

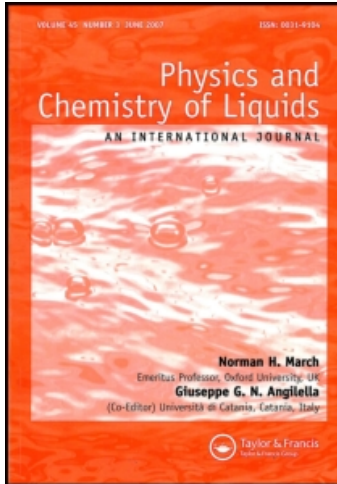
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Review Article

Classical Fluids in Constant External Fields and the Generalizations of the Ornstein-Zernike Relation

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We consider the equilibrium of pure and binary fluids in constant external fields by directly setting up the appropriate distribution functions of Statistical Mechanics. The equilibrium density gradients are obtained in terms of the partial structure factors a_{ij} and by connecting these results with the usual thermodynamic equilibrium conditions we obtain elementary proofs of all the expressions, for the a_{ij} in terms of thermodynamic quantities, usually derived by Fluctuation Theory. We also derive a general form of the Nernst–Einstein relation between mobility and diffusion constant.

The results for the density gradients are exemplified by brief discussions of fluids in gravitational fields and electromigration in a binary alloy.

1 INTRODUCTION

The problem under discussion is that of a classical pure or multi-component fluid under the influence of uniform external fields, so that each particle of a particular species i suffers the same constant force F_i . In considering the equilibrium of the fluid under these forces one may approach the problem thermodynamically, as, for example, Landau and Lifshitz¹ do in finding the change in concentration with height for a solution in the field of gravity. By imposing the condition that the chemical potential of every component is constant throughout the system they are able to find an expression for the concentration gradient (their final expression is valid, however, for weak solutions only). Alternatively, one can approach the problem directly by means of statistical mechanics, obtaining the equilibrium concentration gradients in terms of the distribution functions, and it is this latter approach we shall pursue here. As we shall see, this brings us three major advantages:

i) We straightforwardly obtain simple expressions for the concentration gradients in terms of the long wavelength limits a_{ij} of the partial structure

factors, that is, in terms of physical quantities which are in principle directly measurable in the laboratory.

ii) The form of these expressions can be interpreted very readily in physical terms.

iii) By connecting the equilibrium conditions obtained by means of statistical mechanics with those obtained thermodynamically one is afforded elementary proofs of all the results for the a_{ij} , in terms of thermodynamic quantities, usually obtained by employing fluctuation theory.² The prototype of these relations is of course that shown by Ornstein and Zernike to exist between the long wavelength limit of the structure factor of a pure fluid and its isothermal compressibility. A useful form of the general Nernst–Einstein relation between the mobility and diffusion coefficient will also be shown to follow in simple fashion.

As far as applications of the equilibrium conditions to particular cases is concerned, we shall briefly consider a solution under the action of gravity, showing how the full generalization of the Landau–Lifshitz result follows almost immediately. As a second important example, we shall discuss the reference of our considerations to electromigration, the transport of the ions of an alloy when an electric current is passed.³ This arises because each individual ion suffers a driving force consisting of the applied electric field and an “electron wind” from the scattering of the conduction electrons by ions. Thus by observing the electromigration we hope to obtain information on the scattering, and so improve our knowledge of electronic transport processes.

The plan of the review is as follows. After introducing the many-particle distribution functions we shall outline the physical basis of the approach by showing how it leads to the Ornstein–Zernike relation in a simple way. Before proving in Section 5 the generalizations of this relation to binary fluids, in Section 4 we give a formal proof of the results for the equilibrium concentration gradients. In Section 6 we consider the equilibrium as a balance between transport of particles under the driving forces of the external field and diffusion in the reverse direction. This results in a form of the Nernst–Einstein relation involving the long wavelength limit of the concentration-concentration structure factor S_{cc} . Finally, in Section 7 we discuss the particular cases of (i) a solution in a gravitational field and (ii) a liquid alloy in which electromigration is taking place.

