

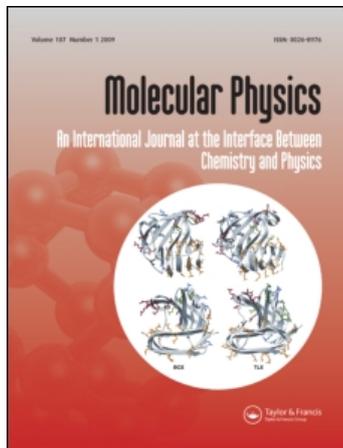
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Thermodynamics and correlation functions of plasmas and electrolyte solutions

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We consider multi-component electrolyte solutions and plasmas in thermal equilibrium and define thermodynamic quantities for number densities which do not necessarily satisfy the condition of charge neutrality. It is shown that these quantities play a role in compressibility theorems for the pair correlation functions and in the generalized Debye shielding length. A fourth moment condition for the pair correlation functions is derived. We discuss to what extent non-uniform systems may be described in terms of local thermodynamics with added coulomb interactions.

1. INTRODUCTION

It is well known that classical equilibrium systems containing freely moving charges are neutral in the bulk [1, 2]. Any net charge distributes itself over the surface of the system; charge fluctuations in the interior are extremely small. Thermodynamic quantities defined from the grand canonical partition function by means of a thermodynamic limiting procedure are dominated by the neutral bulk. In non-uniform systems charge neutrality need not be satisfied locally, e.g. near the boundary of an electrolyte solution electric double layers can be formed [3]. We show in this paper that it is then possible to work with local thermodynamic functions which depend on the local number densities not necessarily satisfying the condition of electroneutrality. The functions can be defined by the methods of statistical mechanics for non-uniform systems. In §§ 2 and 3 we describe the procedure, emphasizing the peculiarities of coulomb systems. For simplicity we use a model in which the solvent influences the coulomb interactions only through the dielectric constant, but the formalism is easily extended to take full account of the polar properties of the solvent.

In § 4 we define correlation functions by functional differentiation of the Helmholtz free energy functional with respect to the density. It is shown that the long range part of the pair correlation functions is conveniently expressed in terms of a renormalized interaction involving the screened electrostatic Green function. The screening length is a generalization of the Debye length to higher density. Under certain conditions it can be expressed in terms of the local thermodynamic functions defined earlier. In § 5 we show that compressibility theorems for the correlation functions also involve these thermodynamic functions. The relation to the usual type of compressibility theorem which follows from the grand canonical partition function is given in the Appendix. In § 6 we show that the pair correlation functions satisfy a fourth moment condition. The moment involves

the local thermodynamic functions and hence is of less universal character than the zeroth and second moment conditions derived previously [4]. In § 7 we treat the Debye–Hückel theory as an example and in § 8 we discuss under what conditions the thermodynamic functions can be used to describe non-uniform situations in terms of local thermodynamics with added coulomb interactions. As an application of the formalism in § 9 we evaluate the fluctuations of the total charge in a spherical volume element in a solution which on average is uniform and neutral. If the radius of the sphere is larger than the Debye length the fluctuations are proportional to the surface area, if it is smaller they are proportional to the volume of the sphere with an amplitude determined by the local thermodynamic functions.

2. EQUILIBRIUM CONDITIONS

We consider an electrolyte solution consisting of ions with charges e_α in a neutral solvent at temperature T . The solution is confined to a vessel of volume V . The polar properties of the system are simplified and taken into account only by including the dielectric constant of the solvent in the coulomb interaction. Moreover we assume that the medium outside V is uniform with the same dielectric constant, so that the coulomb interaction between ions is given by

$$w_{\alpha\beta}(\mathbf{r}_i, \mathbf{r}_j) = \frac{e_\alpha e_\beta}{\varepsilon |\mathbf{r}_i - \mathbf{r}_j|}. \quad (2.1)$$

The short-range interactions between all particles, ions as well as solvent molecules, are fully included in the potential energy. Thus we consider a multi-component system with short-range interactions and with added coulomb interactions between the charged particles. All interactions are assumed to be translationally invariant. Often one considers a further simplified system in which the solvent is treated as a structureless continuum. This is called the primitive model.

We denote the average number densities in thermal equilibrium by an s -component vector $\{n_\alpha(\mathbf{r})\} \equiv \mathbf{n}(\mathbf{r})$ (s is the number of solvent and solute components). As we demonstrate in § 3 these satisfy equilibrium conditions

$$\mu_\alpha(\mathbf{r}, [\mathbf{n}]) + e_\alpha \phi(\mathbf{r}, [\mathbf{n}]) = \mu_\alpha^z, \quad (2.2)$$

where $\mu_\alpha(\mathbf{r}, [\mathbf{n}])$ is the chemical potential of species α at \mathbf{r} . The latter has a functional dependence on the densities $\mathbf{n}(\mathbf{r}')$ in a restricted neighbourhood of the point \mathbf{r} . The average coulomb potential $\phi(\mathbf{r})$ also depends on the average densities and in the absence of external electric fields is given by

$$\phi(\mathbf{r}) = \int \frac{\sum_\beta e_\beta n_\beta(\mathbf{r}')}{\varepsilon |\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \quad (2.3)$$

By construction $\phi(\mathbf{r})$ satisfies the electrostatic Maxwell equations in all space.

The values of the constants $\{\mu_\alpha^z\}$ on the right-hand side of (2.2) may be restricted by dissociation equilibria, but it is assumed that otherwise they can be prescribed arbitrarily. The superscript z indicates that the $\{\mu_\alpha^z\}$ are related to the activities $\{z_\alpha\}$ appearing in the grand canonical ensemble by

$$\mu_\alpha^z = kT \ln(z_\alpha \Lambda_\alpha^3), \quad (2.4)$$

where Λ_α is the de Broglie wavelength for species α . For a system of given shape and volume it follows from the grand canonical ensemble that to each set of values μ^z there corresponds a set of average densities $\mathbf{n}(\mathbf{r})$ satisfying (2.2).

The left-hand side of (2.2) will be called the electrochemical potential of species α . Of course at equilibrium this equals μ_α^z , but for non-equilibrium the left-hand side of (2.2) is still defined whereas μ_α^z has no meaning. The equilibrium condition states that at thermal equilibrium the electrochemical potentials are constant throughout the system. For suitable choices of potentials μ^z the system is neutral. Then the ions will be distributed uniformly apart from small boundary effects. The chemical potentials $\mu_0^z(V)$ for which the system is neutral depend slightly on the chosen volume V , because the functional dependence in (2.2) is slightly volume-dependent due to boundary effects, but they tend to a well defined limit $\mu_0^z(\infty)$ as the vessel becomes large in a regular manner [5]. The chemical potentials μ_0^z define a hypersurface S_0 in μ^z -space called the neutral hypersurface.

For values μ^z different from μ_0^z the system is charged. For a sufficiently large system the excess charges distribute themselves along the surface and their effect is screened from the interior within a distance of the order of the Debye length. The bulk of the system is neutral again. The surface charge distribution can be found to a good approximation from the laws of electrostatics for ideal conductors. Suppose μ^z corresponds to a positively charged system. Then by decreasing the μ_α^z of the positively charged species and increasing those of the negatively charged ones the system will be driven back to neutrality. Hence there must be a ϕ_0 such that

$$\mu^z = \mu_0^z + \mathbf{e}\phi_0, \quad (2.5)$$

where $\mathbf{e} \equiv \{e_\alpha\}$. We may compare this equation to (2.2) in the interior of the system where $\mathbf{n}(\mathbf{r})$ reduces to a set of almost uniform bulk densities and $\phi(\mathbf{r}, [\mathbf{n}])$ is almost constant, according to the laws of electrostatics. It follows then that ϕ_0 is the electrostatic potential in the interior and μ^z and μ_0^z , related by (2.5), describe systems with the same bulk densities. The difference between the systems described by μ^z and μ_0^z is that the former possesses a net surface charge which produces an electrostatic potential in the interior, whereas the latter does not. We can define a modified potential

$$\psi(\mathbf{r}) = \phi(\mathbf{r}) - \phi_0 \quad (2.6)$$

and rewrite the equilibrium condition in the form

$$\mu(\mathbf{r}, [\mathbf{n}]) + \mathbf{e}\psi(\mathbf{r}) = \mu_0^z. \quad (2.7)$$

In the interior the modified potential $\psi(\mathbf{r})$ vanishes approximately. From electrostatics one finds that the total charge is $Q \approx C\phi_0$ where C is the capacity of the ideal conductor with the same volume. The capacity is of order ϵL , where L is the linear dimension of the system, so that for fixed ϕ_0 the total coulomb energy $Q^2/2C$ is also of order L . Hence in the thermodynamic limit the coulomb energy does not contribute to the thermodynamic properties per unit volume (with the exception of the specific Gibbs free energies $g_\alpha = \mu_\alpha^z$), nor to those of the surface per unit area. The thermodynamic properties per unit volume are entirely dominated by the neutral bulk of the system. In particular the pressure $p(\mu^z)$, as found from the grand canonical partition function, equals $p(\mu_0^z)$ for μ^z and μ_0^z related by (2.5).

We shall denote this pressure function by $p_0(\boldsymbol{\mu}^z)$. It has the obvious property

$$\sum_{\alpha} e_{\alpha} (\partial p_0 / \partial \mu_{\alpha}^z) = \sum_{\alpha} e_{\alpha} n_{0\alpha} = 0, \quad (2.8)$$

which is nothing else than the well known electroneutrality condition. This statement was proven rigorously by Lieb and Lebowitz [5]. We note that for systems with a finite geometry, boundary effects can influence significantly the composition of the bulk. For a treatment of systems with a plane geometry see reference [6].

