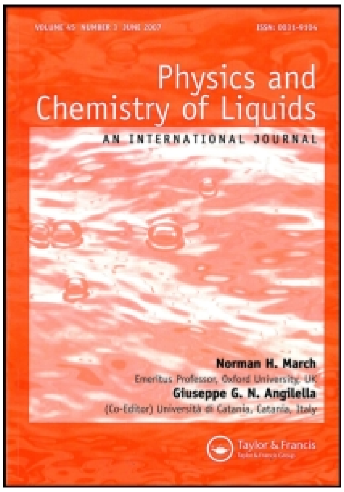

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W. Jones[a]; G. C. Barker[ab]
[a] Physics Department, The University, Sheffield, UK [b] Agriculture and Food Research Council, Institute of Food Research, Colney Lane, Norwich, UK

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The Response of a Liquid to Relative Forces With Application to Electromigration

W. JONES and G. C. BARKER

Physics Department, The University, Sheffield S7 3RH, UK and
Agriculture and Food Research Council, Institute of Food Research,
Colney Lane, Norwich NR4 7UA, UK

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We discuss the motion of the particles of a liquid under the influence of driving forces depending on the relative positions of pairs of particles. We show that generalised reciprocal relations exist which relate the response to velocity distributions around a diffusing particle. The theory is applied to the electromigration of a K impurity in Na, where hitherto the configuration dependence of the driving forces has been ignored. We approximate as simply as possible, the new element in the calculation being to recognise that solvent ions in the vicinity of the impurity will suffer different driving forces from those in the bulk of the fluid, and this will directly influence the impurity migration. Our calculations indicate this to be of considerable importance.

We also indicate how results relating diffusion coefficients to current–current correlation functions, of a type obtained previously be a velocity-field approach, may be obtained from the present formalism.

Key Words: Particle motion, electromigration, driving forces.

1 INTRODUCTION

While of general interest, the problem of the response of a classical liquid to relative (configuration-dependent) driving forces is of particular relevance to the theory of electromigration in alloys. In recent years the Faber–Ziman theory of the resistivity has been extended to yield expressions for the electromigration driving forces (Faber 1972, Sorbello 1978). Within this theory the total force on ion i is of the form $\sum_j \mathbf{F}^{ij}$ where (using the convention of summation over a repeated suffix)

$$F_\alpha^{ij} = f_{\alpha\beta}^{ij} E_\beta + ze\delta_{ij}E_\alpha \tag{1.1}$$

Here **E** is the electric field and

$$f^{ij}_{\alpha\beta} = \frac{e\tau}{m} \sum_{k<2k_f} \frac{k_\alpha k_\beta}{k} v_i^*(\mathbf{k}) v_j(\mathbf{k}) e^{i\mathbf{k}\mathbf{r}_{ij}} \tag{1.2}$$

where τ is the relaxation time, $v_i(\mathbf{k})$ the scattering form factor for ion i (in practice we use single-centre t matrices) and $\mathbf{r}_{ij}$ is the position of i relative to j.

It is evident from these equations that the driving forces are configuration dependent, but hitherto the response of the ions has been analysed as if the driving forces were constant at the values given by configuration averaging. In the following we shall develop the formal theory of the response to relative forces with a pairwise dependence as in eq. (1.1). In applying the theory to a K impurity in Na, as a first attempt to include configuration dependence as an actual calculation, we shall use the simplest set of approximations possible. With these approximations the driving force on the impurity itself will be averaged as before, the new element of the calculation being to recognise that solvent ions in the vicinity of the impurity will suffer different driving forces from those in the bulk of the fluid and this will indirectly influence the impurity migration.

We have chosen Na–K for a particular reason. Using scattering form factors given by Mayer, Nestor and Young (1967), corresponding to a bare ion crudely screened by a shell of charge positioned so as to satisfy the Friedel sum rule, the correct direction of migration (in the same direction as the electrons) is predicted for the K impurity without introducing configuration-dependence (Sorbello 1978, Jones and Dunleavy 1979). This is in contrast to potentials constructed in a much more sophisticated manner by Rasolt and Taylor (1975) following the procedure of Dagens, Rasolt and Taylor (1975); here the direction of migration is incorrect despite an accurate prediction of the total resistivity (Barker and Jones, 1984).