2 DISTRIBUTION FUNCTIONS IN THE PRESENCE OF EXTERNAL FIELDS

We may write the many-body potential governing the motion of the N particles of the fluid as

$$\Phi(\mathbf{r}_1 \mathbf{r}_2 \cdots \mathbf{r}_N) = \Phi_0(\mathbf{r}_1 \mathbf{r}_2 \cdots \mathbf{r}_N) + \Phi_1(\mathbf{r}_1 \mathbf{r}_2 \cdots \mathbf{r}_N) \quad (1)$$

where Φ_0 is the many-body potential of the unperturbed fluid and

$$\Phi_1(\mathbf{r}_1 \mathbf{r}_2 \cdots \mathbf{r}_N) = \sum_{i=1}^N \mathbf{F}_i \mathbf{r}_i \tag{2}$$

where \mathbf{F}_i is the steady external force on particle i . We can now write down the N -particle distribution function by using a standard result of Statistical Mechanics.¹ The probability-density for the configuration $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$ is

$$\begin{aligned} n(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) &= A \exp[-\beta\Phi] \\ &= \frac{A}{A_0} n_0(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \exp[-\beta\Phi_1(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)] \end{aligned} \tag{3}$$

where $\beta = 1/k_B T$; A is constant for given \mathbf{F}_i and A_0, n_0 correspond to the case where all external forces are zero. The number-density $n_1(\mathbf{r}_1)$ of particles of type 1 may now be found by integrating out the positions of all other particles. Let us introduce the quantity $u_1(\mathbf{r}_1)$ through

$$\frac{1}{n_1} \frac{\partial n_1}{\partial \mathbf{r}_1} = -\beta \frac{\partial u}{\partial \mathbf{r}_1}(\mathbf{r}_1) \tag{4}$$

so that, evidently, $n_1(\mathbf{r}_1) \propto \exp[-\beta u_1(\mathbf{r}_1)]$. We can see that

$$\frac{\partial u_1}{\partial \mathbf{r}_1}(\mathbf{r}_1) = \frac{\int \frac{\partial \Phi}{\partial \mathbf{r}_1}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) n(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_2, \dots, d\mathbf{r}_N}{\int n(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_2, \dots, d\mathbf{r}_N} \tag{5}$$

so that u_1 may be interpreted as a ‘‘potential of mean force.’’

We shall work throughout to first order in the external forces \mathbf{F}_i . In the interior of a fluid of volume v , where the unperturbed mean density is constant, Eq. (5) may then be written as

$$\begin{aligned} \frac{\partial u_1}{\partial \mathbf{r}_1}(\mathbf{r}_1) &= v \int \frac{\partial \Phi_1}{\partial \mathbf{r}_1}(\mathbf{r}_1, \dots, \mathbf{r}_N) n_0(\mathbf{r}_1, \dots, \mathbf{r}_N) d\mathbf{r}_2, \dots, d\mathbf{r}_N \\ &\quad - v\beta \int \frac{\partial \Phi_0}{\partial \mathbf{r}_1}(\mathbf{r}_1, \dots, \mathbf{r}_N) n_0(\mathbf{r}_1, \dots, \mathbf{r}_N) \Phi_1(\mathbf{r}_1, \dots, \mathbf{r}_N) d\mathbf{r}_2, \dots, d\mathbf{r}_N \end{aligned} \tag{6}$$

or

$$\begin{aligned} \frac{\partial u_1}{\partial \mathbf{r}_1}(\mathbf{r}_1) &= v \int \frac{\partial \Phi_1}{\partial \mathbf{r}_1}(\mathbf{r}_1, \dots, \mathbf{r}_N) n_0(\mathbf{r}_1, \dots, \mathbf{r}_N) d\mathbf{r}_2, \dots, d\mathbf{r}_N \\ &\quad + v \int \Phi_1(\mathbf{r}_1, \dots, \mathbf{r}_N) \frac{\partial n_0}{\partial \mathbf{r}_1}(\mathbf{r}_1, \dots, \mathbf{r}_N) d\mathbf{r}_2, \dots, d\mathbf{r}_N \end{aligned} \tag{7}$$

so that we may put

$$u_1(\mathbf{r}_1) = v \int \Phi_1(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) n_0(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_2, \dots, d\mathbf{r}_N \quad (8)$$