When additional one-body potentials $\{\Phi_{\alpha}(\mathbf{r})\}$ are imposed the equilibrium condition (2.2) is changed to

$$\boldsymbol{\mu}(\mathbf{r}, [\mathbf{n}]) + \mathbf{e}\phi(\mathbf{r}, [\mathbf{n}]) + \Phi(\mathbf{r}) = \boldsymbol{\mu}^z. \quad (2.9)$$

The solution $\mathbf{n}(\mathbf{r})$ is modified accordingly and by suitable choice of the potentials $\Phi(\mathbf{r})$ any equilibrium distribution can in principle be achieved.

3. FREE ENERGY FUNCTIONAL

The statistical mechanics of non-uniform systems has been developed by Morita and Hiroike [7], De Dominicis [8], Percus [9], Stell [10], and others [11]. The grand canonical partition function Ξ is considered as a functional of the generalized activities

$$z_{\alpha}^*(\mathbf{r}) = z_{\alpha} \exp[-\beta\Phi_{\alpha}(\mathbf{r})] \quad (3.1)$$

or of their logarithms

$$\gamma_{\alpha}(\mathbf{r}) = \ln z_{\alpha}^*(\mathbf{r}) = \beta(\mu_{\alpha}^z - \Phi_{\alpha}(\mathbf{r})). \quad (3.2)$$

As shown for example in the review by Stell [10] the grand canonical distribution functions can be obtained from Ξ by functional differentiation with respect to $z_{\alpha}^*(\mathbf{r})$ or $\gamma_{\alpha}(\mathbf{r})$. Here we shall explicitly need the first two functional derivatives of $\ln \Xi$ with respect to $\gamma_{\alpha}(\mathbf{r})$, which are

$$\frac{\delta \ln \Xi}{\delta \gamma_{\alpha}(\mathbf{r})} = n_{\alpha}(\mathbf{r}), \quad (3.3 a)$$

$$\begin{aligned} \frac{\delta^2 \ln \Xi}{\delta \gamma_{\alpha}(\mathbf{r}) \delta \gamma_{\beta}(\mathbf{r}')} &= \hat{F}_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = n_{\alpha}(\mathbf{r}) \delta_{\alpha\beta} \delta(\mathbf{r} - \mathbf{r}') + F_{\alpha\beta}(\mathbf{r}, \mathbf{r}') \\ &= n_{\alpha\beta}(\mathbf{r}, \mathbf{r}') + n_{\alpha}(\mathbf{r}) \delta_{\alpha\beta} \delta(\mathbf{r} - \mathbf{r}') - n_{\alpha}(\mathbf{r}) n_{\beta}(\mathbf{r}'), \end{aligned} \quad (3.3 b)$$

where $n_{\alpha\beta}$ is the two-particle distribution function for species α and β .

The Helmholtz free energy is defined as a functional of the one-particle densities $n_{\alpha}(\mathbf{r})$ by a Legendre transformation

$$\mathcal{F}([\mathbf{n}]) = \mathcal{F}^{\text{int}}([\mathbf{n}]) + \mathcal{F}^{\text{ext}}([\mathbf{n}]), \quad (3.4 a)$$

$$\beta \mathcal{F}^{\text{int}}([\mathbf{n}]) = -\ln \Xi([\gamma]) + \sum_{\alpha} \int_V n_{\alpha}(\mathbf{r}) \gamma_{\alpha}(\mathbf{r}) d\mathbf{r}, \quad (3.4 b)$$

$$\mathcal{F}^{\text{ext}}([\mathbf{n}]) = \sum_{\alpha} \int_V n_{\alpha}(\mathbf{r}) \Phi_{\alpha}(\mathbf{r}) d\mathbf{r}. \quad (3.4 c)$$

In equation (3.4 a) the free energy \mathcal{F} is separated into an internal and an external part. The latter is simply the total potential energy due to the external potentials $\Phi(\mathbf{r})$. In (3.4 c) the Φ_{α} must be considered as given functions, not as functions of the density. The functional derivatives of \mathcal{F}^{int} with respect to the densities can be

expressed in terms of direct correlation functions. Specifically we have for the first two derivatives

$$\beta \frac{\delta \mathcal{F}^{\text{int}}}{\delta n_{\alpha}(\mathbf{r})} = \gamma_{\alpha}(\mathbf{r}), \quad (3.5 a)$$

$$\begin{aligned} \beta \frac{\delta^2 \mathcal{F}^{\text{int}}}{\delta n_{\alpha}(\mathbf{r}) \delta n_{\beta}(\mathbf{r}')} &= \beta \frac{\delta^2 \mathcal{F}}{\delta n_{\alpha}(\mathbf{r}) \delta n_{\beta}(\mathbf{r}')}, \\ &= -\hat{c}_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = -c_{\alpha\beta}(\mathbf{r}, \mathbf{r}') + \delta_{\alpha\beta} \delta(\mathbf{r} - \mathbf{r}') / n_{\alpha}(\mathbf{r}). \end{aligned} \quad (3.5 b)$$

Note that $\hat{c}_{\alpha\beta}$ and $\hat{F}_{\alpha\beta}$ satisfy the Ornstein–Zernike relation [12]

$$\begin{aligned} - \sum_{\gamma} \int \hat{F}_{\alpha\gamma}(\mathbf{r}, \mathbf{r}'') \hat{c}_{\gamma\beta}(\mathbf{r}'', \mathbf{r}') d\mathbf{r}'' &= \sum_{\gamma} \int \frac{\delta n_{\alpha}(\mathbf{r})}{\delta \gamma_{\gamma}(\mathbf{r}'')} \frac{\delta \gamma_{\gamma}(\mathbf{r}')}{\delta n_{\beta}(\mathbf{r}')} d\mathbf{r}'' \\ &= \delta_{\alpha\beta} \delta(\mathbf{r}' - \mathbf{r}''). \end{aligned} \quad (3.6)$$

For systems with coulomb interactions we can separate the internal free energy as

$$\mathcal{F}^{\text{int}}([\mathbf{n}], T) = \mathcal{F}^0([\mathbf{n}], T) + E^{\text{coul}}([\mathbf{n}]), \quad (3.7)$$

where the coulomb energy is given by

$$E^{\text{coul}}([\mathbf{n}]) = \frac{1}{2} \sum_{\alpha\beta} \iint_V w_{\alpha\beta}(\mathbf{r}, \mathbf{r}') n_{\alpha}(\mathbf{r}) n_{\beta}(\mathbf{r}') d\mathbf{r} d\mathbf{r}', \quad (3.8)$$

with $w_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ as defined in (2.1). The chemical potentials $\mu_{\alpha}(\mathbf{r}, [\mathbf{n}])$ can be defined as

$$\mu_{\alpha}(\mathbf{r}, [\mathbf{n}]) = \frac{\delta \mathcal{F}^0}{\delta n_{\alpha}(\mathbf{r})}. \quad (3.9)$$

The reason for making the separation (3.7) is that the chemical potentials defined by (3.9), as well as all other thermodynamic quantities which can be obtained from the free energy functional \mathcal{F}^0 , are local functionals of the densities. This means that $\mu(\mathbf{r})$ depends only on the density fields $\mathbf{n}(\mathbf{r}')$ in the neighbourhood of \mathbf{r} with a radius proportional to the Debye shielding length. Mayer [13] has shown this first by devising a resummation of the divergent virial expansion for the pressure of an infinite system with coulomb interactions. He found indeed that the pressure, and as a consequence also the free energy density, separated into a coulomb contribution of type (3.8) and a contribution which for uniform systems could be made plausible to have a range on the order of the Debye length. Especially at low densities Mayer's results coincide with those of Debye–Hückel theory.

Equation (3.9) together with (3.2), (3.5 a), (3.7) and (3.8) leads to the equilibrium condition (2.9). As explained in the preceding section, in the absence of external potentials the bulk of the system will be uniform, with electric double layers near the boundaries. At the boundaries there will be characteristic wall effects which are conveniently described by the introduction of a surface phase with corresponding thermodynamic functions [6].

In a non-uniform system we can measure the densities relative to a reference state $\mathbf{n}_0(\mathbf{r})$ by writing

$$\mathbf{n}(\mathbf{r}) = \mathbf{n}_0(\mathbf{r}) + \mathbf{n}_1(\mathbf{r}). \quad (3.10)$$

By expansion about the reference state we obtain for the chemical potentials

$$\begin{aligned} \mu_\alpha(\mathbf{r}, [\mathbf{n}]) = & \mu_\alpha(\mathbf{r}, [\mathbf{n}_0]) - kT \sum_\beta \int \hat{c}_{\alpha\beta}^0(\mathbf{r}, \mathbf{r}') n_{1\beta}(\mathbf{r}') d\mathbf{r}' \\ & - \frac{1}{2} kT \sum_{\beta\gamma} \iint \hat{c}_{\alpha\beta\gamma}^0(\mathbf{r}, \mathbf{r}', \mathbf{r}'') n_{1\beta}(\mathbf{r}') n_{1\gamma}(\mathbf{r}'') d\mathbf{r}' d\mathbf{r}'' + \dots, \end{aligned} \quad (3.11)$$

where the \hat{c}^0 are the direct correlation functions for the reference state. The superscript 0 indicates that these functions are obtained from \mathcal{F}^0 by functional derivation with respect to the densities, but of course $\hat{c}_{\alpha\beta\gamma}^0 \dots = \hat{c}_{\alpha\beta\gamma}^0 \dots$ for three or more indices because of (3.8). From (3.11) one may conclude that μ is a short-ranged functional of the densities also in non-uniform systems, provided all the direct correlation functions in the reference state are sufficiently short ranged.