We shall begin (in Section 2) with a formulation of linear response theory appropriate to our problem. In section 3 we introduce the approximations we shall make, these being correct in the hydrodynamic limit. We then (Section 4) apply our results in K in Na, while finally (Section 5) we discuss the significance of our results. We should also remark that, as a matter of general interest, in an appendix we shall show how results, relating diffusion coefficients to current-current correlation functions, and of a type obtained previously by Gaskell and Miller (1978) using a velocity field approach, may be obtained from the formulation for the response to relative forces.

2 LINEAR RESPONSE

Let us suppose a force $\mathbf{F}_k(\mathbf{r}_{10}, \mathbf{r}_{20}, \ldots)$ is applied to particle k, the force depending on the positions of the particles relative to the particular particle **0**. The general result of linear response theory for f_1, the change from the equilibrium distribution functions f_0 describing the ensemble, has been given previously (Jones and Barker 1985). If the $\mathbf{F}_k$ are independent of velocity one finds

$$f_1 = \frac{-1}{k_B T} \int_{-\infty}^{t} \mathrm{d}s f_0 \exp[iL(t-s)] \mathbf{F}_\mathbf{k} \cdot \mathbf{V}_\mathbf{k} \tag{2.1}$$

Here L is the appropriate Liouville operator (so $Lf_0 = 0$) and $\mathbf{V}_\mathbf{k}$ the velocity of particle k evaluated, like $\mathbf{F}_k$, at $s = 0$. We have omitted a convergence factor $e^{\eta t}$ ($\eta \to +0$) which may be reinserted if necessary.

If the $\mathbf{F}_k$ are independent of the time, a change of variable brings (2.1) into the form

$$f_1 = \frac{1}{k_B T} \int_0^\infty f_0 \exp(-iLt) \mathbf{F}_k \cdot \mathbf{V}_k \, \mathrm{d}t \tag{2.2}$$

As we have previously shown (Jones and Barker, 1985) the above results for f_1 do not rely on the existence of a classical hamiltonian giving rise to $\mathbf{F}_k$. In fact, while the electromigration driving forces cannot be written as gradients of a many-body potential, they do arise from a hamiltonian involving vector-potentials. These give rise to velocity dependent forces, which, however, are of second order in the electric field. The mean velocity of particle **0** may now be written as

$$\bar{V}_{\beta 0} = \int f_1 V_{\beta 0} \, \mathrm{d}T = \frac{1}{k_B T} \int_0^\infty \mathrm{d}t \int \mathrm{d}\Gamma f_0 V_{\beta 0} e^{-iLt} F_{k\alpha} V_{\alpha_k} \tag{2.3}$$

where $\mathrm{d}\Gamma$ denotes integration over all positions and momenta. On expanding e^{-iLt} in powers of L, the resulting integrations may be performed by parts to yield

$$\bar{V}_{\beta 0} = \frac{1}{k_B T} \int_0^\infty \mathrm{d}t \int \mathrm{d}\Gamma F_{k\alpha} V_{k\alpha} e^{iLt} V_{\beta 0} \tag{2.4}$$

or

$$\bar{V}_{\beta 0} = \frac{1}{k_B T} \int_0^\infty \mathrm{d}t \langle F_{\alpha k}(\mathbf{r}_{10}, \mathbf{r}_{20}, \ldots) \, V_{\alpha k}(0) V_{\beta 0}(t) \rangle \tag{2.5}$$

where $\langle \; \rangle$ denotes the usual equilibrium statistical average, with momenta and co-ordinates at $t = 0$ and $\mathbf{V}(t) = e^{iLt}\mathbf{V}(0)$.

We shall specifically discuss the electromigration of an isolated impurity, in which case, as we can see from Eq. (1.2), we are interested in forces with four different types of dependence.

