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Note on the Onsager symmetry of the kinetic coefficients for sedimentation and diffusion in a dilute bidispersion

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The effect of gravity on a statistically homogeneous dispersion of small particles in fluid is to disturb the thermodynamic equilibrium slightly when the Reynolds and Péclet numbers associated with the resulting motion are small. In these circumstances the kinetic coefficients for the sedimentation velocities of two different species of particle should satisfy the Onsager reciprocal relation. It is shown analytically that the explicit expressions for the sedimentation velocities of the two species of spherical particle in a dilute bidispersion at small Péclet number found previously (Batchelor 1982) are in fact consistent with the reciprocal relation. It follows that the known kinetic coefficients for the Brownian diffusion of the particles down concentration gradients in a dilute bidispersion (Batchelor 1983) likewise satisfy the reciprocal relation.

1. Introduction

When a statistical system in equilibrium is disturbed by the application of an external force or influence, a transport or flux of some conserved quantity is normally generated in the system. There may be several independent 'forces' (the word being used in a generalized sense to mean an externally controlled agency causing change in the system), and a corresponding number of 'fluxes'. The fluxes represent irreversible thermodynamic processes, and for a wide class of systems and of forces the expression for the rate of change of entropy of the system is of the form

$$\frac{\mathrm{d}\sigma}{\mathrm{d}t} = \frac{1}{T}\sum_{i=1}^{m} \boldsymbol{J}_i\cdot\boldsymbol{X}_i, \tag{1.1}$$

where $\boldsymbol{X}_i$ is one of the m independent forces and $\boldsymbol{J}_i$ is the associated flux, said to be conjugate to the force $\boldsymbol{X}_i$. The forces and fluxes are written here as vectors since that is the case of interest to us, but they could be tensors of rank other than one.

If now the forces are small in magnitude and cause only a small departure from the state of equilibrium, we may suppose the relation between cause (the forces) and effect (the fluxes) to be linear, that is

$$\boldsymbol{J}_i = \sum_{j=1}^{m} \boldsymbol{L}_{ij}\cdot\boldsymbol{X}_j \quad (i = 1, 2, \ldots, m) \tag{1.2}$$

correct to the first order in the $\boldsymbol{X}_i$. The so-called kinetic or phenomenological coefficients $\boldsymbol{L}_{ij}$ representing (when $i \neq j$) the coupling between the effects of the applied forces are parameters of the equilibrium system, and here are tensors of rank two. By postulating reversibility of the microscopic entities of the system Onsager (1931) was able to establish the reciprocal relation

$$\boldsymbol{L}_{ij} = \tilde{\boldsymbol{L}}_{ji}, \tag{1.3}$$

where the tilde denotes the transpose of the tensor. Onsager's original derivation and later modifications have been extensively discussed in the literature of statistical physics. Our concern, however, is with the application of the reciprocal relation, itself the subject of many papers and books, of which the most relevant to considerations of dispersions of particles in fluid is perhaps de Groot & Mazur (1962).

A few years ago I derived analytical expressions for the mean velocity of the different species of spherical particle in a dilute polydispersion falling under gravity with small Reynolds number of the motion in the fluid (Batchelor 1982, to be referred to henceforth as Paper I). These expressions, which are correct to terms of the first degree in the (small) volume fractions of the different species, contain the probability density function for the separation of particle pairs. This function is determined by the relative motion of two particles due to the applied forces, interparticle forces, and Brownian diffusion, and is not known in general, but asymptotic forms for small and large values of the Péclet number were computed in a companion paper and used to obtain numerical values of the mean velocities in the two limits (Batchelor & Wen 1982, hereinafter referred to as Paper II). There is a close connection between the response of particles to the effect of an applied force at small Péclet number and the diffusive flux of particles down a concentration gradient, and in a third paper (Batchelor 1983, hereinafter referred to as Paper III) the results for the sedimentation velocity were used to obtain analytical expressions for, and numerical values of, the Brownian diffusivities of the different particle species in a dilute polydispersion. At the time I had not realised that the hydrodynamic interaction of the different particle species falling under gravity is an example of the type of coupling of the effects of independent forces acting on a statistical system to which the Onsager reciprocal relation applies. The reciprocal relation is applicable to *small* departures from equilibrium, and hence to sedimentation in a polydisperse system at small values of the Péclet number only.