Consider in particular the thermodynamic limit of a large neutral system with uniform densities $\mathbf{n}_0 \equiv \{n_{0\alpha}\}$ satisfying the condition of electroneutrality $\mathbf{e} \cdot \mathbf{n}_0 = \sum_\alpha e_\alpha n_{0\alpha} = 0$. In such a state the chemical potentials $\mu(\mathbf{n}_0) = \mu_0^z$ lie on the neutral hypersurface S_0 , and the direct correlation functions \hat{c}^0 are translationally invariant and short ranged. Choosing the densities $\mathbf{n}_1(\mathbf{r})$ to be spatially uniform we see that the chemical potentials $\mu([\mathbf{n}_0 + \mathbf{n}_1])$ are also uniform. Thus by Taylor expansion we have derived chemical potentials $\mu(\mathbf{n})$ as functions of \mathbf{n} which do not necessarily satisfy the electroneutrality condition. Equivalently the chemical potentials can be defined in terms of (resummed) Mayer functions by extending these definitions to non-uniform and/or non-neutral systems. Either way it follows that for a system with uniform densities, but not necessarily satisfying the electroneutrality condition, the chemical potentials can be obtained from the free energy density $\mathbf{f}^0(\mathbf{n}) = \mathcal{F}^0(\mathbf{n})/V$ as

$$\mu(\mathbf{n}) = \partial f^0 / \partial \mathbf{n}. \quad (3.12)$$

By Legendre transformation we can define the pressure as a function of the chemical potentials.

$$p(\boldsymbol{\mu}) = -f^0 + \sum_\alpha n_\alpha \mu_\alpha, \quad (3.13)$$

where \mathbf{n} as a function of $\boldsymbol{\mu}$ has to be solved from (3.12). From the equilibrium condition (2.2) it follows that in a non-uniform system with $\Phi = 0$ the gradient of p is locally balanced by the electrostatic field. Note that $p(\boldsymbol{\mu})$ differs from the function $p_0(\boldsymbol{\mu}^z)$ defined in the previous section from the thermodynamic limit in the grand canonical ensemble. Considering these functions in the same $\boldsymbol{\mu}$ -space we see that

$$p(\boldsymbol{\mu}) = p_0(\boldsymbol{\mu}) \text{ on } S_0, \quad \frac{\partial p}{\partial \boldsymbol{\mu}} = \frac{\partial p_0}{\partial \boldsymbol{\mu}} = \mathbf{n}_0 \text{ on } S_0. \quad (3.14)$$

The function $p_0(\boldsymbol{\mu})$ is degenerate in the sense that $\sum_\alpha e_\alpha (\partial p_0 / \partial \mu_\alpha) = 0$ everywhere in $\boldsymbol{\mu}$ -space. We contend that the function $p(\boldsymbol{\mu})$ contains more physical information.

4. RELATIONS BETWEEN CORRELATION FUNCTIONS

For systems with coulomb interactions it follows from (3.5 *b*) and (3.7) that the direct correlation functions $\hat{c}_{\alpha\beta}$ can be split into a part given by the long-range

interaction and a part of short range

$$\hat{c}_{\alpha\beta} = \hat{c}_{\alpha\beta}^0 - \beta w_{\alpha\beta}. \quad (4.1)$$

Corresponding to the short-range direct correlation functions $\hat{c}_{\alpha\beta}^0$, we define a set of auxiliary quantities $\hat{F}_{\alpha\beta}^0$, called the short range pair cluster functions (this nomenclature does not imply that the $\hat{F}_{\alpha\beta}^0$ are long-ranged functions, they have a longer range than the $\hat{F}_{\alpha\beta}^0$ however) and connected to the $\hat{c}_{\alpha\beta}^0$ by the Ornstein–Zernike relation

$$-\sum_{\gamma} \int \hat{F}_{\alpha\beta}^0(\mathbf{r}, \mathbf{r}'') \hat{c}_{\gamma\beta}^0(\mathbf{r}'', \mathbf{r}') d\mathbf{r}'' = \delta_{\alpha\beta} \delta(\mathbf{r} - \mathbf{r}'). \quad (4.2)$$

We may represent $\hat{F}_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$, $\hat{c}_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$, etc., as matrix kernels $\hat{\mathbf{F}}$ and $\hat{\mathbf{C}}$. The multiplication of two of these kernels is defined by

$$(\mathbf{M}\mathbf{N})_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = \sum_{\gamma} \int M_{\alpha\gamma}(\mathbf{r}, \mathbf{r}'') N_{\gamma\beta}(\mathbf{r}'', \mathbf{r}') d\mathbf{r}''. \quad (4.3)$$

With these conventions the Ornstein–Zernike relations (3.6) and (4.2) can be rewritten as

$$\hat{\mathbf{F}} = -\hat{\mathbf{C}}^{-1}, \quad (4.4 a)$$

$$\hat{\mathbf{F}}^0 = -(\hat{\mathbf{C}}^0)^{-1}. \quad (4.4 b)$$

Since we see from (3.5 *b*) and (3.11) that the short-range direct correlation functions $\hat{\mathbf{C}}^0$ are functional derivatives of the chemical potentials

$$\hat{c}^0(\mathbf{r}, \mathbf{r}') = -\beta(\delta\mu(\mathbf{r})/\delta\mathbf{n}(\mathbf{r}')), \quad (4.5)$$

it follows that the short-range pair cluster functions $\hat{\mathbf{F}}^0$ are given by the inverse functional derivatives

$$\hat{\mathbf{F}}^0(\mathbf{r}, \mathbf{r}') = kT(\delta\mathbf{n}(\mathbf{r})/\delta\mu(\mathbf{r}')). \quad (4.6)$$

From (4.1) and (4.4) it follows that $\hat{\mathbf{F}}$ is related to $\hat{\mathbf{F}}^0$ by

$$\hat{\mathbf{F}} = (\mathbf{I} + \beta\hat{\mathbf{F}}^0\mathbf{W})^{-1}\hat{\mathbf{F}}^0. \quad (4.7)$$

A more convenient relation is found by expressing the pair function $\hat{\mathbf{F}}$ in the form

$$\hat{\mathbf{F}} = \hat{\mathbf{F}}^0 - \beta\hat{\mathbf{F}}^0\mathbf{U}\hat{\mathbf{F}}^0, \quad (4.8)$$

where the renormalized interaction \mathbf{U} must satisfy

$$\mathbf{U} = \mathbf{W} - \beta\mathbf{W}\hat{\mathbf{F}}^0\mathbf{U} \quad (4.9)$$

or equivalently

$$\mathbf{U} = (\mathbf{I} + \beta\mathbf{W}\hat{\mathbf{F}}^0)^{-1}\mathbf{W}. \quad (4.10)$$

Equations (4.7) and (4.10) show that $\hat{\mathbf{F}}$ and \mathbf{U} develop from $\hat{\mathbf{F}}^0$ resp. \mathbf{W} by an alternating chain of short-range correlations and long-range interactions. Similar relations were previously derived by one of us in a semi-macroscopic theory [14].

For \mathbf{W} given by (2.1) we can express the renormalized interaction \mathbf{U} in terms of a scalar function g^E as

$$U_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = e_{\alpha}e_{\beta}g^E(\mathbf{r}, \mathbf{r}'). \quad (4.11)$$

From (4.9) it follows that g^E satisfies the integral equation

$$g^E(\mathbf{r}, \mathbf{r}') = \frac{1}{\varepsilon |\mathbf{r} - \mathbf{r}'|} - \beta \int \int \frac{1}{\varepsilon |\mathbf{r} - \mathbf{r}''|} \sum_{\alpha\beta} e_\alpha e_\beta \hat{F}_{\alpha\beta}^0(\mathbf{r}'', \mathbf{r}''') g^E(\mathbf{r}''', \mathbf{r}') d\mathbf{r}'' d\mathbf{r}''', \quad (4.12)$$

from which we find, by acting with the Laplace operator,

$$\nabla^2 g^E(\mathbf{r}, \mathbf{r}') - \frac{4\pi}{\varepsilon} \beta \int \sum_{\alpha\beta} e_\alpha e_\beta \hat{F}_{\alpha\beta}^0(\mathbf{r}, \mathbf{r}'') g^E(\mathbf{r}'', \mathbf{r}') d\mathbf{r}'' = -\frac{4\pi}{\varepsilon} \delta(\mathbf{r} - \mathbf{r}'). \quad (4.13)$$

This is a generalization of the linear Poisson–Boltzmann equation occurring in Debye–Hückel theory [15] and $g^E(\mathbf{r}, \mathbf{r}')$ can be identified with the electrostatic Green function for the geometry under consideration. As a consequence of (4.8) and (4.11) the long-distance behaviour of all pair functions $\hat{F}_{\alpha\beta}^0(\mathbf{r}, \mathbf{r}')$ is given by the same scalar function $g^E(\mathbf{r}, \mathbf{r}')$. For uniform systems this is most easily seen by Fourier transforming (4.8), with the result

$$\hat{\mathbf{F}}(\mathbf{k}) = \hat{\mathbf{F}}^0(\mathbf{k}) - \beta \hat{\mathbf{F}}^0(\mathbf{k}) \mathbf{U}(\mathbf{k}) \hat{\mathbf{F}}^0(\mathbf{k}). \quad (4.14)$$

The Fourier transform $\mathbf{U}(\mathbf{k})$ is found from (4.13) as

$$U_{\alpha\beta}(\mathbf{k}) = \frac{(4\pi/\varepsilon) e_\alpha e_\beta}{k^2 + (4\pi\beta/\varepsilon) \sum_{\alpha\beta} e_\alpha e_\beta \hat{F}_{\alpha\beta}^0(\mathbf{k})}. \quad (4.15)$$