Setting $i = j = 0$ we have the direct scattering force on ion **0**, and there is no configuration dependence at all. Then since the liquid is isotropic,

$$\bar{V}_{\alpha 0} = F_{\alpha}^{00}\mu \tag{2.6}$$

where

$$\mu = \frac{1}{k_B T}\int_0^\infty \langle V_{\alpha 0}(0)V_{\alpha 0}(t)\rangle \mathrm{d}t \tag{2.7}$$

is just the mobility of the impurity **0**.

Secondly, setting $i = 0$ and $j = k \neq i$ in (1.1) and (1.2) a total force on **0** of $\sum_j F_0^{0j}(\mathbf{r}_{i0})$, where j represents the solvent ions. We may write the response to this as

$$\bar{V}_{\beta 0} = \int \mathrm{d}\mathbf{r}\; F_{\alpha 0}^{0j}(\mathbf{r})\mu_{\alpha\beta}(\mathbf{r}) \tag{2.8}$$

where

$$\mu_{\alpha\beta}(\mathbf{r}) = \frac{1}{k_B T}\sum_i \int_0^\infty \langle \delta(\mathbf{r} - \mathbf{r}_k + \mathbf{r}_0)V_{\alpha 0}(0)V_{\beta 0}(t)\rangle \mathrm{d}t \tag{2.9}$$

Next, setting $i = k$, $j = 0$, we have forces $\mathbf{F}_k^{ko}(\mathbf{r}_{k0})$ acting on the particles of the solvent. Each of these produces a drift velocity

$$\bar{V}_{\beta 0} = \int \mathrm{d}\mathbf{r}\; F_{\alpha k}^{k0}(\mathbf{r})\mu_{\alpha\beta}^{0k}(\mathbf{r}) \tag{2.10}$$

where

$$\mu_{\alpha\beta}^{0k}(\mathbf{r}) = \frac{1}{k_B T}\int_0^\infty \mathrm{d}t\langle \delta(\mathbf{r} - \mathbf{r}_k + \mathbf{r}_0)V_{\alpha k}(0)V_{\beta 0}(t)\rangle \tag{2.11}$$

Lastly, when $i, j \neq 0$, we are also concerned with forces $\mathbf{F}_k^{jk}(\mathbf{r}_{kj})$ where $\mathbf{r}_{kj}$ is the position of particle k relative to a second solvent particle j. Such a force produces a drift velocity of the impurity given by

$$\bar{V}_{\beta 0} = \int \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\; F_{\alpha k}^{jk}(\mathbf{r} - \mathbf{r}')\mu_{\alpha\beta}^{kj}(\mathbf{r}', r) \tag{2.12}$$

with

$$\mu_{\alpha\beta}^{kj}(\mathbf{r}, \mathbf{r}') = \int_0^\infty \mathrm{d}t\langle \delta(\mathbf{r} - \mathbf{r}_{k0})\delta(\mathbf{r}' - \mathbf{r}_{j0})V_{\alpha k}(0)V_{\beta 0}(t)\rangle \tag{2.13}$$

We should note at this point the existence of generalised reciprocal relations for $\mu_{\alpha\beta}^{0k}$ and $\mu_{\alpha\beta}^{kj}$. For example, if a constant force $\mathbf{F}_0$ is applied to the impurity then from (2.1) the velocity distribution of the solvent ions relative to the impurity is given by

$$\bar{V}_{\beta k}(r) = \frac{1}{k_B T}\int_0^\infty \mathrm{d}t \int \mathrm{d}\Gamma\, f_0 \delta(\mathbf{r} - \mathbf{r}_k) f_0 V_{k\beta} e^{-iLt} V_{\alpha 0} F_{\alpha 0} \tag{2.14}$$

Time reversal symmetry implies that e^{-iLt} may be replaced by e^{iLt} under the integral sign $\int \mathrm{d}\Gamma$, so that

$$\bar{V}_{\beta k}(\mathbf{r}) = F_{\alpha 0}\mu_{\beta\alpha}^{0k}(\mathbf{r}) \tag{2.15}$$