The analytical expressions for the kinetic coefficients obtainable from the published expressions for the mean particle velocities do not obviously satisfy the Onsager reciprocal relation, and this may have puzzled those who are more at home in statistical physics and could see immediately the need to satisfy this relation.

The purpose of this note, which is essentially an addendum to the three previous papers on sedimentation and diffusion in a polydispersion, is to provide an explicit proof that the results are in fact consistent with the Onsager reciprocal relation. We do not learn anything new from this proof, although the new analytical form of the kinetic coefficients that shows the Onsager symmetry explicitly is of some interest. It is reassuring that the published results for the sedimentation velocities at small values of the Péclet number pass one important test of correctness and that, in consequence of the linear relation between the particle diffusivities in a polydispersion and the low-Péclet number sedimentation coefficients, the same is true of the formulae for the diffusivities.

The argument necessary to establish that the published formulae for the sedimentation velocities at small Péclet number satisfy the Onsager reciprocal relation is presented here with only as much detail as is needed for the proof to be intelligible. A more didactic version, which does not assume familiarity with the previously published papers and which discusses the relevance of reciprocal relations – Lorentz as well as Onsager – to statistical hydrodynamics problems in colloid science, was presented in a lecture to the 17th Polish Biennial Fluid Mechanics Symposium in September 1985 and will be published in the proceedings of that Symposium (Batchelor 1986). The proof in the present note is more general in that it allows for the existence of interparticle forces.

2. The kinetic coefficients for sedimentation in a dilute bidispersion

It has been seen (Paper I, §6.3) that when a steady external force $\boldsymbol{F}_j$ is applied to each of the spherical particles of species j in a statistically homogeneous dilute dispersion, with $|\boldsymbol{F}_j|$ being small enough to ensure that the Péclet number of the resulting motion is small, the mean velocity $\langle \boldsymbol{U}_i\rangle$ of the particles of species i, relative to axes such that the flux of material (i.e. both fluid and particle) volume in any direction is zero, is given by

$$6\pi\eta a_i\langle \boldsymbol{U}_i\rangle = \boldsymbol{F}_i+\sum_{j=1}^{m}\phi_j(S'_{ij}\boldsymbol{F}_i+\lambda_{ij}^{-2}S''_{ij}\boldsymbol{F}_j) \quad (i = 1,2\ldots m) \quad (2.1)$$

correct to terms of the first degree in the particle volume fractions, where η is the fluid viscosity, a_i is the particle radius, n_i is the number density of particles of species i, and

$$\lambda_{ij} = a_j/a_i, \quad \phi_i = \tfrac{4}{3}\pi a_i^3 n_i.$$

The dimensionless coefficients S'_{ij}, S''_{ij} are determined by the interaction of a sphere of species i with a sphere of species j, and analytical expressions for them have been obtained. To the above order of approximation only pair interactions are relevant, and we may take the number of particle species (m) to be 2 without loss of generality. The condition to be satisfied by the external forces may be written as

$$\mathbb{P}_{ij} = \frac{\tfrac{1}{2}(a_i+a_j)\,|\boldsymbol{U}_j^{(0)}-\boldsymbol{U}_i^{(0)}|}{\dfrac{kT}{6\pi\eta}\left(\dfrac{1}{a_i}+\dfrac{1}{a_j}\right)} \ll 1, \tag{2.2}$$

where $\boldsymbol{U}_j^{(0)} = \boldsymbol{F}_j/6\pi\eta a_j$. Note that although the external forces represent gravity, and so are parallel, in the case for which the calculations of mean particle velocity were made, the forces $\boldsymbol{F}_j$ are independent perturbations of an isotropic equilibrium state and (2.1) holds for arbitrary directions of the $\boldsymbol{F}_j$.