To obtain the long range behaviour of $\hat{\mathbf{F}}$ we have to find the singularity of the right-hand side of (4.14) which is closest to the real axis. If indeed $\hat{\mathbf{F}}^0$ is of shorter range than \mathbf{U} (in the Debye–Hückel case $\hat{\mathbf{F}}^0(\mathbf{r}, \mathbf{r}')$ is proportional to a δ -function $\delta(\mathbf{r} - \mathbf{r}')$!) then this singularity is found as a zero point of the denominator in (4.15). Hence both \mathbf{U} and $\hat{\mathbf{F}}$ decay asymptotically as $\exp(-\tilde{K}r)$ for large r , where \tilde{K} has to be determined from

$$\tilde{K}^2 - (4\pi\beta/\varepsilon) \sum_{\alpha\beta} e_\alpha e_\beta \hat{F}_{\alpha\beta}^0(i\tilde{K}) = 0. \quad (4.16)$$

If the range of $\hat{\mathbf{F}}^0$ is much shorter than \tilde{K}^{-1} we may replace $\hat{F}_{\alpha\beta}^0(i\tilde{K})$ approximately by $\hat{F}_{\alpha\beta}^0(0)$ and (4.16) simplifies

$$-\tilde{K}^2 \approx K^2 \equiv \frac{4\pi}{\varepsilon} \sum_{\alpha\beta} e_\alpha e_\beta \frac{\partial n_\alpha}{\partial \mu_\beta}, \quad (4.17)$$

where we have used (4.6) and the fact that in a uniform system

$$\partial \mathbf{n} / \partial \mu = \int (\delta \mathbf{n}(\mathbf{r}) / \delta \mu(\mathbf{r}')) d\mathbf{r}'.$$

In the sequel we shall refer to $\Lambda = K^{-1}$ as the generalized Debye–Hückel screening length. We have to keep in mind however that in fact \tilde{K} describes the asymptotic exponential decay of the pair correlation function and K equals \tilde{K} only if the range of the short range correlation functions $\hat{F}_{\alpha\beta}^0$ is much smaller than \tilde{K}^{-1} . Stell and Lebowitz [16] have introduced a generalized Debye screening length which looks very similar to (4.17), but instead of our $\hat{\mathbf{F}}^0$ they used the pair correlation function of a reference system in which only short-range interactions are present. Furthermore Høye and Stell [17] derived a quantity similar to K for a one-component system with neutralizing background, but they expressed little hope of generalizing their relation to many-component systems [18].

5. COMPRESSIBILITY THEOREMS

In the preceding section we have shown that the pair correlations and re-normalized interactions can be calculated from the short-range direct correlation functions \mathbf{C}^0 and the long-range interactions \mathbf{W} . The derived expressions are valid for arbitrary geometry. Here we consider the thermodynamic limit of a neutral system where all the above functions become translationally invariant. We show that the integrals of the various correlation functions can be related to thermodynamic derivatives by generalized compressibility theorems.

From (4.5) we see that

$$\int \hat{\mathbf{c}}^0(\mathbf{r}-\mathbf{r}')d\mathbf{r}' = -\beta(\partial\boldsymbol{\mu}/\partial\mathbf{n})_0, \quad (5.1)$$

where the subscript 0 indicates that the derivative is to be evaluated for the neutral state. From (4.6) it follows immediately that correspondingly

$$\int \hat{\mathbf{F}}^0(\mathbf{r}-\mathbf{r}')d\mathbf{r}' = kT(\partial\mathbf{n}/\partial\boldsymbol{\mu})_0. \quad (5.2)$$

In (4.17) we have defined a screening parameter K in terms of these derivatives. It follows from (4.11) and (4.15) that

$$\int g^E(\mathbf{r}-\mathbf{r}')d\mathbf{r}' = (4\pi/\varepsilon K^2). \quad (5.3)$$

From (4.8), (4.11), and (5.3) we find

$$\begin{aligned} \int \hat{\mathbf{F}}(\mathbf{r}-\mathbf{r}')d\mathbf{r}' &= kT\left(\frac{\partial\mathbf{n}}{\partial\boldsymbol{\mu}}\right)_0 - kT\left(\frac{\partial\mathbf{n}}{\partial\boldsymbol{\mu}}\right)_0 \cdot \frac{4\pi\mathbf{e}\mathbf{e}}{\varepsilon K^2} \cdot \left(\frac{\partial\mathbf{n}}{\partial\boldsymbol{\mu}}\right)_0, \\ &= kT\left(\frac{\partial\mathbf{n}}{\partial\boldsymbol{\mu}}\right)_0 - \frac{4\pi kT}{\varepsilon K^2} \mathbf{d}\mathbf{d}, \end{aligned} \quad (5.4)$$

where we have introduced the vector

$$\mathbf{d} = (\partial\mathbf{n}/\partial\boldsymbol{\mu})_0 \cdot \mathbf{e}. \quad (5.5)$$

With the aid of (3.3 *b*) and (3.5 *b*) the theorems (5.1) and (5.2) can be rewritten as

$$\begin{aligned} \mathbf{n}_0^{-1} - \int \mathbf{c}^0(\mathbf{r}-\mathbf{r}')d\mathbf{r}' &= \beta(\partial\boldsymbol{\mu}/\partial\mathbf{n})_0, \\ \mathbf{n}_0 + \int \mathbf{F}^0(\mathbf{r}-\mathbf{r}')d\mathbf{r}' &= kT(\partial\mathbf{n}/\partial\boldsymbol{\mu})_0, \end{aligned} \quad (5.6)$$

where we have introduced the diagonal matrix \mathbf{n}_0 with elements $n_{0\alpha\beta} = n_{0\alpha}\delta_{\alpha\beta}$. If we further introduce the pair correlation functions $h_{\alpha\beta}(r)$ by

$$F_{\alpha\beta}(r) = n_{0\alpha}n_{0\beta}h_{\alpha\beta}(r), \quad (5.7)$$

then theorem (5.4) becomes

$$n_{0\alpha}\delta_{\alpha\beta} + n_{0\alpha}n_{0\beta} \int h_{\alpha\beta}(\mathbf{r}-\mathbf{r}')d\mathbf{r}' = kT\left(\frac{\partial n_\alpha}{\partial\mu_\beta}\right)_0 - \frac{4\pi kT}{\varepsilon K^2} d_\alpha d_\beta. \quad (5.8)$$

The second term on the right represents a peculiar modification of the usual form of fluctuation theorem. From (3.2), (3.3) and (5.7) it follows that (5.8) can also be written

$$n_{0\alpha}\delta_{\alpha\beta} + n_{0\alpha}n_{0\beta} \int h_{\alpha\beta}(\mathbf{r}-\mathbf{r}')d\mathbf{r}' = kT(\partial n_{0\alpha}/\partial\mu_\beta)_0. \quad (5.9)$$

In the Appendix we show this on the basis of purely thermodynamic arguments. The form (5.9) agrees with the usual derivation of the fluctuation theorem from the grand canonical ensemble.

Letting both sides of (5.8) act on \mathbf{e} and using (4.17) and (5.5) we find

$$\int \sum_{\beta} e_{\beta} n_{0\beta} h_{\alpha\beta}(r_{12}) d\mathbf{r}_2 = -e_{\alpha}. \quad (5.10)$$

This shows that the average charge of the screening cloud about each ion is equal and opposite to that of the ion, i.e. in the neutral state each ion is fully screened. Using $\mathbf{e} \cdot \mathbf{n}_0 = 0$ this relation also follows immediately from (5.9). The relation (5.10) is known as the zeroth-moment condition. In the next section we derive corresponding second and fourth-moment conditions.

Finally we derive an expression for the inverse of the compressibility, using (3.14) and (5.6)

$$\begin{aligned} \left(\frac{\partial p}{\partial n_0} \right)_{\mathbf{x}} &= \sum_{\alpha} \left(\frac{\partial p}{\partial \mu_{\alpha}} \right) \left(\frac{\partial \mu_{\alpha}}{\partial n_0} \right)_{\mathbf{x}}, \\ &= \sum_{\alpha\beta} \frac{n_{0\alpha} n_{0\beta}}{n_0} \left(\frac{\partial \mu_{\alpha}}{\partial n_{\beta}} \right)_0, \\ &= \sum_{\alpha\beta} \frac{n_{0\alpha} n_{0\beta}}{n_0} kT [n_{0\alpha}^{-1} \delta_{\alpha\beta} - \int c_{\alpha\beta}^0(\mathbf{r} - \mathbf{r}') d\mathbf{r}']. \end{aligned} \quad (5.11)$$

Here $x_{\alpha} = n_{0\alpha}/n_0$ is the concentration of species α . In the next section we show how (5.11) can be transformed to an expression involving the pair correlation functions $h_{\alpha\beta}$ instead of the direct correlation functions $c_{\alpha\beta}^0$.

6. SECOND AND FOURTH MOMENT CONDITION

The second and fourth moment conditions give relations similar to (5.10) with additional factors r_{12}^2 and r_{12}^4 in the integrand. We follow the method of Mitchell *et al.* [19], who used it to derive the second-moment condition, first found in a different fashion by Stillinger and Lovett [4].

