6)$$

where, again, the second term is formally identical to the result of Bhatia et al¹ for the surface tension of a neutral mixture.

Equation (4.3), and eqn. (3.9) with $\tilde{\mu}_Q(x)$ given by eqn. (4.4), must in general be solved simultaneously to determine the total density profile $\rho_N(x)$ and the charge density profile $\rho_Q(x)$. Use of these profiles in eqn. (3.11), with $\tilde{P}(x)$ given by eqn. (4.5), yields the pressure P, and their use in eqn. (4.6) yields the surface tension. We note here two special cases in which the problem simplifies considerably:

(i) in the case of a classical one-component plasma on a semi-infinite background, the total density ρ_N and the functions associated with it lose meaning. The equilibrium conditions reduce to eqn. (3.9) with $\tilde{\mu}_Q(x)$ given by the first three terms on the r.h.s. of eqn. (4.4). In this equation as well as in the expressions for the pressure and the surface tension, one should set $\rho_N = 0$ and ρ_Q equal to the density of the plasma in all terms except the Hartree terms, which still contain the full ρ_Q inclusive of the charge density of the semi-infinite background.

(ii) in the case of a symmetric system, in which the two component species are identical except for the signs of their charges, the charge density $\rho_Q(x)$ vanishes by symmetry. The r.h.s. of eqn. (4.3) reduces to the first three terms, and the problem reduces to that of a neutral one-component fluid. We shall exploit this fact below to develop a perturbative treatment of the liquid-vapour interface in alkali halide systems.

5. Nearly symmetric molten salts

A symmetric model of a molten alkali halide, in which a single potential function describes the short range interactions between the various ion pairs, has been considered by Hansen and McDonald¹³ in simulation work on the structural and dynamical properties of bulk ionic liquids. Molten salts of isoelectronic alkali and halogen ions are not very far from this idealized model, especially molten NaF in which the electronic polarizabilities of the ions are small. The great simplification in the theory of the bulk properties of the model arises from the fact that its Hamiltonian is invariant under exchange of the two ionic species. This fact implies, in particular, that the static correlations between total density and charge density fluctuations vanish exactly in the bulk.

From our viewpoint, the general property of the Hamiltonian that we have recalled above for such a symmetric system has the following consequences. First of all, the chemical potential μ_Q defined in eqn. (2.16), with $Z_1 = -Z_2$, vanishes. Furthermore, the function $A_{NQ}(\{\rho\})$ vanishes with ρ_Q , while the functions $\tilde{\Psi}(\{\rho\})$ and $A_{NN}(\{\rho\})$ vary quadratically with ρ_Q . Clearly, the equilibrium condition (3.9) then admits a solution with $\rho_Q(x) = 0$.

We thus expect that in a nearly symmetric molten salt the charge density $\rho_Q(x)$ will be small everywhere across the surface region, so that the problem can be linearized in $\rho_Q(x)$. The form taken by the equilibrium condition (3.9) within the gradient expansion scheme is

$$\mu_Q = \phi(x) + f(x) + g(x) \rho_Q(x) - \frac{d}{dx} \left[A_{QQ}^0(\rho_N(x)) \frac{d\rho_Q(x)}{dx} \right] \quad (5.1)$$

where $A_{QQ}^0(\rho_N(x))$ refers to the bulk molten salt and

$$f(x) = f(\rho) \Big|_{\rho_a=0}, \quad (5.2)$$

$$g(x) = \frac{\partial f(\rho)}{\partial \rho_a} \Big|_{\rho_a=0}, \quad (5.3)$$

with

$$f(\rho) = \frac{\partial \tilde{\Psi}(\rho)}{\partial \rho_a} - A_{Na} \rho_N'' + \left(\frac{1}{2} \frac{\partial A_{NN}}{\partial \rho_a} - \frac{\partial A_{Ng}}{\partial \rho_N} \right) (\rho_N')^2. \quad (5.4)$$

A similar linearization of eqn. (4.3) in $\rho_Q(x)$ clearly allows one to determine the surface density profiles self-consistently, starting from the total density profile in the absence of a surface dipole layer. The problem thus posed requires a knowledge of the free energy density and of the direct correlation functions for the bulk molten salt and of their variation under a small relative change of the ionic densities $\delta(\rho_i - \rho_j)$, neutralized by the addition of a uniform background.

An additional simplification is possible, however, since the differences between the two ionic species are small by assumption and can thus be treated perturbatively. As we noted above, both μ_Q and $f(x)$ in eqn. (5.1) vanish in the limit of a symmetric system, so that only their variation with a difference between the two ionic species is involved. The functions $g(x)$ and $A_{QQ}^0(\rho_N(x))$, on the other hand, can be replaced in eqn. (5.1) by their values in the symmetric system. A similar linearization of eqn. (4.3) then allows one to treat the surface properties of a nearly symmetric system by a full perturbative scheme, starting from the density profile and the surface tension of the symmetric system.

