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Brownian Motion in Many-Particle Systems. I. Forced Interdiffusion of Two Species

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In this paper we discuss a system consisting of two species, α and β , whose molecules are subjected to opposing external forces $\mathbf{A}^{(\alpha)}$ and $\mathbf{A}^{(\beta)}$, causing α to move relative to β with a mean velocity \mathbf{u} . On the assumption that each molecule is undergoing a Brownian motion biased by the external forces and its interactions with other molecules, it is possible to derive a rigorously valid upper bound on the magnitude of \mathbf{u} , a bound which can be expressed in terms of *equilibrium* two- and three-particle distribution functions. Explicit calculations are given for the case where the α -species is present at very low concentrations and the β -molecules do not interact with one another.

Introduction

For the past two decades, interest in the statistical mechanics of irreversible processes has centered almost entirely on systems in which the constituent particles move in one another's fields of force according to the laws of classical dynamics. Even the question of how irreversibility arises in the first place is already controversial for these systems, and more practical matters such as the calculation of transport coefficients have been investigated in a rigorous manner only in the limit of low density or weak interactions between the particles.

At the same time there has existed, ever since Professor Debye's work on electrolytic conduction,¹ a whole class of systems which, though sharing many features of the dynamical systems mentioned above, are very much more tractable. In these systems the particles still interact with one another, but, instead of obeying Newton's laws, undergo Brownian motion. The source of this motion is some agency outside the system itself; for example, if our system consists of solute particles, Brownian motion can be considered as being induced by collisions with solvent molecules. The Brownian movement of an isolated particle is characterized by an intrinsic diffusion coefficient which must be known *a priori*. External and interparticle forces bias the intrinsic diffusion, causing each particle to drift in the direction of the total instantaneous force acting upon it, with a speed proportional to the magnitude of the force.

Just as the behavior of an N -particle dynamical system is described through an N -particle distribution function in phase space, so will the behavior of a Brownian system be described through an N -particle distribution function $F^{(N)}$ in configuration space. The temporal development of the former is given by the Liouville equation; the corresponding relation for the latter is the $3N$ -dimensional diffusion equation

$$\frac{\partial F^{(N)}}{\partial t} = \sum_{i=1}^N D_i \frac{\partial}{\partial \mathbf{r}_i} \cdot \left(\frac{\partial F^{(N)}}{\partial \mathbf{r}_i} - \zeta_i F^{(N)} / kT \right) \quad (1)$$

in which D_i is the intrinsic diffusion coefficient of the i th particle, \mathbf{r}_i its position vector, and ζ_i ($\mathbf{r}_1, \dots, \mathbf{r}_N$) the total force acting upon it.

At first glance it does not appear that eq. 1 should be any easier to treat than the Liouville equation. True, by working in configuration space rather than in phase space we have cut the number of independent variables in half, but we are still left with a many-particle prob-

lem. Furthermore, except for the trivial case where ζ_i involves external forces only, there is no possibility of a separation of (1) into single particle equations.

Indeed, the standard treatments of the Liouville equation can also be applied to eq. 1 and lead to comparable difficulties. For example, if the particle interactions are pairwise additive, we may integrate (1) with respect to the position coordinates of some of the particles to obtain a series of relations between lower order distribution functions, analogous to the BBGKY hierarchy.² Just as in the case of the BBGKY hierarchy, the series does not constitute a closed system of equations, and so cannot be used to determine, say, the pair distribution function without some supplementary assumption, like the Kirkwood superposition approximation.³ Although the validity of results obtained through such approximations is, to say the least, hard to evaluate, it seems that the only alternative is to confine ourselves once again to the region of low concentrations.