Now the force $\boldsymbol{F}_j$ applied to each particle of species j and the density of flux of number of particles of this species, $n_j\langle \boldsymbol{U}_j\rangle$, may be identified, in conformity with (1.1), with the generalized force and flux considered in the Onsager theory. The kinetic coefficients for sedimentation are thus defined by

$$n_i\langle \boldsymbol{U}_i\rangle = \sum_{j=1}^{2}\boldsymbol{L}_{ij}^{(\mathrm{S})}\cdot\boldsymbol{F}_j \quad (i = 1,2). \tag{2.3}$$

We obtain coefficients with a clear physical meaning by making the slight transformation

$$\boldsymbol{L}_{ij}^{(\mathrm{S})} = \frac{n_i}{6\pi\eta a_i}\boldsymbol{B}_{ij}, \tag{2.4}$$

for we then have

$$6\pi\eta a_i\langle \boldsymbol{U}_i\rangle = \sum_{j=1}^{2}\boldsymbol{B}_{ij}\cdot\boldsymbol{F}_j, \tag{2.5}$$

showing that the $\boldsymbol{B}_{ij}$ are dimensionless *bulk mobility coefficients*. The Onsager reciprocal relation (1.3) is hence equivalent to

$$\frac{n_i}{a_i}\boldsymbol{B}_{ij} = \frac{n_j}{a_j}\tilde{\boldsymbol{B}}_{ji} \quad (i,j = 1,2). \tag{2.6}$$

On comparing (2.1) and (2.5) we find for the case of a dilute dispersion

$$\boldsymbol{B}_{ij} = \boldsymbol{I}\left\{\delta_{ij}\left(1+\sum_{k=1}^{2}\phi_k S'_{ik}\right)+\lambda_{ij}^{-3}\phi_j S''_{ij}\right\} \quad (i,j = 1,2), \tag{2.7}$$

where $\boldsymbol{I}$ is the unit isotropic tensor and $\delta_{ij} = 1$ when $i = j$ and is zero otherwise. The Onsager reciprocal relation (2.6) has consequences only for the non-diagonal elements of this matrix of tensor mobilities, and is seen to be satisfied provided

$$\frac{n_1\phi_2}{a_1\lambda_{12}^3}S''_{12} = \frac{n_2\phi_1}{a_2\lambda_{21}^3}S''_{21},$$

that is, on changing to the notation $\lambda = a_2/a_1$, provided

$$\frac{S''_{12}}{\lambda} = \frac{S''_{21}}{\lambda^{-1}}. \tag{2.8}$$

We now examine the expression for S''_{12} published previously to see whether it is consistent with (2.8). It was shown (Paper I, §6.3) that

$$S''_{12} = S''^{(\mathrm{G})}_{12}+S''^{(\mathrm{I})}_{12}+S''^{(\mathrm{B})}_{12}, \tag{2.9}$$

where the three contributions on the right-hand side have different physical origins. The first term, given explicitly by

$$S''^{(\mathrm{G})}_{12} = \left(\frac{1+\lambda}{2}\right)^2\int_2^\infty\left\{(A_{12}+2B_{12})\exp\left(\frac{-\varPhi_{12}}{kT}\right)-\frac{3}{s}\right\}s^2\,\mathrm{d}s-(\lambda^2+3\lambda+1), \tag{2.10}$$

represents the contribution to the mean velocity of the particles of one species due to the application of the external force to the particles of the other species. In (2.10) $A_{12}(s)$ and $B_{12}(s)$ are two-sphere mobility functions defined in Paper I and known numerically, $\varPhi_{12}(s)$ is the potential of the force exerted between a sphere of species 1 and a sphere of species 2 (a force which may be of electrostatic or van der Waals type), and $s = 2r/(a_1+a_2)$. Note that the small departure of the pair-distribution function from its equilibrium form caused by the application of the external forces does not appear in the integral in (2.10) because it is of the order $\boldsymbol{F}_{12}$ and makes a negligible contribution.