It is convenient to introduce the Fourier transforms

$$\begin{aligned} C_{\alpha\beta}(\mathbf{k}) &= \sqrt{(n_{0\alpha} n_{0\beta})} \int \exp(-i\mathbf{k} \cdot \mathbf{r}_{12}) c_{\alpha\beta}(r_{12}) d\mathbf{r}_{12}, \\ H_{\alpha\beta}(\mathbf{k}) &= \sqrt{(n_{0\alpha} n_{0\beta})} \int \exp(-i\mathbf{k} \cdot \mathbf{r}_{12}) h_{\alpha\beta}(r_{12}) d\mathbf{r}_{12}. \end{aligned} \quad (6.1)$$

With these definitions the Ornstein-Zernike equation (3.6) for a uniform system can be written as

$$\sum_{\gamma} [\delta_{\alpha\gamma} - C_{\alpha\gamma}(\mathbf{k})] [\delta_{\gamma\beta} + H_{\gamma\beta}(\mathbf{k})] = \delta_{\alpha\beta}, \quad (6.2)$$

or in matrix notation

$$[\mathbf{I} - \mathbf{C}(\mathbf{k})][\mathbf{I} + \mathbf{H}(\mathbf{k})] = \mathbf{I}. \quad (6.3)$$

It is plausible that $\mathbf{C}(\mathbf{k})$ has a k -expansion of the form

$$C_{\alpha\beta}(\mathbf{k}) = -4\pi \frac{\sqrt{(n_{0\alpha} n_{0\beta})} e_{\alpha} e_{\beta}}{\epsilon k T} k^{-2} + \sum_{n=0}^{\infty} C_{\alpha\beta}^{(2n)} k^{2n} \equiv \sum_{n=-1}^{\infty} C_{\alpha\beta}^{(2n)} k^{2n}. \quad (6.4)$$

The first term originates from the long-range coulomb interaction in (4.1), whereas the remaining series represents the Fourier transform of the short-range direct correlation function $c_{\alpha\beta}^0(r_{12})$. The Mayer resummation of the cluster expansion for coulomb systems [13, 20–23] strongly suggests that the latter decays as $\exp(-2\kappa r_{12})$ at large distance, where κ is the Debye shielding parameter

$$\kappa = \left[\frac{4\pi}{\epsilon k T} \sum_{\alpha} n_{0\alpha} e_{\alpha}^2 \right]^{1/2}. \tag{6.5}$$

If this is correct all moments of this function exist and its Fourier transform can be expanded as

$$\int \exp(-i\mathbf{k} \cdot \mathbf{r}_{12}) c_{\alpha\beta}^0(r_{12}) d\mathbf{r}_{12} = \sum_{m=0}^{\infty} \frac{(-1)^m}{(2m+1)!} k^{2m} \int r_{12}^{2m} c_{\alpha\beta}^0(r_{12}) d\mathbf{r}_{12}, \tag{6.6}$$

where we have used the isotropy of $c_{\alpha\beta}^0$. Hence we have

$$C_{\alpha\beta}^{(2n)} = \sqrt{(n_{0\alpha} n_{0\beta})} \frac{(-1)^n}{(2n+1)!} \int r_{12}^{2n} c_{\alpha\beta}^0(r_{12}) d\mathbf{r}_{12}. \tag{6.7}$$

From (6.2) and (6.4) it follows that the series expansion of the pair correlation function must have the form

$$H_{\alpha\beta}(\mathbf{k}) = \sum_{n=0}^{\infty} H_{\alpha\beta}^{(2n)} k^{2n}, \tag{6.8 a}$$

$$H_{\alpha\beta}^{(2n)} = \sqrt{(n_{0\alpha} n_{0\beta})} \frac{(-1)^n}{(2n+1)!} \int r_{12}^{2n} h_{\alpha\beta}(r_{12}) d\mathbf{r}_{12}. \tag{6.8 b}$$

If the coefficients $C_{\alpha\beta}^{(2n)}$ are known, then the $H_{\alpha\beta}^{(2n)}$ can be found with the aid of (6.2). As was shown by Mitchell *et al.* [19], knowledge of $C_{\alpha\beta}^{(-2)}$, as given in (6.4), is sufficient to obtain $H_{\alpha\beta}^{(0)}$ and a special linear combination of the $H_{\alpha\beta}^{(2)}$. The resulting expressions are called the zeroth and second-moment conditions. Here we use the knowledge of $C_{\alpha\beta}^{(0)}$, as given by (5.6), to express a special linear combination of the $H_{\alpha\beta}^{(4)}$ in terms of thermodynamic derivatives.

It is convenient for the analysis of (6.3) to write $C_{\alpha\beta}^{(-2)}$ as

$$\mathbf{C}^{(-2)} = -\kappa^2 \mathbf{c}\mathbf{c}, \tag{6.9}$$

where \mathbf{c} has components $c_{\alpha} = \kappa^{-1} (4\pi n_{0\alpha} e_{\alpha}^2 / \epsilon k T)^{1/2}$. Apparently $\mathbf{c} \cdot \mathbf{c} = 1$ so that $\mathbf{c}\mathbf{c}$ is a projector. We introduce the complementary projector

$$\mathbf{P} = \mathbf{I} - \mathbf{c}\mathbf{c}, \tag{6.10}$$

which projects onto the space of neutral compositions in the sense that $\sum_{\beta} P_{\alpha\beta} (\delta n_{\beta} / \sqrt{n_{0\beta}}) = \delta n_{\alpha} / \sqrt{n_{0\alpha}}$ implies $\sum_{\alpha} e_{\alpha} \delta n_{\alpha} = 0$.

We start solving (6.3) by comparing coefficients of k^{2n} . For $n = -1$ we find

$$\mathbf{C}^{(-2)} (\mathbf{I} + \mathbf{H}^{(0)}) = -\kappa^2 \mathbf{c}\mathbf{c} (\mathbf{I} + \mathbf{H}^{(0)}) = 0, \tag{6.11}$$

so that

$$\mathbf{H}^{(0)} \cdot \mathbf{c} = -\mathbf{c}, \tag{6.12 a}$$

$$\mathbf{I} + \mathbf{H}^{(0)} = \mathbf{P} (\mathbf{I} + \mathbf{H}^{(0)}) = (\mathbf{I} + \mathbf{H}^{(0)}) \mathbf{P}, \tag{6.12 b}$$

where we have used the symmetry of $\mathbf{H}(k)$. The property (6.12 *a*) is equivalent to the zeroth-moment condition (5.10).

Comparing coefficients of k^0 in (6.3) we find

$$(\mathbf{I} - \mathbf{C}^{(0)})(\mathbf{I} + \mathbf{H}^{(0)}) - \mathbf{C}^{(-2)}\mathbf{H}^{(2)} = \mathbf{I}. \quad (6.13)$$

Multiplication by $\mathbf{I} - \mathbf{P}$ from right and left and use of (6.12 *b*) yields

$$-(\mathbf{I} - \mathbf{P})\mathbf{C}^{(-2)}\mathbf{H}^{(2)}(\mathbf{I} - \mathbf{P}) = \mathbf{I} - \mathbf{P}, \quad (6.14)$$

$$\kappa^2 \mathbf{c} \cdot \mathbf{H}^{(2)} \cdot \mathbf{c} = 1. \quad (6.15)$$

The latter equation is the second-moment condition [4]

$$\sum_{\alpha\beta} e_\alpha e_\beta n_{0\alpha} n_{0\beta} \int r_{12}^2 h_{\alpha\beta}(r_{12}) dr_{12} = -3\epsilon kT/2\pi. \quad (6.16)$$

Multiplication of (6.13) from the left with $\mathbf{I} - \mathbf{P}$ and from the right with \mathbf{P} yields a relation

$$(\mathbf{I} - \mathbf{P})(\mathbf{I} - \mathbf{C}^{(0)})(\mathbf{I} + \mathbf{H}^{(0)}) = -\kappa^2(\mathbf{I} - \mathbf{P})\mathbf{H}^{(2)}\mathbf{P} \quad (6.17)$$

which will be used later. Multiplication of (6.13) to the left and to the right with \mathbf{P} finally yields

$$\mathbf{P}(\mathbf{I} - \mathbf{C}^{(0)})\mathbf{P}(\mathbf{I} + \mathbf{H}^{(0)}) = \mathbf{P}. \quad (6.18)$$

This shows that $\mathbf{H}^{(0)}$ can be obtained by inversion of $\mathbf{I} - \mathbf{C}^{(0)}$ within neutral space. Equation (6.18) may be checked explicitly with the aid of (5.6), (5.8), (6.1), and (6.10).

We may use (6.18) to express the compressibility theorem (5.11) in terms of the pair correlation functions \mathbf{H} . With the aid of (6.1) this equation can be rewritten as

$$\frac{\partial p}{\partial n} = \frac{kT}{n} \mathbf{n}_0^{1/2} \cdot (\mathbf{I} - \mathbf{C}(0)) \cdot \mathbf{n}_0^{1/2}, \quad (6.19)$$

where the vector $\mathbf{n}_0^{1/2}$ is given by $(n_0^{1/2})_\alpha = \sqrt{n_{0\alpha}}$. We have $\mathbf{P}\mathbf{n}_0^{1/2} = \mathbf{n}_0^{1/2}$, hence we can use (6.18) to re-express (6.19) as

$$\begin{aligned} \frac{\partial p}{\partial n} &= \frac{kT}{n} \mathbf{n}_0^{1/2} \cdot \mathbf{P}(\mathbf{I} - \mathbf{C}(0))\mathbf{P} \cdot \mathbf{n}_0^{1/2}, \\ &= \frac{kT}{n} \mathbf{n}_0^{1/2} \cdot (\mathbf{I} + \mathbf{H}(0))^{-1} \cdot \mathbf{n}_0^{1/2}. \end{aligned} \quad (6.20)$$

The inverse of $\mathbf{I} + \mathbf{H}^{(0)}$ has to be taken in neutral space, that is the space of all matrices which are both to the left and to the right orthogonal to \mathbf{c} .