Suppose we define $\mathbf{v}(\mathbf{u}, \mathbf{r})$ as the velocity distribution around the impurity, which has a drift velocity $\mathbf{u}$. Thus $\mathbf{v}(\mathbf{u}, \mathbf{r})$ is the expectation value of the velocity given that the particle is at relative position $\mathbf{r}$. From (2.11) we may then write

$$\mu_{\alpha\beta}^{0i}(\mathbf{r}) = n\mu v_\beta(\mathbf{u}, \mathbf{r}) g_0(\mathbf{r}) \tag{2.16}$$

where $\hat{\mathbf{u}}$ is a unit vector in the direction α and $ng_0(\mathbf{r})$ gives the distribution of solvent ions around the impurity. Equation (2.12) is the form we shall use below.

One may similarly write

$$\mu_{\alpha\beta}^{ij}(\mathbf{r}, \mathbf{r}') = \mu V_\beta(\hat{\mathbf{u}}, \mathbf{r}, \mathbf{r}')\, n_0(\mathbf{r}, \mathbf{r}') \tag{2.17}$$

where $\mathbf{V}(\mathbf{u}, \mathbf{r}, \mathbf{r}')$ is the expectation value of the velocity of a particle at position $\mathbf{r}$ relative to the impurity diffusing with mean velocity $\mathbf{u}$, given that there is a third particle at relative position $\mathbf{r}'$. The function $n_0(\mathbf{r}, \mathbf{r}')$ is the probability of the presence of solvent ions at $\mathbf{r}$ and $\mathbf{r}'$, given that there is an impurity at the origin.

3 HYDRODYNAMIC APPROXIMATION

To make progress in investigating the response of an impurity we shall approximate by setting

$$\mu_{\alpha\beta}(\mathbf{r}) = \mu\delta_{\alpha\beta} \tag{3.1}$$

and

$$\mathbf{V}_\beta(\hat{\mathbf{u}}, \mathbf{r}, \mathbf{r}') = \mathbf{V}_\beta(\hat{\mathbf{u}}, \mathbf{r}) \tag{3.2}$$

As some justification for (3.1) we note that in a liquid the environment of the impurity will remain roughly constant during diffusion (unlike that of an impurity diffusing by jumping through a lattice). We might therefore hope that the driving force on the impurity, $\sum_i \mathbf{F}_0(\mathbf{r}_{i0})$, also remains roughly constant, so that the response is given by μ. As far as (3.2) is concerned, we argue that the dense packing effects existing in liquids (see Balucani *et al.*) imply that given the position of a particle at relative position $\mathbf{r}$ the distribution of other particles around the impurity is to a considerable extent determined, in which case (3.2) follows as a reasonable approximation. These arguments will eventually require further examination but for the present we shall accept (3.1) and (3.2) as the simplest approximations we can make. We should note that (3.1) forms the basis of the usual analysis of the response to electromigration. The new element here is that we no longer ignore the effects of forces on ions near the impurity.

Equations (3.1) and (3.2) are what we would expect if **0** were a relatively large particle, in which case one could take for $V(\mathbf{u}, \mathbf{r})$ the hydrodynamic (Stokes flow) result. In this connection one might note that by taking the hydrodynamic approximation for $\int_0^\infty dt \langle j_\alpha(q) j_\beta(\mathbf{q}, t)\rangle$ one obtains from (A.13) of the appendix the usual Stokes-Einstein formula for the diffusion coefficient of a sphere in a fluid (see Balucani *et al.* 1985) and, with a equal to the mean interparticle spacing one finds surprisingly good agreement with experiment. Computer experiments (Alley and Alder 1983) also show that flow is hydrodynamic-like on a much smaller scale than might have been anticipated. This encourages us to use the form

$$\mathbf{V}_H(\mathbf{u}, \mathbf{r}) = A\left(\frac{\mathbf{u}}{r}, + \mathbf{r}\,\frac{\mathbf{u}\cdot\mathbf{r}}{\mathbf{r}^3}\right) + \mathrm{B}\left(\frac{\mathbf{u}}{r^3} - \mathbf{r}\cdot\frac{\mathbf{u}\cdot\mathbf{r}}{r^5}\right) \tag{3.3}$$

which is in the standard result for hydrodynamic flow around a sphere of velocity $\mathbf{u}$ (Landau and Lifshitz 1962). Here A and B are constants with respective values 3R/4 and R3/4 (R being the radius of the sphere) for stick boundary conditions. For slip boundary conditions the values are a little different, but this is of no consequence to an order-of-magnitude calculation, as here.