The second term, given explicitly by†

$$S''^{(\mathrm{I})}_{12} = \frac{1}{2}\left(\frac{1+\lambda}{2\lambda}\right)^2\int_2^\infty\left(\frac{2A_{12}}{1+\lambda}-A_{11}\right)\frac{\mathrm{d}\exp(-\varPhi_{12}/kT)}{\mathrm{d}s}Q''(s)\,s^2\,\mathrm{d}s, \tag{2.11}$$

represents the direct contribution to the mean velocity of the particles of species 1 due to the force exerted by particles of species 2. This contribution would be zero if the pair-distribution function had spherical symmetry, as it does in the equilibrium state. However, there is a departure here from spherical symmetry

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† I take this opportunity of correcting a transcription error in the previous papers: the factor λ in the expression for $S''^{(\mathrm{I})}_{12}$ given in (6.11) in Paper I, and again in (3.8) in Paper III, should be replaced by $(1+\lambda)^2/4\lambda^2$. The numerical values calculated in Paper II were confined to the case $\lambda = 1$ and are not affected.

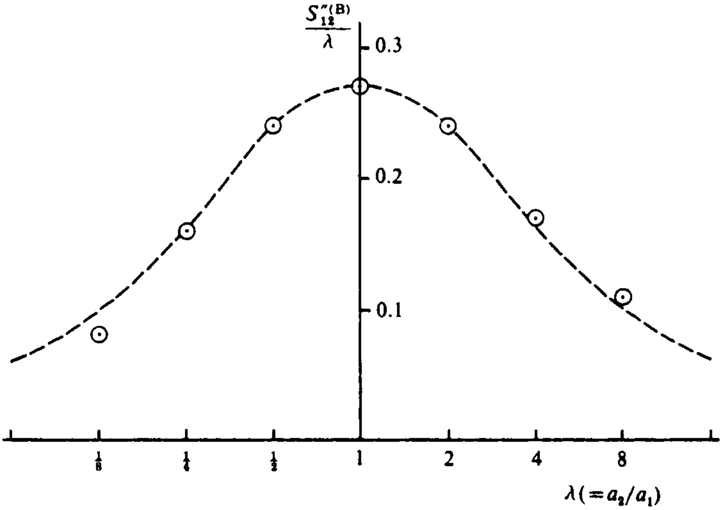

FIGURE 1. The circles indicate calculated values of $S''^{(B)}_{12}/\lambda$ as a function of λ ($= a_2/a_1$) for particles which exert no direct force on each other. The broken curve has been drawn through the points with the symmetry about $\lambda = 1$ that is required by the Onsager reciprocal relation for two species of particle acted on by small external forces.

caused by the applied forces (and represented in (2.11) by $Q''(s)$, which will be defined in (3.1)) which although of the order of the Péclet number leads to a non-small contribution to the mean particle velocities from the interparticle force if $|\Phi_{12}|$ is of the order of kT, as it may be in practice.

The third term, given explicitly by

$$S''^{(B)}_{12} = -\left(\frac{1+\lambda}{2\lambda}\right)^2 \int_2^\infty \left\{\frac{A_{11}-B_{11}}{s} + \frac{1}{2}\frac{\mathrm{d}A_{11}}{\mathrm{d}s} - \frac{2(A_{12}-B_{12})}{(1+\lambda)s} - \frac{1}{1+\lambda}\frac{\mathrm{d}A_{12}}{\mathrm{d}s}\right\} \times \exp\left(\frac{-\Phi_{12}}{kT}\right) Q''(s)\, s^2\, \mathrm{d}s, \quad (2.12)$$

is the contribution due to the relative diffusion of pairs of particles. Here a large diffusivity acts on a pair-distribution function made slightly non-isotropic by the effect of the applied forces, yielding a product of order unity.

Similar decompositions of S''_{11} and S''_{22} and of S'_{ij} may be made but are not needed here.