That this limitation can be partially overcome for Brownian systems is due to an important difference between the diffusion and the Liouville equations: under steady-state conditions, where the distribution functions become time independent, eq. 1 can be replaced by an equivalent variational principle which permits us to place bounds on transport coefficients.⁴ These bounds can be expressed in terms of averages taken with respect to *equilibrium* distribution functions, so that, although an exact treatment of transport rates runs into much the same difficulties whether we are dealing with Brownian or with dynamical systems, in the former case we can obtain rigorously valid *inequalities* without leaving the domain of equilibrium statistical mechanics.

Interdiffusion of Two Species

To illustrate our approach, we shall in this paper consider a two-component system, consisting of $N^{(\alpha)}$ particles of species α and $N^{(\beta)}$ particles of species β , uniformly distributed over a volume V , with external forces $\mathbf{A}^{(\alpha)}$ and $\mathbf{A}^{(\beta)}$ acting, respectively, on each α - and each β -particle; since the total force acting on the system must vanish, $\mathbf{A}^{(\alpha)}$ and $\mathbf{A}^{(\beta)}$ satisfy the relation

$$N^{(\alpha)} \mathbf{A}^{(\alpha)} + N^{(\beta)} \mathbf{A}^{(\beta)} = 0 \quad (2)$$

If the over-all concentration gradients are maintained at zero, these external forces produce a steady relative

(2) H. S. Green, "The Molecular Theory of Fluids," North-Holland Publishing Co., Amsterdam, 1952, Chapter V.

(3) J. G. Kirkwood and E. M. Boggs, *J. Chem. Phys.*, **10**, 394 (1942).

(4) A preliminary communication outlining the main results of this paper appeared previously: G. W. Woodbury, Jr., and S. Prager, *ibid.*, **38**, 1446 (1963).

(1) P. Debye and H. Falkenhagen, *Physik. Z.*, **29**, 401 (1928); L. Onsager, *ibid.*, **28**, 277 (1927).

motion of α with respect to β . In the absence of interactions between the particles, the mean velocity \mathbf{u}_0 of the motion is given by

$$\mathbf{u}_0 = (D^{(\alpha)}\mathbf{A}^{(\alpha)} - D^{(\beta)}\mathbf{A}^{(\beta)})/kT \quad (3)$$

where $D^{(\alpha)}$ and $D^{(\beta)}$ are the intrinsic diffusion coefficients for the two species. When interparticle forces are brought into play, the mean relative velocity will change to \mathbf{u} , and we wish to calculate $\mathbf{u} - \mathbf{u}_0$. The most common example of this type of problem is, of course, electrolytic conduction.

Once a steady state has been reached, the N -particle distribution function must satisfy the diffusion equation with the time derivative set equal to zero. In terms of the external force \mathbf{A}_i on the i th particle and the total internal potential $\Phi(\mathbf{r}_1, \dots, \mathbf{r}_N)$, the force ζ_i can be written

$$\zeta_i = -\frac{\partial\Phi}{\partial\mathbf{r}_i} + \mathbf{A}_i \quad (4)$$

and eq. 1 becomes

$$\sum_{i=1}^N D_i \frac{\partial}{\partial\mathbf{r}_i} \cdot \left(\frac{\partial F^{(N)}}{\partial\mathbf{r}_i} + \frac{\partial\Phi}{\partial\mathbf{r}_i} F^{(N)}/kT - \mathbf{A}_i F^{(N)}/kT \right) = 0 \quad (5)$$

If no external forces are acting on the particles ($\mathbf{A}_i = 0$), the solution to (5) is the equilibrium distribution function

$$F_e^{(N)} = (1/Q) \exp(-\Phi/kT) \quad (6)$$

Q being the configurational partition function. In what follows we shall, as is customary, assume that the external forces, though not zero, are very small, so that $F^{(N)}$ differs only slightly from $F_e^{(N)}$. This permits us to replace $F^{(N)}$ by $F_e^{(N)}$ in the last term of (5), which, together with the substitution $G^{(N)} \equiv [(F^{(N)}/F_e^{(N)}) - 1]$, leads to

$$\sum_{i=1}^N D_i \frac{\partial}{\partial\mathbf{r}_i} \left[F_e^{(N)} \left(\frac{\partial G^{(N)}}{\partial\mathbf{r}_i} - \mathbf{A}_i/kT \right) \right] = 0 \quad (7)$$

It is this form of the N -particle diffusion equation that we propose to replace by a variation principle.