We thus see that to first order in the \mathbf{F}_i the quantity $u_1(\mathbf{r}_1)$ is simply the mean potential energy of the unperturbed fluid in the external field when there is a particle of type 1 at \mathbf{r}_1 .

3 THE ORNSTEIN-ZERNIKE RELATION

We are now in a position to illustrate the basic approach of this review by obtaining the relationship between the isothermal compressibility K_T and the long wavelength limit of the structure factor. Consider each molecule of a pure fluid to be subjected to a steady force \mathbf{F} , for definiteness the force of gravity. Let the equilibrium number density at height x be $n(x)$ and let the pair distribution function of the unperturbed fluid be $g(r)$, so that the probability density for finding a particle at a distance r from some given particle is $\bar{n}g(r)$, where \bar{n} is the unperturbed mean density. It can now be shown that, to first order in F ,

$$\frac{1}{n} \frac{dn}{dx} = \frac{F}{k_B T} \left\{ 1 + n \int [g(r) - 1] dr \right\}. \quad (9)$$

A formal proof of this will be given in the following section but the relationship may readily be understood as follows. From the results of the last section $n(x) = n_0 e^{-\beta u(x)}$ where n_0 is the density at $x = 0$ and $u(x)$ is the mean change in potential energy on moving a molecule from zero altitude to x . This change in potential consists of two terms, the first being the work Fx done against the direct gravitational force on the molecule. To see the origin of the second term, we note that the molecule creates a disturbance $n[g(r) - 1]$ in its surroundings and this disturbance is also moved from zero altitude to x with a consequent change in potential energy. Hence

$$u(x) = Fx \left\{ 1 + n \int [g(r) - 1] dr \right\} \quad (10)$$

from which Eq. (9) follows.

But elementary hydrostatics also tells us that the pressure varies with height as

$$dP = -Fn dx \quad (11)$$

so that the compressibility is

$$K_T = \frac{1}{n} \frac{dn}{dp} = \frac{1}{Fn^2} \frac{dn}{dx} \quad (12)$$

This is the isothermal compressibility since at equilibrium the temperature will be constant throughout the system. We already have $1/n(dn/dx)$ from Eq. (9), whence we find

$$nk_BTK_T = 1 + n \int [g(r) - 1]d\mathbf{r} \tag{13}$$

which is the famous Ornstein–Zernike relation.

4 EQUILIBRIUM CONDITIONS IN A BINARY FLUID

The following derivation of expressions for the equilibrium density gradients in a binary fluid may easily be specialised to a pure fluid or generalized to a multi-component system, as required. For simplicity we shall assume all external forces \mathbf{F}_i to lie in the x -direction; again, this restriction is readily removed if necessary.

From Eqs. (2), (4) and (7) we find the concentration gradient of particles of type 1 to be given, to first order in the external forces, by

$$\frac{1}{n_1} \frac{dn_1}{dx} = -\frac{F_1}{k_B T} - \frac{V}{k_B T} \sum_i' F_i \int x_i \frac{\partial n_0}{\partial x_1}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_2, \dots, d\mathbf{r}_N \tag{14}$$

where F_i is the component of the force in the x -direction, so that $\mathbf{F}_i = F_i \hat{\mathbf{x}}$. Let us calculate the contribution of all particles of type 2 to the second term on the right-hand side. We first introduce the number concentration c_i of particles of type i , so that $n_i = c_i n$, and also the partial distribution function $g_{12}(r_{12})$ such that in the thermodynamic limit the probability density for a particle of type 2 at \mathbf{r}_2 , given that there is a particle of type 1 at \mathbf{r} , is $c_2 n g_{12}(r_{12})$. Thus in the limit $N, v \rightarrow \infty, N/v \rightarrow n$

$$v \int n_0(\mathbf{r}_1, r_2, r_3, \dots, \mathbf{r}_N) d\mathbf{r}_3, \dots, d\mathbf{r}_N = \frac{1}{v} g_{12}(r_{12}) \tag{15}$$