Comparing coefficients of k^2 in (6.3) we find

$$(\mathbf{I} - \mathbf{C}^{(0)})\mathbf{H}^{(2)} - \mathbf{C}^{(-2)}\mathbf{H}^{(4)} - \mathbf{C}^{(2)}(\mathbf{I} + \mathbf{H}^{(0)}) = 0. \quad (6.21)$$

Multiplication with $\mathbf{I} - \mathbf{P}$ from left and right yields

$$\begin{aligned} -\kappa^2(\mathbf{I} - \mathbf{P})\mathbf{H}^{(4)}(\mathbf{I} - \mathbf{P}) &= (\mathbf{I} - \mathbf{P})(\mathbf{I} - \mathbf{C}^{(0)})\mathbf{P}\mathbf{H}^{(2)}(\mathbf{I} - \mathbf{P}) \\ &\quad + (\mathbf{I} - \mathbf{P})(\mathbf{I} - \mathbf{C}^{(0)})(\mathbf{I} - \mathbf{P})\mathbf{H}^{(2)}(\mathbf{I} - \mathbf{P}); \end{aligned} \quad (6.22)$$

this equation was already obtained in reference [19]. Substituting (6.15) and the

adjoint of (6.17) we find

$$\kappa^4(\mathbf{I}-\mathbf{P})\mathbf{H}^{(4)}(\mathbf{I}-\mathbf{P})=(\mathbf{I}-\mathbf{P})[(\mathbf{I}-\mathbf{C}^{(0)})(\mathbf{I}+\mathbf{H}^{(0)})(\mathbf{I}-\mathbf{C}^{(0)}) - (\mathbf{I}-\mathbf{C}^{(0)})](\mathbf{I}-\mathbf{P}). \quad (6.23)$$

From (4.17), (5.6) and (5.8) we obtain

$$(\mathbf{I}-\mathbf{C}^{(0)})(\mathbf{I}+\mathbf{H}^{(0)})(\mathbf{I}-\mathbf{C}^{(0)})=\mathbf{I}-\mathbf{C}^{(0)}-(\kappa^2/K^2)\mathbf{c}\mathbf{c} \quad (6.24)$$

so that

$$\mathbf{c} \cdot \mathbf{H}^{(4)} \cdot \mathbf{c} = -(\kappa^2 K^2)^{-1}. \quad (6.25)$$

Using (6.8) we can write this as the fourth moment condition

$$\sum_{\alpha\beta} e_\alpha e_\beta n_{0\alpha} n_{0\beta} \int r_{12}^4 h_{\alpha\beta}(r_{12}) d\mathbf{r}_{12} = -30\epsilon kT/\pi K^2. \quad (6.26)$$

From (4.17) and (5.1) it follows that the integral can be expressed in terms of thermodynamic derivatives, or alternatively in terms of an integral over the short-range part of the direct correlation function. As Mitchell *et al.* [19] remarked, the fourth moment condition cannot be expressed in terms of the coulomb interaction alone, but also involves the short-range interactions. Hence it does not have the universal character of the zeroth and second moment conditions (5.10) and (6.16). Nonetheless the condition may provide a useful consistency check in approximate calculations. We can see that higher moments of the pair correlation function cannot be expressed in terms of thermodynamic derivatives only.

7. DEBYE-HÜCKEL THEORY

Let us consider how Debye-Hückel theory fits in with the formalism described in the preceding sections. This theory is based on the assumption that to lowest approximation in the densities the chemical potentials of the ionic species are given by

$$\mu_\alpha(\mathbf{r}) = kT \ln [n_\alpha(\mathbf{r})/n_\alpha^+] + u_\alpha(n_1, T), \quad \alpha = 2, \dots, s, \quad (7.1)$$

where the n_α^+ are standard densities and the functions $u_\alpha(n_1, T)$ refer to the behaviour of a single α -ion in the pure solvent. It is convenient to choose the standard densities n_α^+ such that they satisfy the electroneutrality condition $\sum_\alpha e_\alpha n_\alpha^+ = 0$. It follows from (3.11) and (7.1) that in Debye-Hückel theory the short-range direct correlation functions in a neutral state \mathbf{n}_0 show ideal gas behaviour

$$\hat{c}_{\alpha\beta}^0(\mathbf{r}-\mathbf{r}') = -n_{0\alpha}^{-1} \delta_{\alpha\beta} \delta(\mathbf{r}-\mathbf{r}'), \quad (\alpha, \beta = 2, \dots, s). \quad (7.2)$$

Correspondingly we find from (4.2) for the short-range pair cluster functions $\hat{\mathbf{F}}^0$

$$\hat{\mathbf{F}}_{\alpha\beta}^0(\mathbf{r}-\mathbf{r}') = n_{0\alpha} \delta_{\alpha\beta} \delta(\mathbf{r}-\mathbf{r}'), \quad (\alpha, \beta = 2, \dots, s) \quad (7.3)$$

and for the pair correlation functions from (3.3 b), (4.8) and (5.7)

$$h_{\alpha\beta}(\mathbf{r}-\mathbf{r}') = -\beta e_\alpha e_\beta g^E(|\mathbf{r}-\mathbf{r}'|) \quad (\alpha, \beta = 2, \dots, s), \quad (7.4)$$

where the Green function is given by

$$g^E(r) = \exp(-\kappa r)/\epsilon r, \quad (7.5)$$

with the Debye–Hückel parameter

$$\kappa = (4\pi \sum_{\alpha} n_{0\alpha} e_{\alpha}^2 / \epsilon k T)^{1/2}.$$

For the functions $\mathbf{C}(\mathbf{k})$ and $\mathbf{H}(\mathbf{k})$ defined in (6.1), (6.3) we obtain the following expressions with the aid of (2.1), (3.5 b), (4.1) and (7.4)

$$\mathbf{C}(\mathbf{k}) = -\frac{\kappa^2}{k^2} \mathbf{c}\mathbf{c}, \quad \mathbf{H}(\mathbf{k}) = -\frac{\kappa^2}{k^2 + \kappa^2} \mathbf{c}\mathbf{c}, \quad (7.6)$$

with \mathbf{c} defined below (6.9). By expanding \mathbf{H} in powers of k we easily check that the moment conditions (6.12), (6.15) and (6.25) are all fulfilled. Furthermore (6.18) is trivially satisfied.

The compressibility of a Debye–Hückel system follows from (5.11) to have the ideal gas form

$$\partial p / \partial n = kT. \quad (7.7)$$

By integration we obtain the ideal gas expression $p = nkT$ for the pressure. Together with (7.1) this is sufficient to obtain all desired thermodynamic functions for a neutral Debye–Hückel system. All of these turn out to have the ideal gas form.

On the other hand we may compute corrections to the ideal gas thermodynamics from the pair correlation functions $h_{\alpha\beta}$, e.g. by a charging procedure or by using the virial equation of state or the energy equation of state, given respectively as

$$p = n_0 k T - \frac{1}{6} \sum_{\alpha\beta} \int n_{0\alpha} n_{0\beta} [1 + h_{\alpha\beta}(r)] \mathbf{r} \cdot \frac{\partial \varphi_{\alpha\beta}(r)}{\partial \mathbf{r}} d\mathbf{r}, \quad (7.8 a)$$

$$u = \frac{3}{2} n_0 k T + \frac{1}{2} \sum_{\alpha\beta} \int n_{0\alpha} n_{0\beta} [1 + h_{\alpha\beta}(r)] \varphi_{\alpha\beta}(r) d\mathbf{r}. \quad (7.8 b)$$

For example, for the free energy density we find the Debye–Hückel correction

$$f^{\text{DH}} = -kT\kappa^3/12\pi \quad (7.9)$$

and hence we may obtain similar corrections for pressure, chemical potentials, etc.

This leads us to the following remark: it is often said that Debye–Hückel theory is asymptotically exact as the ion-densities approach zero. What is meant is that this theory correctly produces the leading corrections to the ideal gas expressions for the thermodynamic quantities of a dilute ionic solution. It does not mean that the theory is completely internally consistent. That is clearly not the case; starting from the ideal gas expressions (like (7.1)) for the thermodynamic quantities we arrive through (7.8 a) or (7.8 b) at expressions like (7.9), which embody corrections to the ideal gas laws.

It is worth mentioning that precisely the same internal inconsistencies exist in the mean spherical model, introduced by Waisman and Lebowitz [24]. Indeed in the limit of vanishing ion diameters this model becomes identical to Debye–Hückel theory.

8. LOCAL THERMODYNAMICS AND GENERALIZED SCREENING LENGTH

The formalism developed in §§ 3–6 can be regarded as a natural extension of Debye–Hückel theory to higher ion densities. If the range of the short-range correlation functions is much shorter than the generalized Debye shielding length \tilde{K}^{-1} defined by (4.16), some drastic simplifications are possible.

First, as discussed already in § 4, \tilde{K} may be replaced by K , which was defined by (4.17) in terms of thermodynamic quantities.

Secondly, the Debye shielding length is the typical length scale for spatial non-uniformities involving deviations from electroneutrality, as can be seen for example from the theory of electrical double layers [3]. The reason, of course, is that all local charges are shielded by a cloud of opposite charge with an extension of a few Debye lengths. If the range of the short-range correlation functions is much shorter than the Debye length, non-local thermodynamic relations of the type (3.11) may be replaced by local equilibrium relations (that is all thermodynamic quantities at a given position depend only on thermodynamic variables at the same position and the functional relations between these quantities are the same as in uniform equilibrium). To the local thermodynamics the coulomb interactions must be added, just as in Debye–Hückel theory.