The queston now is whether the sum of the three expressions (2.10), (2.11), (2.12) when divided by λ is invariant to the exchange of the suffixes 1 and 2. The function $\Phi_{12}(s)$ is so invariant by definition. And for the two-sphere mobility functions, it can be shown by use of the Lorentz reciprocal theorem (Paper I) that

$$\left.\begin{aligned} A_{11}(s,\lambda) &= A_{22}(s,\lambda^{-1}), \quad A_{12}(s,\lambda) = A_{21}(s,\lambda) = A_{21}(s,\lambda^{-1}),\\ B_{11}(s,\lambda) &= B_{22}(s,\lambda^{-1}), \quad B_{12}(s,\lambda) = B_{21}(s,\lambda) = B_{21}(s,\lambda^{-1}).\end{aligned}\right\} \quad (2.13)$$

However, there are no evident invariant properties of the function $Q''(s,\lambda)$, which satisfies a linear second-order differential equation with coefficients that are linear combinations of the two-sphere mobility functions.

It is clear by inspection and the use of (2.13) that the one contribution to S''_{12} that does not depend on Q'', viz. $S''^{(G)}_{12}$, has the required invariance. This is actually to be expected on grounds other than the Onsager reciprocal relation, for it can be shown from the Lorentz reciprocal theorem that when external forces are applied to particles in a configuration whose statistical properties are given, independently of the applied forces, the instantaneous sedimentation coefficient S''_{12} satisfies the reciprocal relation (2.8) (Batchelor 1986).

On the other hand, neither separately nor in sum do the two contributions $S''^{(I)}_{12}$ and $S''^{(B)}_{12}$ show the required invariance, at any rate not in their present forms. This is puzzling at first sight, until it is realized that we could not expect to be able to prove the invariance without making some use of the differential equation of which Q'' is the solution. We obtain some encouragement to seek an analytical proof from the numerical values of $S''^{(B)}_{12}$ for the case $\Phi_{12} = 0$ (in which event $S''^{(I)}_{12} = 0$) which were found in Paper II and are reproduced here in figure 1.† Despite a little difference between the values for $\lambda = 8$ and $\lambda = \frac{1}{8}$, where the accuracy of the calculation is not high, the numerical values are clearly consistent with the requirement of the Onsager reciprocal relation.

3. Proof that S''_{12} satisfies the Onsager symmetry relation

There is no reason to expect the contributions $S''^{(I)}_{12}$ and $S''^{(B)}_{12}$ separately to satisfy Onsager symmetry, and we therefore consider their sum. The proof is a matter of manipulation of the integrals in (2.11) and (2.12), and involves use of the differential equation for the departure of the pair-distribution function from its equilibrium form. At small Péclet number the pair-distribution function may be written as

$$p_{12}(\mathbf{s}) = n_1 n_2 \left\{1 + \mathbb{P}_{12} \frac{\mathbf{s}\cdot(\mathbf{U}^{(0)}_1 Q' + \lambda^{-2}\, \mathbf{U}^{(0)}_2 Q'')}{s|\mathbf{U}^{(0)}_2 - \mathbf{U}^{(0)}_1|} + O(\mathbb{P}^2_{12})\right\} \tag{3.1}$$

for $s \geqslant 2$, where $\mathbf{U}^{(0)}_2$and $\mathbf{U}^{(0)}_1$ are being used, as in (2.2), as measures of the external forces. The non-dimensional functions $Q'(s, \lambda)$ and $Q''(s, \lambda)$ enter into the expressions for the coefficients S'_{12} and S''_{12} respectively defined in (2.1). Now the condition of conservation of particle pairs leads to differential equations for Q' and Q'' which may conveniently be written together as

$$\frac{\mathrm{d}}{\mathrm{d}s}\left(s^2 G \frac{\mathrm{d}Q'^{,\,''}}{\mathrm{d}s}\right) - \frac{\mathrm{d}(\Phi_{12}/kT)}{\mathrm{d}s}\, s^2 G \frac{\mathrm{d}Q'^{,\,''}}{\mathrm{d}s} - 2HQ'^{,\,''}$$
$$= 2s(L'^{,\,''} - M'^{,\,''}) + s^2 \frac{\mathrm{d}L'^{,\,''}}{\mathrm{d}s} - \frac{\mathrm{d}(\Phi_{12}/kT)}{\mathrm{d}s}\, s^2 L'^{,\,''}, \tag{3.2}$$