4 ELECTROMIGRATION OF K IN Na

Electromigration experiments are analysed under the assumption that the driving force is steady and it is usual to write this force as $\bar{\mathbf{F}} = eZ^*\mathbf{E}$ where Z^* is an effective valence for the impurity. (The drift velocity is then $\mu\bar{\mathbf{F}}$ where the mobility μ may be obtained in terms of the diffusion coefficient by means of the Nernst-Einstein relation). We are now in a position to write down an expression for Z^* taking some account of configuration dependence of the actual driving forces. We write

$$Z^* = Z_d^* + Z_{\text{ind}}^* \tag{4.1}$$

where Z_d^* is the usual expression for the effective valence, so that $EZ_d^*\mathbf{E}$ is the electrostatic force on the ion $ez\mathbf{E}$ (where Z is the actual valence) plus the force due to electron scattering, averaged over configuration. We shall correct this by adding on the contribution $Z_{\text{ind}}^*\mathbf{E}$. To obtain this we use the approximations (3.1) and (3.2) and the Kirkwood superposition approximation for $n_0(\mathbf{r}, \mathbf{r}')$ in (2.16). For simplicity we shall use a substitutional model in which the three independent pair correlations are represented by a single function (apart from a factor of the density). This approximation is known to be a good one for binary alloys in which the two species are chemically similar and particularly so for Na–K (Ashcroft and Langreth 1967). Then if $\mathbf{E}$ is in the α direction (the direction of $\mathbf{u}$), we find

$$Z_{\text{ind}}^* = n \int d\mathbf{r}\, g(\mathbf{r}) V_\beta(\hat{\mathbf{u}}, \mathbf{r})\Big[f_{\alpha\beta}^{0i}(\mathbf{r}) + \delta_{\alpha\beta} ze + n \int d\mathbf{r}'\, f_{\alpha\beta}^{ij}(\mathbf{r}') g(\mathbf{r}') g(\mathbf{r} - \mathbf{r}')\Big] \tag{4.2}$$

where i, j refer to Na ions and $g(\mathbf{r})$ is the pair function for Na. In the pure liquid the electrostatic force on an ion will, on average, be balanced by the force due to the scattering of the conduction electrons (see for example, Jones and Dunleavy 1979), so that

$$ZeE_\alpha + nE_\beta \int f_{\alpha\beta}^{ij}(\mathbf{r}) g(\mathbf{r})\, d\mathbf{r} = 0 \tag{4.3}$$

Thus equation (4.2) becomes

$$Z_{\text{ind}}^* = n \int d\mathbf{r}\, g(\mathbf{r}) V_\beta(\hat{\mathbf{u}}, \mathbf{r})\Big[f_{\alpha\beta}^{0i}(\mathbf{r}) + n \int d\mathbf{r}'\, f_{\alpha\beta}^{ij}(\mathbf{r}') g(\mathbf{r}')[g(\mathbf{r} - \mathbf{r}') - 1]\Big] \tag{4.4}$$