In fact, if we look at the length scale of the Debye length the complete formalism can be reduced entirely to Debye–Hückel theory involving what might be called dressed ions. To see this first notice that on this length scale the short-range pair cluster functions are of the form

$$\hat{F}_{\alpha\beta}^0(\mathbf{r}, \mathbf{r}') = \hat{F}_{\alpha\beta}^0 \delta(\mathbf{r} - \mathbf{r}') \quad (8.1)$$

with

$$\hat{F}_{\alpha\beta}^0 = kT \partial n_\alpha / \partial \mu_\beta \quad (8.2)$$

according to (4.6). Hence $\hat{\mathbf{F}}^0$ is a real, symmetric $s \times s$ -matrix and can be diagonalized by an orthogonal transformation, viz.

$$\hat{\mathbf{F}}^{0'} = \mathbf{A} \hat{\mathbf{F}}^0 \mathbf{A}^\dagger, \quad (8.3)$$

where \mathbf{A} is some orthogonal matrix. The eigenvectors $\mathbf{v}^{(v)}$ of $\hat{\mathbf{F}}^0$, with elements $v_\mu^{(v)} = A_{\mu\nu}^\dagger$, can be interpreted as classical quasi-particles, which are just linear combinations of the s particle species present in the solution. Especially if the off-diagonal elements of $\hat{\mathbf{F}}^0$ are relatively small, $\mathbf{v}^{(v)}$ can be interpreted as a dressed ion of species v , in which a particle of species v is surrounded by a cloud of other particles generated by the short-range pair cluster functions $\hat{\mathbf{F}}^0$. Densities and charges of the quasi-particles v are given by the relations

$$\mathbf{n}' = \mathbf{A} \cdot \mathbf{n}, \quad \mathbf{e}' = \mathbf{A} \cdot \mathbf{e}. \quad (8.4)$$

We can easily check that in this representation the matrix \mathbf{W} given by (2.1) transforms to

$$\mathbf{W}'(r) = \mathbf{A} \mathbf{W}(r) \mathbf{A}^\dagger = \frac{\mathbf{e}' \mathbf{e}'}{\epsilon r}. \quad (8.5)$$

From (4.7), (4.10) and (4.13) it follows then that the matrices $\hat{\mathbf{F}}'$ and \mathbf{U}' , as well as the Green function g^E , are of the Debye–Hückel form. However the charges

must be replaced by the renormalized charges \mathbf{e}' , and κ^2 by

$$K^2 = (4\pi/\varepsilon kT) \sum_{\nu} e_{\nu}'^2 \hat{F}_{\nu\nu}{}^{0'} = (4\pi/\varepsilon kT) \sum_{\nu\mu} e_{\nu}' \hat{F}_{\nu\mu}{}^{0'} e_{\mu}' = (4\pi/\varepsilon kT) \sum_{\nu\mu} e_{\nu} \hat{F}_{\nu\mu}{}^0 e_{\mu}$$

in accordance with (4.6) and (4.17).

Now the question arises under what circumstances the range of the short-range correlation functions is indeed much shorter than the Debye shielding length. The leading correction to the short-range direct correlation function, resulting from the coulomb interactions between the ions and consistent with (3.5) and the Debye–Hückel correction (7.9) to the free energy density, is

$$c_{\alpha\beta}{}^0(r) = \frac{1}{2} \left[\frac{e_{\alpha} e_{\beta} \exp(-\kappa r)}{\varepsilon k T r} \right]^2. \quad (8.6)$$

The typical range of this function is $\frac{1}{2}\kappa^{-1}$, which is not small compared to the Debye shielding length. In addition to (8.6) there exist contributions to the short-range direct correlation functions resulting from short-ranged interactions like hard core repulsions, which have a typical range of the order of the hard core diameter d . If these contributions dominate the electrical contributions the condition for the validity of the Debye–Hückel approximation may still be satisfied. To obtain a criterion for this we may compare the contributions to $\partial\mu/\partial\mathbf{n}$ from the two parts of the short-range direct correlation function. The electrical part contributes on the order of $kT\kappa^3/50n^2$, whereas the hard core part contributes on the order kTd^3 . Hence we obtain the condition

$$50nd^3n\kappa^{-3} \gg 1. \quad (8.7)$$

Of course we have to require, in addition,

$$\kappa d \ll 1. \quad (8.8)$$

In laboratory plasmas the densities are usually far too small (typically $n \approx 10^{16} \text{ cm}^{-3}$) to satisfy (8.7). Perhaps the plasmas generated by pellet implosion are an exception, but these certainly are quite far removed from equilibrium. In the interior of stars we can easily find densities in the order of $n \approx 10^{21} \text{ cm}^{-3}$, such as needed to obtain appreciable contributions to $\partial\mu/\partial\mathbf{n}$ from the hard-core parts of $\hat{\mathbf{c}}^0$ (assuming $d \approx 5\text{Å}$). In that case (8.7) is fulfilled if we require $\kappa^{-1} \geq 50\text{Å}$. The latter requirement leads to temperatures $> 5 \times 10^6 \text{ K}$, as follows from (6.5). Such temperatures do occur in the interior of stars, but then light elements like hydrogen and helium are completely ionized and the remaining nuclei have an effective hard core diameter $\ll 1\text{Å}$. So we have to require in addition the presence in fair amounts of relatively heavy elements to satisfy (8.7) at these temperatures.

In aqueous electrolyte solutions the large value of ε , which is about 88, helps to increase κ^{-1} , but the comparatively low temperature makes it impossible to satisfy (8.8) at densities where the short-range interactions contribute appreciably to $\partial\mu/\partial\mathbf{n}$. Yet there is one interesting case where a non-trivial reduction to a Debye–Hückel system may, at least in principle, be possible. This is the case where there exists a strong tendency to form dimers between ions of opposite charge. We could imagine oppositely charged ions to have a coulomb energy $\gg kT$ if they are close enough together (this was suggested by Mayer [13] already in 1950). In that case the main contributions to the direct correlation function of these particles may come from the coulomb interaction in configurations where the particles are within a distance much smaller than the Debye length from each other.

We estimate this effect by assuming that for short distances the short-range direct correlation function, due to coulomb interactions is given approximately by

$$c_{\alpha\beta}^0(r) = \exp\left(-\frac{e_\alpha e_\beta}{\varepsilon k T r}\right) - 1 = \exp\left(-\frac{Z_\alpha Z_\beta e^2}{\varepsilon k T r}\right) - 1. \quad (8.9)$$

For $Z_\alpha Z_\beta = -4$ and $Z_\alpha Z_\beta = -6$ and for some values of r between 4 and 6 Å the magnitude of C^0 is given in the table. The contributions to $\partial\mu_\alpha/\partial n_\beta$ from this can be estimated as follows: $\beta\partial\mu_\alpha/\partial n_\beta \approx 10^5 \text{ Å}^3$ for $Z_\alpha Z_\beta = -4$ and $\approx 10^6 \text{ Å}^3$ for $Z_\alpha Z_\beta = -6$. For this to amount to at least 10 per cent of the ideal gas contribution, one must have $n_\alpha, n_\beta > 10^{-6} \text{ Å}^{-3}$ for $Z_\alpha Z_\beta = -4$ and $n_\alpha, n_\beta > 10^{-7} \text{ Å}^{-3}$ for $Z_\alpha Z_\beta = -6$. For the Debye length this leads to $\kappa^{-1} < 40 \text{ Å}$ for $Z_\alpha Z_\beta = -4$ and $\kappa^{-1} < 90 \text{ Å}$ for $Z_\alpha Z_\beta = -6$. This would imply that for 2-2 and 2-3 electrolytes it would indeed be possible to have appreciable corrections to Debye-Hückel theory with a good separation between the range of the short-range correlation functions and the Debye length.

$c_{\alpha\beta}^0(r)$ for $Z_\alpha Z_\beta = -4$ and $Z_\alpha Z_\beta = -6$.

$r/\text{Å}$	$Z_\alpha Z_\beta = -4$	$Z_\alpha Z_\beta = -6$
4.0	550	12900
4.2	407	8220
4.4	310	5450
4.8	192	2660
5.2	128	1451
5.6	90	863

However we have to be very cautious for a number of reasons. First we see from the table that the value of $c^0(r)$ changes dramatically in the range about $r \approx 4 \text{ Å}$. In model calculations values of about 4 Å are commonly used for the effective hard core diameter, but it is clear that the results sketched here are extremely sensitive to this value. A somewhat larger diameter could completely destroy the influence of the dimerization effect, whereas a slightly smaller diameter would enhance it drastically.

Secondly, if the potential energy of an ion pair is $\ll -kT$ this pair is very likely in a bound state. So we must wonder if we should not regard the pair as a molecule under these circumstances and if we should not use quantum mechanics instead of classical mechanics. However, if we calculate the radial quantum number for a state of energy $-10kT$, treating the ion-pair as a pair of point charges with coulomb interaction $Z_\alpha Z_\beta e^2/\varepsilon r$, we find an estimate of $n \approx 100-500$. For such large quantum numbers the classical approximation should be very good. In addition we find that the energy difference between neighbouring quantum states is only a fraction of kT so that indeed the ions can move rather freely with respect to each other. It looks as though the concept of molecule formation is not needed to describe the ion pairs, as long as they stay so far apart from each other that their interaction is purely coulombic.

Finally we must ask the question if, for interactions which are so short ranged, the influence of the solvent on the coulomb interactions can be described simply by means of a dielectric constant. In any case we ought to take into account the

molecular structure of the solvent in the case of small separations between the ions.