The contribution in question is therefore

$$\begin{aligned} & -\beta F_2 c_2 N v \int x_2 \frac{\partial n_0}{\partial x_1}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_2, \dots, d\mathbf{r}_N \\ & = -\beta F_2 c_2 n \int x_2 \frac{\partial}{\partial x_1} g_{12}(r_{12}) d\mathbf{r}_2 \end{aligned} \tag{16}$$

We may perform a partial integration by noting first that $x_1 \int \partial g / \partial x_1 (r_{12}) d\mathbf{r}_2 = 0$, so that

$$\begin{aligned} \int x_2 \frac{\partial}{\partial x_1} g_{12}(g_2) d\mathbf{r}_2 &= - \int x \frac{\partial}{\partial x} g_{12}(r) d\mathbf{r} = - \int x \frac{\partial}{\partial x} [g_{12}(r) - 1] d\mathbf{r} \\ &= \int [g_{12}(r) - 1] d\mathbf{r} \end{aligned} \quad (17)$$

We can similarly calculate the contributions of particles of type 1 to finally obtain

$$\frac{1}{n_1} \frac{dn_1}{dx} = \frac{F_1}{k_B T} + \frac{c_1 n}{k_B T} F_1 \int [g_{11}(r) - 1] d\mathbf{r} + \frac{c_2 n}{k_B T} F_2 \int [g_{12}(r) - 1] d\mathbf{r} \quad (18)$$

In terms of the long wavelength limits of the partial structure factors,

$$a_{ij} = 1 + n \int [g_{ij}(r) - 1] d\mathbf{r}, \quad (19)$$

we have

$$\begin{aligned} \frac{1}{n_1} \frac{dn_1}{dx} &= \beta [F_1 (c_2 + c_1 a_{11}) + c_2 F_2 (a_{12} - 1)] \\ \frac{1}{n_2} \frac{dn_2}{dx} &= \beta [F_2 (c_1 + c_2 a_{22}) + c_1 F_1 (a_{12} - 1)] \end{aligned} \quad (20)$$

From these we obtain the gradient of the logarithm of the total number density as

$$\frac{1}{n} \frac{dn}{dx} = \beta [c_1 F_1 (c_1 a_{11} + c_2 a_{12}) + c_2 F_2 (c_2 a_{22} + c_1 a_{12})] \quad (21)$$

Noting that

$$\frac{1}{n_i} \frac{dn_i}{dx} = \frac{1}{c_i} \frac{dc_i}{dx} + \frac{1}{n} \frac{dn}{dx} \quad \text{and} \quad c_1 + c_2 = 1$$

we can obtain the concentration gradient from Eqs. (20) in the form

$$\frac{1}{c_1 c_2} \frac{dc_1}{dx} = \frac{1}{C} \frac{dC}{dx} = \beta \{ F_1 [1 + c_1 (a_{11} - a_{12})] - F_2 [1 + c_2 (a_{22} - a_{12})] \} \quad (22)$$

where $C = c_1/c_2$. Anticipating the results of the following section this may be rewritten in terms of thermodynamic quantities. Introducing the molecular volumes v_1 and v_2 and the Gibbs free energy per particle G , we shall

see that

$$\frac{1}{C} \frac{dC}{dx} = \beta[v_2 F_1 - v_1 F_2] n f \tag{23}$$

where the quantity f is

$$f = \frac{S_{cc}}{c_1 c_2} = 1 + c_1 c_2 (a_{11} + a_{22} - 2a_{12}) \tag{24}$$

or, in thermodynamic terms,

$$f = \frac{k_B T}{c_1 c_2} \left(\frac{\partial^2 G}{\partial c_1^2} \right)_{P, T} \tag{25}$$