The perturbative scheme proposed above clearly involves only the variations of the free energy density and of the direct correlation functions of a bulk symmetric molten salt under a relative change of the short-range interaction potentials of the ionic species and a neutralized change of the relative ionic densities. Such variations could be estimated by the use of a

charged-hard-spheres model. The necessary theoretical input is already available in the literature¹⁴⁻¹⁶ for the mean spherical approximation to this model. A refinement of this approximation could be based on an extension of the so-called self-consistent Ornstein-Zernike approximation developed by Høje and Stell¹⁷ for a bulk fluid of charged hard spheres of equal diameters.

6. Simple liquid metals

Numerous calculations of the distribution of conduction electrons at a metal surface are already available in the literature^{11,18}, based on either a semi-infinite background model or a rigid-lattice model for the ionic component of the metal. Especially in the case of a liquid metal, however, the ions can be expected to follow to some extent the outward relaxation of the electronic distribution. We wish to indicate in this section how a perturbative treatment of this effect can be given, on the assumption that the electron-ion interactions are weak. This may be expected to be useful for the so-called simple liquid metals, and in particular for the alkali metals.

It is convenient to this end to return to the equilibrium conditions for the individual components of the charged fluid, that we have discussed at the beginning of section 2. As has been recently pointed out¹⁹, the matrix of inverse response functions for the components of the bulk liquid metal takes a very simple form in the cases where the electron-ion interactions can be described by a local pseudopotential $v(\underline{r}-\underline{r}')$ and treated by linear screening theory. The argument can be extended to the inverse response functions of an inhomogeneous ion-electron fluid, with the result

$$\chi_{ij}^{-1}(\underline{r}, \underline{r}') = \begin{pmatrix} \chi_i^{-1}(\underline{r}, \underline{r}') & -v(\underline{r}-\underline{r}') \\ -v(\underline{r}-\underline{r}') & \chi_e^{-1}(\underline{r}, \underline{r}') \end{pmatrix} \quad (6.1)$$

where $\chi_i(\underline{r}, \underline{r}')$ and $\chi_e(\underline{r}, \underline{r}')$ are the response functions for the ionic and the electronic component decoupled from each other, each being neutralized by an appropriate semi-infinite background. The equilibrium conditions (2.4) thus take in the liquid metal the simple form

$$\begin{cases} \int d\underline{r}' \chi_i^{-1}(\underline{r}, \underline{r}') \nabla \rho_i(\underline{r}') = \int d\underline{r}' v(\underline{r}-\underline{r}') \nabla \rho_e(\underline{r}') \\ \int d\underline{r}' \chi_e^{-1}(\underline{r}, \underline{r}') \nabla \rho_e(\underline{r}') = \int d\underline{r}' v(\underline{r}-\underline{r}') \nabla \rho_i(\underline{r}') \end{cases} \quad (6.2)$$

where $\rho_i(\underline{r})$ and $\rho_e(\underline{r})$ are the ionic and the electronic density distribution. These can be replaced in the r.h.s. of eqn. (6.2), to the same order of perturbation theory, by their values in the uncoupled systems ($\rho_i^0(\underline{r})$ and $\rho_e^0(\underline{r})$, say).

The density distributions in the uncoupled systems are, on the other hand, the solutions of two independent equilibrium conditions, which can be written

$$\int d\underline{r}' \chi_i^{-1}(\underline{r}, \underline{r}') \nabla \rho_i^0(\underline{r}') = \nabla U_i(\underline{r}) \quad (6.3)$$

and

$$\int d\underline{r}' \chi_e^{-1}(\underline{r}, \underline{r}') \nabla \rho_e^0(\underline{r}') = \nabla U_e(\underline{r}) \quad (6.4)$$

Here, $U_i(\underline{r})$ and $U_e(\underline{r})$ are the potentials generated by the semi-infinite backgrounds for the ionic and the electronic system, related to each other by

$$U_i(\underline{r}) = Z U_e(\underline{r}) \quad (6.5)$$

if Z is the ionic valence. Subtraction of eqns (6.3) and (6.4) from eqns (6.2) yields

$$\int d\underline{r}' \chi_i^{-1}(\underline{r}, \underline{r}') \nabla [\rho_i(\underline{r}') - \rho_i^0(\underline{r}')] = -\nabla U_i(\underline{r}) + \int d\underline{r}' v(\underline{r}-\underline{r}') \nabla \rho_e^0(\underline{r}') \quad (6.6)$$

and

$$\int d\underline{r}' \chi_e^{-1}(\underline{r}, \underline{r}') \nabla [\rho_e(\underline{r}') - \rho_e^0(\underline{r}')] = -\nabla U_e(\underline{r}) + \int d\underline{r}' v(\underline{r}-\underline{r}') \nabla \rho_i^0(\underline{r}'). \quad (6.7)$$

Of course, the Coulomb piece $-Ze^2/|\underline{r}-\underline{r}'|$ in the bare pseudo-potential on the r.h.s. of eqns (6.6) and (6.7) should be combined with the background potentials to cancel divergences.