In spite of these objections it does not seem impossible that certain electrolyte solutions with high ion charges could be described by a generalized Debye-Hückel model and it might be worthwhile to investigate this point in more detail.

9. CHARGE FLUCTUATIONS

Compressibility theorems of the form (5.4) are intimately connected with expressions for the fluctuations $\langle(\Delta N_\alpha)^2\rangle$ in the total number of particles of species α in a volume element larger than the range of the correlation function. By the usual argument we find that $\langle(\Delta N_\alpha)^2\rangle$ is proportional to the size of the volume element. If, however, we calculate the fluctuations of the total charge $\langle(\Delta Q)^2\rangle$ in this way, we find from (5.4) that a cancellation occurs so that the charge fluctuations vanish. This shows that charge neutrality is maintained to a strict degree. We demonstrate here that $\langle(\Delta Q)^2\rangle$ is proportional to the surface area of the volume element under consideration.

We calculate in particular the charge fluctuations in a sphere of volume V in a spatially uniform neutral solution. We use local thermodynamics, as described in the last section, and assume that the short-range pair cluster function $\hat{\mathbf{F}}^0$ can be replaced by a delta function. Then it follows from (4.8), (4.11), (4.17) and (5.2) that

$$\langle(\Delta Q)^2\rangle = \iint_V \mathbf{e} \cdot \hat{\mathbf{F}}(\mathbf{r}-\mathbf{r}') \cdot \mathbf{e} \, d\mathbf{r} \, d\mathbf{r}', \quad (9.1 a)$$

$$\approx V k T \frac{\varepsilon K^2}{4\pi} \left[1 - \frac{\varepsilon K^2}{4\pi} S_V \right], \quad (9.1 b)$$

with

$$S_V = \frac{1}{V} \iint_V g^E(\mathbf{r}-\mathbf{r}') \, d\mathbf{r} \, d\mathbf{r}'. \quad (9.2)$$

The integral S_V can be calculated from (4.13) where again we replace $\hat{\mathbf{F}}^0$ by a delta function. In order to find the integral $\int_V g^E(\mathbf{r}-\mathbf{r}') \, d\mathbf{r}'$ it then suffices to solve the equation

$$\nabla^2 \phi - K^2 \phi = -(4\pi/\varepsilon)\rho, \quad (9.3)$$

for a charge density $\rho(r)$ which is uniform inside the sphere and vanishes outside. Integrating the result

$$\phi(r) = \frac{4\pi\rho}{\varepsilon K^2} \left[1 - (1+KR) \exp(-KR) \frac{\sinh Kr}{Kr} \right] \quad (r < R) \quad (9.4)$$

once more over the sphere, we find

$$S_V = \frac{4\pi}{\varepsilon K^2} \left[1 - 3 \frac{1+KR}{K^3 R^3} \exp(-KR)(KR \cosh KR - \sinh KR) \right], \quad (9.5)$$

where R is the radius of the sphere. Hence

$$\langle(\Delta Q)^2\rangle = \frac{\varepsilon k T}{K} (1+KR) \exp(-KR)(KR \cosh KR - \sinh KR), \quad (9.6)$$

which shows that for $R \gg K^{-1}$

$$\langle (\Delta Q)^2 \rangle \approx \frac{1}{2} \epsilon k T K R^2, \quad (R \gg K^{-1}). \tag{9.7}$$

For $R \ll K^{-1}$

$$\langle (\Delta Q)^2 \rangle \approx \frac{1}{3} \epsilon k T K^2 R^3 = V \mathbf{e} \cdot \frac{\partial \mathbf{n}}{\partial \boldsymbol{\mu}} \cdot \mathbf{e} \quad (R \ll K^{-1}) \tag{9.8}$$

so that in this limit screening has no effect and the size of the charge fluctuations is determined by the local thermodynamics.

If we do not make the assumption that $\hat{\mathbf{F}}^0$ can be replaced by a delta-function, but still require that $\hat{\mathbf{F}}(r)$ decays exponentially for large r with a decay length Λ , our results remain qualitatively the same. From (9.1 a), which is always valid, it follows that also in that case only a surface layer with a width proportional to Λ contributes to the charge fluctuations. Hence for a volume with a radius $\gg \Lambda$ the charge fluctuations are proportional to the surface area again. On the other hand for a volume with a radius $\ll \Lambda$ it is still true that shielding is not effective and the result (9.8) will be approximately valid.

10. CONCLUSIONS

As we have shown, in ionic solution theory it is possible and useful to introduce local thermodynamic functions, e.g. the chemical potentials, which depend on the local number densities of all components. The latter need not satisfy the charge neutrality condition. The functions are defined with the aid of the statistical mechanics of non-uniform systems, but only for the neutral case do they coincide with the thermodynamic functions obtained from the grand canonical partition function in the thermodynamic limit. We have shown that they occur naturally in compressibility theorems for the various correlation functions, as well as in a fourth moment condition on the pair distribution function, and a generalized screening parameter. If there is a separation of length scales between short-range correlations and the range given by the generalized Debye shielding length, then it is possible to develop a theory for non-uniform systems combining local thermodynamics and coulomb interactions.

APPENDIX

In this appendix we prove by thermodynamic arguments that the right hand sides of (5.8) and (5.9) are identical. We recall from (3.14) that on the neutral hypersurface S_0 in $\boldsymbol{\mu}$ -space the pressure $p(\boldsymbol{\mu})$ is identical to $p_0(\boldsymbol{\mu}^z)$ when the variables $\boldsymbol{\mu}$ and $\boldsymbol{\mu}^z$ are identified. In addition the densities $\mathbf{n} = \partial p / \partial \boldsymbol{\mu}$ and $\mathbf{n}_0 = \partial p_0 / \partial \boldsymbol{\mu}^z$ are identical on S_0 , so that the derivatives of the densities with respect to the chemical potentials along S_0 must also be equal. The latter property will be exploited in our proof. Consider the following set of infinitesimal variations of the chemical potentials

$$\delta \mu_\lambda = \delta \mu, \quad \delta \mu_\beta = -(e_\beta d_\lambda / N_\lambda) \delta \mu \quad (\beta \neq \lambda), \tag{A 1}$$

with

$$d_\lambda = \mathbf{e} \cdot (\partial \mathbf{n} / \partial \mu_\lambda), \quad N_\lambda = \sum_{\gamma \neq \lambda} e_\gamma d_\gamma. \tag{A 2}$$

We can easily check that this is a variation on S_0 : the variation in charge density is given by

$$\begin{aligned}\delta\rho &= \mathbf{e} \cdot \frac{\partial \mathbf{n}}{\partial \boldsymbol{\mu}} \cdot \delta\boldsymbol{\mu} = d_\lambda \delta\mu - \sum_{\beta \neq \lambda} \mathbf{e} \cdot \frac{\partial \mathbf{n}}{\partial \mu_\beta} \frac{e_\beta d_\lambda}{N_\lambda} \delta\mu, \\ &= d_\lambda \delta\mu [1 - (\sum_{\beta \neq \lambda} e_\beta d_\beta) / N_\lambda] = 0.\end{aligned}\quad (\text{A } 3)$$

The resulting variations in the number densities can be calculated as

$$\begin{aligned}\delta n_\alpha &= \sum_\beta \frac{\partial n_\alpha}{\partial \mu_\beta} \delta\mu_\beta = \frac{\partial n_\alpha}{\partial \mu_\lambda} \delta\mu - \sum_{\beta \neq \lambda} \frac{\partial n_\alpha}{\partial \mu_\beta} \frac{e_\beta d_\lambda}{N_\lambda} \delta\mu, \\ &= \left[\frac{\partial n_\alpha}{\partial \mu_\lambda} N_\lambda - \sum_{\beta \neq \lambda} \frac{\partial n_\alpha}{\partial \mu_\beta} e_\beta d_\lambda \right] \frac{\delta\mu}{N_\lambda}, \\ &= \left[\frac{\partial n_\alpha}{\partial \mu_\lambda} \mathbf{e} \cdot \mathbf{d} - \sum_\beta \frac{\partial n_\alpha}{\partial \mu_\beta} e_\beta d_\lambda \right] \frac{\delta\mu}{N_\lambda}, \\ &= \left[\frac{\partial n_\alpha}{\partial \mu_\lambda} \mathbf{e} \cdot \mathbf{d} - d_\alpha d_\lambda \right] \frac{\delta\mu}{N_\lambda},\end{aligned}\quad (\text{A } 4)$$

where we have used the symmetry of $\partial \mathbf{n} / \partial \boldsymbol{\mu}$. If we apply the same variation to the $\mathbf{n}_0 = \partial p_0 / \partial \boldsymbol{\mu}$ the same density variations have to result. All the calculations performed in (A 4) go through as before with the exception that in the last line we have to replace d_α by zero since

$$\sum_\beta (\partial n_{0\alpha} / \partial \mu_\beta) e_\beta = \sum_\beta (\partial n_{0\beta} / \partial \mu_\alpha) e_\beta = 0.$$

Hence

$$\delta n_{0\alpha} = \frac{\partial n_{0\alpha}}{\partial \mu_\lambda^z} \mathbf{e} \cdot \mathbf{d} \frac{\delta\mu}{N_\lambda}.\quad (\text{A } 5)$$

Identification of (A 4) and (A 5) yields

$$\frac{\partial n_{0\alpha}}{\partial \mu_\lambda^z} = \frac{\partial n_\alpha}{\partial \mu_\lambda} - \frac{d_\alpha d_\lambda}{\mathbf{e} \cdot \mathbf{d}}\quad (\text{A } 6)$$

which is the desired relation.

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