Variational Formulation

The principle in question is essentially that of Dirichlet,⁵ extended to the $3N$ -dimensional configuration space of the system. Let us consider the problem of finding the function $G^{(N)}(\mathbf{r}_1, \dots, \mathbf{r}_N)$ which minimizes the integral

$$s = \sum_{i=1}^N D_i \int_{V^N} F_e^{(N)} \left[\left(\frac{1}{2} \right) \frac{\partial G^{(N)}}{\partial\mathbf{r}_i} \cdot \frac{\partial G^{(N)}}{\partial\mathbf{r}_i} - (\mathbf{A}_i/kT) \cdot \frac{\partial G^{(N)}}{\partial\mathbf{r}_i} \right] d\mathbf{r} \quad (8)$$

subject to the restrictions

$$\sum_{i=1}^{N^{(\alpha)}} \int_{V^N} \frac{\partial}{\partial\mathbf{r}_i^{(\alpha)}} (F_e^{(N)} G^{(N)}) d\mathbf{r} = \sum_{i=N^{(\alpha)}+1}^N \int_{V^N} \frac{\partial}{\partial\mathbf{r}_i^{(\beta)}} (F_e^{(N)} G^{(N)}) d\mathbf{r} = 0 \quad (9)$$

(5) R. Courant and D. Hilbert, "Methods of Mathematical Physics," Interscience Publishers, Inc., New York, N. Y., 1953, p. 240.

The first summation in (9) extends over α -particles only, the second over β -particles, and the notation $\int_{V^N} d\mathbf{r}$ indicates the $3N$ -fold integration $\int_V \dots \int_V d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N$. Equation 9 merely serves to ensure the absence of an over-all concentration gradient in either species.

To take (9) into account, we introduce the Lagrangian multipliers $\xi^{(\alpha)}$ and $\xi^{(\beta)}$ and proceed to minimize the quantity

$$\sigma = s + \sum_{i=1}^N \xi_i \cdot \int_{V^N} \frac{\partial}{\partial\mathbf{r}_i} (F_e^{(N)} G^{(N)}) d\mathbf{r} \quad (10)$$

where ξ_i is either $\xi^{(\alpha)}$ or $\xi^{(\beta)}$, depending on the species of the i th particle. The variation of σ is

$$\delta\sigma = \sum_{i=1}^N \int_{V^N} \left[D_i F_e^{(N)} \left(\frac{\partial G^{(N)}}{\partial\mathbf{r}_i} - \mathbf{A}_i/kT \right) \cdot \frac{\partial}{\partial\mathbf{r}_i} (\delta G^{(N)}) + \xi_i \cdot \frac{\partial}{\partial\mathbf{r}_i} (F_e^{(N)} \delta G^{(N)}) \right] d\mathbf{r} \quad (11)$$

and application of Gauss' theorem allows us to transform this to give

$$\delta\sigma = - \int_{V^N} \delta G^{(N)} \sum_{i=1}^N D_i \frac{\partial}{\partial\mathbf{r}_i} \cdot \left[F_e^{(N)} \left(\frac{\partial G^{(N)}}{\partial\mathbf{r}_i} - \mathbf{A}_i/kT \right) \right] d\mathbf{r} + \sum_{i=1}^N \int_{V^N} \int_S \delta G^{(N)} \left[F_e^{(N)} \left(D_i \frac{\partial G^{(N)}}{\partial\mathbf{r}_i} - D_i \mathbf{A}_i/kT + \xi_i \right) \cdot \mathbf{v} \right] dS d\mathbf{r}_i \quad (12)$$

The second integral in (12) extends over all configurations in which particle i is located on the surface S of the region V ; \mathbf{v} is the unit normal to the surface at \mathbf{r}_i .