5 GENERALIZATIONS OF THE ORNSTEIN-ZERNIKE RELATION

In general there must be a pressure gradient in the system at equilibrium to balance the effect of the external forces; in fact,

$$\delta p = \left(\frac{\partial p}{\partial n_1} \right)_{n_2, T} \delta n_1 + \left(\frac{\partial p}{\partial n_2} \right)_{n_1, T} \delta n_2 = (n_1 F_1 + n_2 F_2) \delta x \tag{26}$$

or

$$n_1 \left(\frac{\partial p}{\partial n_1} \right)_{n_2, T} \left[\frac{1}{n_1} \frac{dn_1}{dx} \right] - n_2 \left(\frac{\partial p}{\partial n_2} \right)_{n_1, T} \left[\frac{1}{n_2} \frac{dn_2}{dx} \right] = n_1 F_1 + n_2 F_2 \tag{27}$$

We can impose the condition $dn_2/dx = 0$ by setting

$$F_2 = - \frac{c_1 F_1 (a_{12} - 1)}{(c_1 + c_2 a_{22})} \tag{28}$$

so obtaining the “partial compressibility”

$$\left[n_1 \left(\frac{\partial p}{\partial n_1} \right)_{n_2, T} \right]^{-1} = \frac{(c_2 + c_2 a_{11})(c_1 + c_2 a_{22}) - c_1 c_2 (a_{12} - 1)^2}{nk_B T c_1 (1 + c_2 (a_{22} - a_{12}))} \tag{29}$$

with a similar expression for $n_2(\partial p/\partial n_2)_{n_1, T}$. By using

$$n \left(\frac{\partial p}{\partial n} \right)_{T, c_1} = n_1 \left(\frac{\partial p}{\partial n_1} \right)_{T, n_2} + n_2 \left(\frac{\partial p}{\partial n_2} \right)_{T, n_1}$$

we now immediately find

$$nk_B T K_T = \frac{(c_2 + c_1 a_{11})(c_1 + c_2 a_{22}) - c_1 c_2 (a_{12} - 1)^2}{1 + c_1 c_2 (a_{11} + a_{22} - 2a_{12})} \tag{30}$$

the expression for the isothermal compressibility K_T as given by Kirkwood and Buff.⁴

Given the total compressibility from experiment the partial compressibilities may be found from data on the variation of the total number density n with concentration. Varying c_i at constant temperature and pressure we have $0 = (\partial p/\partial n_1)_{n_2, T} \delta n_1 + (\partial p/\partial n_2)_{n_1, T} \delta n_2$ and the expressions of the form (29) then yield

$$\left(\frac{\partial n_1}{\partial n_2}\right)_{P, T} = -\frac{[n + c_1(\partial n/\partial c_1)_{P, T}]}{n + c_2(\partial n/\partial c_2)_{P, T}} = -\frac{[1 + c_1(a_{11} - a_{12})]}{1 + c_2(a_{22} - a_{12})} \quad (31)$$

This also gives the ratio of the molecular volumes. These are defined such that

$$1 = n_1 v_1 + n_2 v_2 \quad (32)$$

and, with P, T, N constant

$$\frac{\delta v}{v} = \frac{\delta N_1}{v} (v_1 - v_2) = \delta c_1 n (v_1 - v_2) \quad (33)$$

when δN_1 particles of type 2 are replaced by δN_1 particles of type 1. From (32) and (33) we can show that

$$\left(\frac{\partial n_1}{\partial c_1}\right)_{P, T} = n^2 v_2; \quad \left(\frac{\partial n_2}{\partial c_2}\right)_{P, T} = n^2 v_1 \quad (34)$$

so that by reference to (31) we can see that

$$\frac{v_2}{v_1} = \frac{1 + c_1(a_{11} - a_{12})}{1 + c_2(a_{22} - a_{12})} \quad (35)$$