It is thus clear that the effect of ionic relaxation on the electronic distribution at a liquid metal surface can be calculated within a linear response scheme by replacing the potential of the semi-infinite background in the Hohenberg-Kohn-Sham²⁰ Schrodinger equation by the potential of the distorted ionic distribution $\rho_i^0(\underline{x})$. This presupposes, of course, that $\rho_i^0(\underline{x})$ is known through a calculation for the ionic system on a semi-infinite background, based on the gradient-expansion scheme discussed in section 4 for classical charged fluids. The converse is clearly true for the effect of electronic relaxation on the ionic density distribution, as is apparent from eqn. (6.6).

7. Discussion and summary

The formally exact theory of the surface dipole layer in a two-component charged fluid is embodied in the coupled equations (2.20) and (2.21), supplemented by eqn. (3.15) or eqn. (3.18) for the surface tension. These equations involve the inverse response functions of the inhomogeneous fluid, and an implementation of the theory clearly requires approximations. We have therefore resorted to a density gradient expansion to arrive at the equilibrium conditions in the form given by eqn. (4.3) and by eqns (3.9) and (4.4), the corresponding

expression for the surface tension being given in eqn. (4.6). At this stage, the theory still requires knowledge of the free energy density and of the inverse response functions in a homogeneous fluid of charged particles in which the total density of particles ρ_N and the charge density ρ_Q vary independently, ρ_Q being neutralized by the charge density of an inert background.

We have thus examined special cases of charged fluids where additional simplifications become allowed. We have exploited the fact that the surface dipole layer vanishes in a symmetric binary fluid to suggest a perturbative approach for nearly symmetric ionic liquids, such as the molten alkali halides composed of isoelectronic ions. We have also briefly examined the consequences of linear screening theory of the electron-ion coupling in liquid metals in relation to the calculation of their surface dipole layer. This has in turn pointed to the need for a calculation of the surface properties of a classical one-component plasma on a semi-infinite background. An extension of our discussion of the surface structure of a simple liquid metal to a treatment of the surface dynamics of these systems appears possible, and we hope to present it in a future publication.

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Appendix. Derivation of equation (3.18)

A wavelike distortion $\rho_i(k, x)$ of the particle densities is accompanied by a change in Helmholtz free energy given by

$$\Delta F = -\frac{1}{2} A \sum_{ij} \int_{-\infty}^{\infty} dx_1 dx_2 \chi_{ij}^{-1}(k; x_1, x_2) \rho_i^*(k, x_1) \rho_j(k, x_2), \quad (A.1)$$

where $\chi_{ij}^{-1}(k; x_1, x_2)$ is the two-dimensional Fourier transform of $\chi_{ij}^{-1}(R; x_1, x_2)$ with respect to the variable \underline{R} in the y-z plane. With the expansion

$$\chi_{ij}^{-1}(k; x_1, x_2) = \chi_{ij}^{-1}(0; x_1, x_2) - k^2 K_{ij}(x_1, x_2) + \dots \quad (A.2)$$

and proceeding as in Bhatia *et al*¹, one finds the equilibrium conditions for the surface density profiles,

$$\sum_{ij} \int_{-\infty}^{\infty} dx_1 dx_2 \chi_{ij}^{-1}(0; x_1, x_2) \frac{d\rho_i(x_1)}{dx_1} \frac{d\rho_j(x_2)}{dx_2} = 0, \quad (A.3)$$

and the expression for the surface tension,

$$\sigma = \sum_{ij} \int_{-\infty}^{\infty} dx_1 dx_2 K_{ij}(x_1, x_2) \frac{d\rho_i(x_1)}{dx_1} \frac{d\rho_j(x_2)}{dx_2}. \quad (A.4)$$

We now carry out the transformation given in eqns (2.11) and (2.12), and use the definitions (2.22)-(2.26). Equations (2.20) and (2.21) are recovered at once from eqn. (A.3), while eqn. (A.4) yields

$$\sigma = \sigma_H + \sigma_{\text{corr}} \quad (A.5)$$

with the expression for σ_{corr} given in eqn. (3.18). On the other hand,

$$\sigma_H = -\frac{1}{2} \pi e^2 \int_{-\infty}^{\infty} dx_1 dx_2 \frac{d\rho_Q(x_1)}{dx_1} \frac{d\rho_Q(x_2)}{dx_2} \int_0^{\infty} \frac{R^3 dR}{\sqrt{R^2 + (x_1 - x_2)^2}} \quad (A.6)$$

Integration by parts over x_1 and x_2 , and integration over R , lead to

$$\sigma_H = 2\pi e^2 \int_{-\infty}^{\infty} dx_1 dx_2 \rho_Q(x_1) \rho_Q(x_2) |x_1 - x_2|, \quad (A.7)$$

which is equal to $-2f_H$.

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