We take $g(\mathbf{r})$ to agree with the X-ray results from Greenfield *et al.* (1971). The value of R in (4.3) was set at 3.27 Å, the value of which $g(r)$ rises abruptly from zero, as calculated by Hansen and Schiff (1973), whose theoretical results are in good accord with the experimental ones of Greenfield *et al.* The scattering form factors were calculated with two sets of phase shifts, those given by Meyer, Nester and Young (1967) and those calculated by Rasolt and Taylor (1975) following the procedure of Dagens *et al.* (1975). These give $Z_d^* = -1.57$ and $Z_d^* = 1.081$ respectively. Thus the MNY result agrees as to sign with experiment, for which $Z^* = -8$ (see Sorbello 1978)—this sign implying that the impurity moves in the same direction as the conduction electrons—but the ST result does not. However, the respective values of $Z^*_{\rm ind}$ are -2.77 and -2.0. The total Z^* for MNY phase shifts is thus -4.38 while the total ST result is -0.94. These are still well below the experimental value but the important point is that $Z^*_{\rm ind}$ is comparable to Z^*_d and, furthermore, the inclusion of configuration dependence through $Z^*_{\rm ind}$ is sufficient to bring the ST result into agreement with experiment as far as direction of electromigration is concerned.

5 CONCLUSIONS

The exploratory calculation reported above indicates that it is important to take explicit account of the configuration dependence of driving forces in electromigration and that the failure of earlier calculations using an ST potential to give the correct direction of the migration of K in Na is not necessarily a defect of the ST potential in itself. However, in the ST procedure one uses linear screening when extrapolating from the density of the original calculation to other densities. This may not be valid for K in Na and, accordingly, we have embarked on a full self-consistent calculation, with non-linear screening for ions immersed in an electron gas, right across the concentration range of Na-K alloys; we hope to report on this at a later date.

As far as our approximations in calculating the response to relative forces are concerned, our choice of $V(\hat{\mathbf{u}}, \mathbf{r})$ as the hydrodynamic result will of course eventually require improvement. However the assumption most urgently in need of examination is that of (3.1), which is equivalent to configurationally-averaging the direct driving force, as already remarked. Referring to Eq. (2.9), we see that we have a function

$$\langle \delta(\mathbf{r} - \mathbf{r}_k + \mathbf{r}_0) V_{\alpha 0}(0) V_{\beta 0}(t) \rangle = n g_0(\mathbf{r}) \langle V_{\alpha 0}(0) V_{\beta 0}(t) \rangle_{\mathbf{r}} \qquad (5.1)$$

which we have here expressed as the probability $ng_0(\mathbf{r})$, that there is an ion at position $\mathbf{r}$ relative to the impurity, times the self velocity correlation function $\langle V_{\alpha_0}(0) V_{\beta_0}(t) \rangle_{\mathbf{r}}$, which measures the correlation between velocities of the same particle at two different times, given that there is a particle at relative position $\mathbf{r}$ at the earlier time. The most direct way of calculating this quantity would be by means of a molecular dynamics calculation, and one could similarly calculate $\mu_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ and the velocity distributions $\mathbf{V}(\mathbf{u}, \mathbf{r})$ and $\mathbf{V}(\mathbf{u}, \mathbf{r}, \mathbf{r}')$. Such calculations would of course be of much more general interest that simply furnishing the quantities needed in calculating the response to electromigration, but would also give details of the relative diffusion of particles in equilibrium.

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Appendix Connection with results of velocity field approach

Consider the application of impulse forces so that the force on particle i is $\mathbf{F}(\mathbf{r}_{i0})\delta(t)$ and the total force $\sum_i \mathbf{F}(\mathbf{r}_{i0})\delta(t)$. From Eq. (2.1) we obtain (after an integration over Γ by parts, as in Section 2), as the mean (ensemble average) velocity of particle **0** after time t

$$\langle V_{\beta 0}\rangle_t = \frac{1}{k_B T}\int d\mathbf{r}\, F_\alpha(\mathbf{r})\left\langle \sum_i \delta(\mathbf{r} - \mathbf{r}_i + \mathbf{r}_0) V_{\alpha i}(0) V_{\beta 0}(t)\right\rangle \tag{A.1}$$

In fourier transform,

$$\langle V_{\beta 0}\rangle t = \frac{1}{k_{BT}}\int d\mathbf{q}\, F_\alpha(\mathbf{q})\langle j_\alpha(\mathbf{q}) V_{\beta_0}(t) e^{-i\mathbf{q}\cdot\mathbf{r}_0}\rangle \tag{A.2}$$

where

$$\mathbf{j}(\mathbf{q}) = \sum_i \mathbf{V}_i e^{i\mathbf{q}\cdot\mathbf{r}_i} \tag{A.3}$$