Let us next examine the significance of the equilibrium conditions $\mu_i(x) - F_i x = \text{constant}$, where $\mu_i(x)$ is the value of the chemical potential of the unperturbed fluid with the values of P and T holding locally about position x . With n_2 held constant throughout the system by setting F_2 according to Eq. (28) we have

$$\frac{dn_1}{dx} \left(\frac{\partial \mu_i}{\partial n_1}\right)_{n_2, T} = F_i \quad (36)$$

Comparison with the expression for dn_1/dx given by substituting Eq. (28) in (20) now yields

$$\left(\frac{\partial \mu_1}{\partial n_1}\right)_{n_2, T} = \frac{k_B T (c_1 + c_2 a_{22})}{n_1 [(c_1 + c_2 a_{22})(c_2 + c_1 a_{11}) - c_1 c_2 (a_{12} - 1)^2]} \quad (37)$$

and

$$\frac{(\partial\mu_1/\partial n_1)_{n_2, T}}{(\partial\mu_2/\partial n_1)_{n_2, T}} = \frac{c_1 + c_2 a_{22}}{c_1 - c_1 a_{12}} \tag{38}$$

By using

$$\left(\frac{\partial p}{\partial n_1}\right)_{n_2, T} = n_1 \left(\frac{\partial\mu_1}{\partial n_1}\right)_{n_2, T} + n_2 \left(\frac{\partial\mu_2}{\partial n_1}\right)_{n_2, T}$$

we may confirm that these relations are in agreement with Eq. (29).

Instead of n , constant, we can impose constant pressure throughout the system by setting

$$c_1 F_1 + c_2 F_2 = 0 \tag{39}$$

as can be seen from Eq. (26). Equation (22) now gives

$$\frac{1}{c_i} \frac{dc_i}{dx} = \frac{F_i}{k_B T} f \tag{40}$$

Where f is defined by Eq. (24). On the other hand, if P is constant,

$$\mu_i(x) - F_i x = \text{constant}$$

gives

$$\frac{dc_i}{dx} \left(\frac{\partial\mu_i}{\partial c_i}\right)_{P, T} = F_i \tag{41}$$

and hence

$$c_1 \left(\frac{\partial\mu_1}{\partial c_1}\right)_{P, T} = c_2 \left(\frac{\partial\mu_2}{\partial c_2}\right)_{P, T} = \frac{c_1 c_2 k_B T}{S_{cc}} \tag{42}$$

Since the Gibbs function per particle is $G = \mu_1 c_1 + \mu_2 c_2$ Eq. (25) now follows.

We finally observe that given Eq. (35), Eq. (23) now follows readily from Eq. (22).

6 THE NERNST-EINSTEIN RELATION

When density gradients (assumed in the x -direction) are set up in a binary fluid, diffusion takes place and, as is well known,⁵ when no transport of total mass takes place we can describe the situation by a single constant D , the interdiffusion constant. Introducing the drift velocities v_i , mass densities $\rho_i = m_i n_i$ and mass concentrations s_i (so that the total mass-density is

$\rho = \rho_1 + \rho_2$), the mass flux of particles of type i is

$$\rho_i v_i = s_i \rho v_i = D \frac{d\rho_i}{dx} = D\rho \frac{ds_i}{dx} \quad (43)$$

where we have noted the fact that $d\rho/dx = 0$. Thus we evidently have a relative drift velocity of

$$v_D = v_1 - v_2 = \frac{D ds_1}{s_1 dx} - \frac{D ds_2}{s_2 dx} = D \frac{s_2}{s_1} \frac{d}{dx} \left(\frac{s_1}{s_2} \right) \quad (44)$$