where
$$L' = -A_{11} + \frac{2A_{12}}{1+\lambda}, \quad L'' = \lambda^2 A_{22} - \frac{2\lambda^3 A_{12}}{1+\lambda} \tag{3.3}$$

and similarly for the relations between M', M'' and the pair mobility functions B_{11}, etc. The functions $G(s, \lambda)$ and $H(s, \lambda)$ occur in the expression for the tensor relative diffusivity of two spheres, and are known as linear combinations of the A and B functions respectively; and

$$G(s, \lambda) = G(s, \lambda^{-1}), \quad H(s, \lambda) = H(s, \lambda^{-1}).$$

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† In April 1985 I learnt from Dr H. N. W. Lekkerkerker of the Van't Hoff Laboratory at the University of Utrecht that he also had realized that the Onsager reciprocal relation has some consequences for the sedimentation coefficients S''_{12}, and that the symmetry relation (2.8) is indeed satisfied approximately by the numerical values given in Paper II for the case $\Phi_{12} = 0$.

Equations (3.2) can be written more compactly as

$$\frac{\mathrm{d}}{\mathrm{d}s}\left(s^2\tilde{G}\,\frac{\mathrm{d}Q^{\prime,\prime\prime}}{\mathrm{d}s}\right)-2\tilde{H}Q^{\prime,\prime\prime} = 2s(\tilde{L}^{\prime,\prime\prime}-\tilde{M}^{\prime,\prime\prime})+s^2\,\frac{\mathrm{d}\tilde{L}^{\prime,\prime\prime}}{\mathrm{d}s}, \tag{3.4}$$

where $\tilde{G}$, $\tilde{H}$, $\tilde{L}'$, $\tilde{M}'$, $\tilde{L}''$, $\tilde{M}''$ stand for the products of $\exp(-\Phi_{12}/kT)$ and the corresponding symbols without the tilde. We now notice that with the aid of (3.3) the integrands in (2.11) and (2.12) can be rewritten wholly in terms of the L- and M-functions and that

$$S''^{(\mathrm{I})}_{12}+S''^{(\mathrm{B})}_{12} = \frac{1}{2}\left(\frac{1+\lambda}{2\lambda}\right)^2\int_2^\infty \left\{2s(\tilde{L}'-\tilde{M}')+s^2\frac{\mathrm{d}\tilde{L}'}{\mathrm{d}s}\right\}Q''\,\mathrm{d}s. \tag{3.5}$$

This form allows us to use the differential equation for Q' and to find

$$\begin{aligned} S''^{(\mathrm{I})}_{12}+S''^{(\mathrm{B})}_{12} &= \frac{1}{2}\left(\frac{1+\lambda}{2\lambda}\right)^2\int_2^\infty \left\{\frac{\mathrm{d}}{\mathrm{d}s}\left(s^2\tilde{G}\,\frac{\mathrm{d}Q'}{\mathrm{d}s}\right)-2\tilde{H}Q'\right\}Q''\,\mathrm{d}s \\ &= -\frac{1}{2}\left(\frac{1+\lambda}{2\lambda}\right)^2\int_2^\infty \left(s^2\tilde{G}\,\frac{\mathrm{d}Q'}{\mathrm{d}s}\,\frac{\mathrm{d}Q''}{\mathrm{d}s}+2\tilde{H}Q'Q''\right)\mathrm{d}s, \end{aligned} \tag{3.6}$$

since $s^2\tilde{G}\,\mathrm{d}Q'/\mathrm{d}s$ represents the relative diffusive flux of sphere pairs and must be zero at $s = 2$ (where the spheres are touching). The last step in the argument is to deduce from the definition of Q' and Q'' in (3.1) that by exchanging the roles of the two species (and remembering from (2.2) that the Péclet number $\mathbb{P}_{12}$ is a signed quantity), we find

$$Q'(\lambda) = -\lambda^2 Q''(\lambda^{-1}). \tag{3.7}$$

It then follows from (3.6) that $(S''^{(\mathrm{I})}_{12}+S''^{(\mathrm{B})}_{12})/\lambda$ is invariant to the exchange of the 1 and 2 species. Since this has already been found to be true for $S''^{(\mathrm{G})}_{12}/\lambda$, the proof that the Onsager reciprocal relation (2.8) is satisfied by the expressions for the sedimentation coefficients derived in Paper I is complete.