Let us now take $F_\alpha(\mathbf{r}) = f(\mathbf{r})$, where

$$f(\mathbf{r}) = \begin{cases} 1 & r \leqslant a \\ 0 & r > a \end{cases} \tag{A.4}$$

We should note then Eq. (A.1) is valid if we include the possibility $i = 0$. Then if a is less than the minimum separation between particle **0** and any other particle then the only term contributing to the right hand side of (A.1) is in fact that for which $i = 0$, so that

$$\langle V_{\beta 0}\rangle_t = \frac{1}{k_B T}\langle V_{\alpha 0}(0)V_{\beta 0}(t)\rangle \tag{A.5}$$

the correct result when unit impulse force is applied to a single particle. But from (3.2) we also have

$$\langle V_{\beta 0}\rangle_t = \frac{1}{k_B T}\int d\mathbf{q}\, f(\mathbf{q})\langle j_\alpha(\mathbf{q})V_{\beta 0}(t)e^{-i\mathbf{q}\cdot\mathbf{r}_0}\rangle \tag{A.6}$$

and it can be seen, in comparison with (3.5), that the velocity autocorrelation function for particle **0** is given by

$$\langle V_{\alpha 0}(0)V_{\beta 0}(t) = \int d\mathbf{q}\, f(\mathbf{q})\langle j_\alpha(\mathbf{q})V_{\beta 0}(t)e^{-i\mathbf{q}\cdot\mathbf{r}_0}\rangle \tag{A.7}$$

It will further be seen that if only one type of particle exists we may replace 0 by j and sum over all j to obtain

$$N\langle V_\beta(0)\rangle_t = \frac{1}{k_B T}\int d\mathbf{r}\, d\mathbf{r}'\, f(\mathbf{r}-\mathbf{r}')\left\langle j_\alpha(\mathbf{r})\sum_\beta V_{\beta 0}(t)\delta(\mathbf{r}-\mathbf{r}_0)\right\rangle \tag{A.8}$$

so that (2.10) becomes

$$\langle V_{\alpha i}(0)V_{\beta i}(t)\rangle = \int d\mathbf{q}\, f(\mathbf{q})\left\langle j_\alpha(\mathbf{q})\sum_j V_{\beta j}(t)e^{-i\mathbf{q}\cdot\mathbf{r}_j}\right\rangle \tag{A.9}$$

This result (for $\alpha = \beta$) has been obtained by Gaskell and Miller (1978) utilising the velocity-field concept. Gaskell and Miller then assume that the time τ_d taken for an atom to diffuse an interparticle spacing is much longer than the time τ taken for the velocity-correlation function to decay to zero and on that basis replace $r_j \equiv \mathbf{r}_j(0)$ by $\mathbf{r}_j(\mathrm{t})$ in (A.9), so that the equation may be written

$$\langle V_{\alpha i}(0)V_{\beta i}(t)\rangle = \int d\mathbf{q}\, f(\mathbf{q})\langle j_\alpha(\mathbf{q})j_\beta(\mathbf{q}, t)\rangle \tag{A.10}$$

This forms the basis of a successful treatment of the self-diffusion coefficient in a pure fluid. It is usual to fix a as the mean-interparticle spacing (see Balucani *et al.* 1985). In the present approach, a can be less, but if we regard the ionic motion as a combination of vibrational and diffusive motion, then given $\tau \ll \tau_d$ we also require a to be greater than the amplitude of the vibrations about the mean position. Given this we may extend the result (A.10) to binary fluids. For particles of types 1 and 2 we may write

$$\langle V_\alpha^1(0)V_\beta^2(t)\rangle = \int d\mathbf{q}\, f(\mathbf{q})\langle j_\alpha^1(\mathbf{q})j_\beta^2(\mathbf{q}, t)\rangle \tag{A.11}$$