In terms of the number concentrations c_i , the mass concentrations are $s_i = m_i c_i n/l$; thus while s_i/c_i can vary with position, we have $s_i/s_2 = m_1 c_1/m_2 c_2 = m_1/m_2 c$ and Eq. (44) may be rewritten as

$$v_D = \frac{D}{C} \frac{dc}{dx} \quad (45)$$

Supposing now that constant driving forces F_i are applied to a binary fluid, we can expect that after an initial transient the particles of type 1 will have a steady drift velocity v relative to these of type 2, the driving force on any particle being opposed by a mean frictional force:

$$F_1 = \eta_1 v \quad (46)$$

Where η_i is an inverse mobility. We shall take the total external force to be zero so that the total mass transport is zero, and also $c_1 F_1 + c_2 F_2 = 0$ whence

$$c_1 \eta_1 = c_2 \eta_2 = \eta \quad (47)$$

As the concentration gradient builds up back-diffusion will take place until at equilibrium $v = v_D$, as given by Eq. (45), so that

$$v = \frac{F_1}{\eta_1} = \frac{D}{C} \frac{dc}{dx} = \frac{D}{c_1 c_2} \frac{dc_1}{dx} \quad (48)$$

On comparing this with Eq. (40) for the same situation it is evident that

$$\frac{\eta_1 D}{k_B T} = \frac{c_2}{f} = \frac{c_1 c_2^2}{S_{cc}} \quad (49)$$

with a similar relation for η_2 .

For isotopic diffusion $f = 1$ since $a_{11} = a_{12} = a_{22} = a$ and

$$\frac{\eta_1 D}{k_B T} = c_2 \quad (50)$$

As a special case of this, we consider an isolated atom of type 1, when $\eta_1 D/k_B T = 1$, and then let the mass difference go to zero, when D becomes the self-diffusion coefficient. The mobility η_1^{-1} is then to be interpreted as that of an individual particle singled out from the $N - 1$ other identical particles by the application of a driving force to it, and to it alone.

7 APPLICATIONS

a) Fluid in gravitational field

In this case we simply put $F_1 = -m_1 g$, $F_2 = -m_2 g$ where m_1, m_2 are the particle masses and g the acceleration due to gravity. In terms of thermodynamic quantities we immediately obtain from Eq. (23) the full generalization of the result for dilute solutions given by Landau and Lifshitz.¹ We find

$$\frac{1}{c_1 c_2} \frac{dc_1}{dx} = -g\beta(m_1 v_2 - m_2 v_1) n f \tag{51}$$

For a dilute solution ($c_2 \rightarrow 1, f \rightarrow 1$)

$$\frac{1}{c_1} \frac{dc_1}{dx} = -g\beta \left(m_1 - \frac{m_2 v_1}{v_2} \right) \tag{52}$$

which is the Landau-Lifshitz result. As they remark, this is the usual barometric formula corrected according to Archimedes' Law.

For isotopes, we write $\Delta m = m_1 - m_2$, $\bar{m} = c_1 m_1 + c_2 m_2$, $a_{11} = a_{22} = a_{12} = a$ and obtain from Eq. (51)

$$\frac{1}{n_1} \frac{dn_1}{dx} = -\frac{g}{k_B T} (c_2 \Delta m + \bar{m} a) \tag{53}$$

While this involves the compressibility, we have $v_1 = v_2, f = 1$ for an isotopic mixture, and so Eq. (42) becomes

$$\frac{1}{c} \frac{dc}{dx} = -g\beta \Delta m$$

or

$$c = c_0 e^{-g\Delta m/k_B T} \tag{54}$$

irrespective of the character of the interactions between the particles.