Note that the Onsager symmetry of $(S''^{(\mathrm{I})}_{12}+S''^{(\mathrm{B})}_{12})/\lambda$, unlike that of $S''^{(\mathrm{G})}_{12}/\lambda$, involves considerations of the relative diffusion of particles and cannot be proved by use of the Stokes equation of motion of the fluid (from which the Lorentz reciprocal relation follows) alone.

Manipulations similar to those leading to (3.6) also give

$$S'^{(\mathrm{I})}_{12}+S'^{(\mathrm{B})}_{12} = -\frac{1}{2}\left(\frac{1+\lambda}{2\lambda}\right)^2\int_2^\infty \left\{s^2\tilde{G}\left(\frac{\mathrm{d}Q'}{\mathrm{d}s}\right)^2+2\tilde{H}Q'^2\right\}\mathrm{d}s. \tag{3.8}$$

4. The kinetic coefficients for diffusion of the particles in a bidispersion

One of the conditions for thermodynamic equilibrium of a bidispersion is that the chemical potential of each of the three constituents should be uniform. If these chemical potentials are non-uniform, as a consequence of the existence of a spatial gradient of concentration of one or both particle species, diffusive fluxes of the particles (and also of the fluid, but this is not independent in a volume-preserving system) will be generated, and the fluxes of the two species will in general be coupled.

The independent generalized fluxes and forces may here be identified, in conformity with (1.1), as

$$J_i^{(\mathrm{D})} = n_i\langle U_i\rangle, \quad X_i^{(\mathrm{D})} = -\nabla\mu_i-\frac{v_i}{1-\phi}\sum_{j=1}^{2} n_j\nabla\mu_j \quad (i = 1, 2). \tag{4.1}$$

where (as in Paper III) $\langle U_i \rangle$ is the local mean velocity, relative to zero-volume-flux axes, of particles of species i resulting from the existence of the concentration gradients, μ_i and v_i are the local chemical potential and volume of a particle species i, and $\phi = \phi_1 + \phi_2$. Also, if the temperature and pressure are uniform throughout the dispersion, we have

$$\nabla \mu_i = \sum_{j=1}^{2} \left(\frac{\partial \mu_i}{\partial n_j}\right)_{T,p} \nabla n_j \quad (i = 1, 2). \tag{4.2}$$

The kinetic coefficients for diffusion in a bidispersion are thus given by

$$n_i \langle U_i \rangle = \sum_{j=1}^{2} \boldsymbol{L}_{ij}^{(\mathrm{D})} \cdot \boldsymbol{X}_j^{(\mathrm{D})}, \tag{4.3}$$

and the Onsager reciprocal relation (1.3) shows that $\boldsymbol{L}_{ij}^{(\mathrm{D})}$, which is an isotropic tensor in view of the isotropic structure of the dispersion in equilibrium, is symmetrical in the suffixes i and j.

Now for the determination of the kinetic coefficients associated with diffusion, one may use a type of argument due originally to Einstein to show that the thermodynamic or generalized forces $\boldsymbol{X}_i^{(\mathrm{D})}$ given by (4.1) generate diffusive fluxes exactly as if they were actual small steady external forces acting on the particles (Batchelor 1976). It follows that the $\boldsymbol{L}_{ij}^{(\mathrm{D})}$ are *identical* with the kinetic coefficients for sedimentation at small Péclet number defined in (2.3), that $\boldsymbol{L}_{ij}^{(\mathrm{D})}$ is related to the bulk mobility coefficients as in (2.4), that the specific expressions found for $\boldsymbol{B}_{ij}$ and thence for $\boldsymbol{L}_{ij}^{(\mathrm{S})}$ for the case of a dilute dispersion are also applicable to $\boldsymbol{L}_{ij}^{(\mathrm{D})}$, and that as shown in §3 these expressions for $\boldsymbol{L}_{ij}^{(\mathrm{D})}$ do satisfy the Onsager reciprocal relation. There is a mechanical aspect to the process of Brownian diffusion of particles, viz. the way in which the particles respond to the effective forces acting on them in the presence of concentration gradients, and it turns out that the Onsager reciprocal relation involves only this mechanical aspect common to the processes of diffusion and sedimentation.

Nothing more need be said on the matter of satisfaction of the Onsager reciprocal relation, but for completeness we note that the particle diffusivities defined for practical convenience as the coefficients in the relations

$$n_i \langle U_i \rangle = -\boldsymbol{D}_{ij} \cdot \nabla n_j \tag{4.4}$$

may be found in terms of $\boldsymbol{L}_{ij}^{(\mathrm{D})}$ by comparing (4.4) and (4.3). With the help of (4.1) and (4.2) we obtain

$$\boldsymbol{D}_{ij} = \sum_{k=1}^{2} \boldsymbol{L}_{ik}^{(\mathrm{D})} \left\{ \left(\frac{\partial \mu_k}{\partial n_j}\right)_{T,p} + \frac{v_k}{1-\phi} \sum_{l=1}^{2} n_l \left(\frac{\partial \mu_l}{\partial n_j}\right)_{T,p} \right\} \quad (i, j = 1, 2), \tag{4.5}$$

which is valid for arbitrary values of the particle concentrations n_1, n_2. The Onsager symmetry of $\boldsymbol{L}_{ij}^{(\mathrm{D})}$ thus implies a linear relation, with rather complicated coefficients, between the various elements of the diffusivity matrix $\boldsymbol{D}_{ij}$. The complexity of the coefficients in this Onsager relation between the elements of $\boldsymbol{D}_{ij}$ arises from the various derivatives of the chemical potentials present in (4.5) and tends to obscure the simplicity of the reciprocal relation for the kinetic coefficients and its essentially mechanical significance.

In the case of a dilute bidispersion of spherical particles for which only pair interactions are significant, approximate expressions correct to the order of the first power of the volume fractions ϕ_1, ϕ_2 are available for $\boldsymbol{L}_{ij}^{(\mathrm{D})}$ (being the same as those for $\boldsymbol{L}_{ij}^{(S)}$ given in (2.4) with (2.7)) and for $\mu_i - kT \log n_i$ (see Paper III), and hence also for $\boldsymbol{D}_{ij}$. Numerical values of the coefficients of ϕ_1 and ϕ_2 in the expression for $\boldsymbol{D}_{ij}$ for various values of $\lambda (= a_2/a_1)$ are give in Paper III.

REFERENCES

Batchelor, G. K. 1976 Brownian diffusion of particles with hydrodynamic interaction. *J. Fluid Mech.* **74**, 1–29.

Batchelor, G. K. 1982 Sedimentation in a dilute polydisperse system of interacting spheres. Part 1. General theory. *J. Fluid Mech.* **119**, 379–408; and Corrigendum **137**, 1983, 467–469. (Paper I).

Batchelor, G. K. 1983 Diffusion in a dilute polydisperse system of interacting spheres. *J. Fluid Mech.* **131**, 155–175; and Corrigendum **137**, 1983, 467–469. (Paper III).

Batchelor, G. K. 1986 Applications of the Onsager reciprocal relation in colloid science. *Proc. XVIIth Symp. on Advanced Problems and Methods in Fluid Mechanics, Poland, Sept. 1985.*

Batchelor, G. K. & Wen, C.-S. 1982 Sedimentation in a dilute polydisperse system of interacting spheres. Part 2. Numerical results. *J. Fluid Mech.* **124**, 495–528; and Corrigendum **137**, 1983, 467–469. (Paper II).

de Groot, S. R. & Mazur, P. 1962 *Non-equilibrium Thermodynamics*. North-Holland.

Onsager, L. 1931 Reciprocal relations in irreversible processes. *Phys. Rev.* **37**, 405–426 and **38**, 2265–2279.