b) Electromigration

Consider the model of an alloy in which the ions are classical particles. When an electric current is passed ion i is acted upon by a total force we

write as $F_i = z_i^* \mathcal{E}$, where \mathcal{E} is the electric field and z_i^* an *effective charge* which takes account of the force due to the scattering of the conduction electrons by the ions (the "electron wind.") It is of particular interest to attempt to derive z_i^* from experiment in order that comparisons with theoretical calculations of the effect of the electron scattering can be made. We can either measure the equilibrium concentration gradient or the relative drift velocity v long before equilibrium. Since the overall charge neutrality of the system implies $c_1 F_1 + c_2 F_2 = 0$ we have in terms of the concentration gradient (see Eq. (40))

$$z_1^* = \frac{1}{f \mathcal{E} c_1} \frac{dc_1}{dx} \quad (55)$$

while from Eqs. (46) and (50), we have in terms of the drift velocity

$$z_1^* = \frac{c_2 k_B T}{f D \mathcal{E}} v \quad (56)$$

In earlier discussions,³ the factor f^{-1} does not appear in Eq. (55), and similarly⁶ for the factor c_2/f in Eq. (56). These factors can be very different from unity⁷ and in Na-Cs the difference is particularly marked, as Figure 1

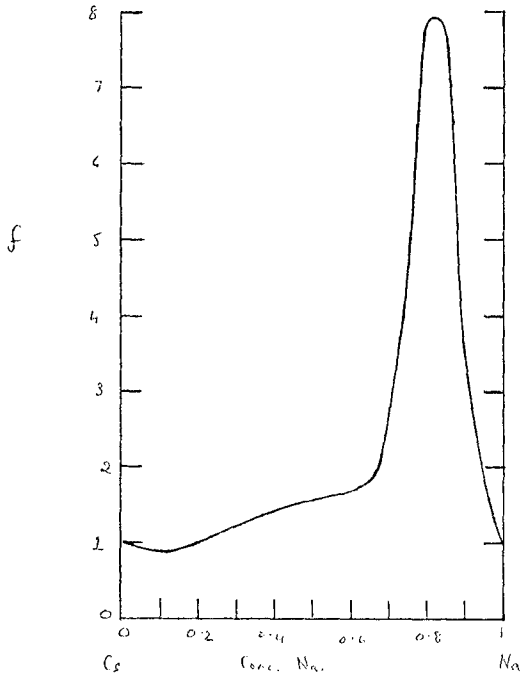


FIGURE 1 $f = S_{ce}/c_1 c_2$ for Na-Cs, from the data of Ichikawa *et al.*⁸

shows. The measurement of electromigration in this system would for this reason be particularly interesting.

One final point is that since the electron scattering will depend on the environment of the ion the z_i^* and the electromigration driving forces will be configuration dependent. The present approach offers a hope of discussing this case, as we attempt elsewhere.⁷

8 SUMMARY

By directly applying the techniques of statistical mechanics, we have obtained expressions for the equilibrium concentration gradients in pure and binary fluids under the influence of uniform external fields. As we have seen these results are very readily interpreted as simply replacing the external force F_i in the elementary expression $1/n_i(dn_i/dx) = F_i/k_B T$ by the *mean force* $-\hat{c}u_i/\partial x$ on an entity composed of particle i and the disturbance, described by the pair functions, it causes in its surroundings. This may be regarded as fully generalizing the correction to the barometric formula by means of Archimedes' Law we found in Eq. (52). Our final results also have the merit of being expressed in terms of the long wavelength limits a_{ij} of the partial structure factors, which are directly measurable physical quantities for liquids contained in the laboratory.

Having obtained our results for the concentration gradients in a binary fluid in terms of the a_{ij} , we can see that they could have been obtained by application of the thermodynamic equilibrium conditions and the use of the generalizations of the Ornstein-Zernike relation. However, the procedure we have reviewed has the further advantage that by comparing our results with the thermodynamic conditions we obtain proofs of all the results for the a_{ij} in terms of thermodynamic quantities; these proofs are elementary, in marked contrast to the usual sophisticated derivations relying on fluctuation theory. For completeness we have also included an elementary proof of the general Nernst-Einstein relation, whereby we directly obtain the result $\eta_1 D/k_B T = c_1 c_2/S_{cc}$.

The equilibrium conditions are of course also of interest in their own right. Apart from their immediate application to a fluid in a gravitational field, for which we have given the general equilibrium conditions, our results are also of relevance to electromigration, a topic of increasing theoretical interest.

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