If $G^{(N)}$ is to be the minimizing function, $\delta\sigma$ must vanish for any choice of $\delta G^{(N)}$. It follows that the coefficients of $\delta G^{(N)}$ in the two integrals on the right-hand side of (12) must each be identically zero, so that $G^{(N)}$ must satisfy the diffusion eq. 7 and the boundary conditions

$$\mathbf{v} \cdot \left[-D_i \left(\frac{\partial G^{(N)}}{\partial\mathbf{r}_i} - \mathbf{A}_i/kT \right) \right] = \mathbf{v} \cdot \xi_i \quad (\mathbf{r}_i \text{ on } S) \quad (13)$$

with the vector constants $\xi^{(\alpha)}$ and $\xi^{(\beta)}$ chosen so that the zero gradient conditions (9) are also obeyed. The mean velocity \mathbf{v}_i of particle i for a given configuration of the system is

$$\mathbf{v}_i = -D_i \left(\frac{\partial G^{(N)}}{\partial\mathbf{r}_i} - \mathbf{A}_i/kT \right) \quad (14)$$

and (13) may therefore be interpreted as requiring that the mean velocity with which a particle passes through the surface S be $\xi^{(\alpha)}$ for an α -particle, or $\xi^{(\beta)}$ for a β -particle. Such a requirement is certainly far more detailed than any conditions actually imposed in practice; however, we shall rely on the reasonable assumption that the details of the boundary conditions exert an appreciable influence on the distribution functions only in the immediate vicinity of the surface where they are imposed. Thus, whether we use (13) or some other condition (such as requiring $G^{(N)}$ to vanish whenever a particle is on S), we expect to get

the same results for the bulk properties of the system, so long as the basic condition of zero over-all concentration gradient is fulfilled for each species.

The next point concerns the physical significance of s : only if s is simply related to the mean relative velocity \mathbf{u} which we wish to calculate can we claim that our variation principle is truly useful, for only then can bounds on s be translated into bounds on, say, the magnitude of \mathbf{u} . To establish such a relationship, we begin by noting that, of the two terms under the integral sign in (8), the first is of order two and the second of order one in $G^{(N)}$. Furthermore, if $\bar{G}^{(N)}$ is a legitimate trial function satisfying (9), then $\lambda \bar{G}^{(N)}$, where λ is a constant, will also satisfy (9). We may substitute $\lambda \bar{G}^{(N)}$ for $G^{(N)}$ in (8) and minimize the resulting quadratic expression in λ ; the value of λ so obtained is

$$\lambda = \frac{(1/kT) \sum_{i=1}^N D_i \mathbf{A}_i \cdot \int_{V^N} F_e^{(N)} \frac{\partial \bar{G}^{(N)}}{\partial \mathbf{r}_i} d\mathbf{r}}{\sum_{i=1}^N D_i \int_{V^N} F_e^{(N)} \frac{\partial \bar{G}^{(N)}}{\partial \mathbf{r}_i} \cdot \frac{\partial \bar{G}^{(N)}}{\partial \mathbf{r}_i} d\mathbf{r}} \quad (15)$$

When $\bar{G}^{(N)}$ is the solution $G^{(N)}$ of our variational problem, the optimum value of λ must be unity, so that the numerator and the denominator in (15) are equal, allowing us to write

$$s = -(1/2kT) \sum_{i=1}^N D_i \mathbf{A}_i \cdot \int_{V^N} F_e^{(N)} \frac{\partial G^{(N)}}{\partial \mathbf{r}_i} d\mathbf{r} \quad (16)$$

which can be transformed further, using eq. 14 and 2, to give the desired relation between s and \mathbf{u}

$$s = (1/2kT) \sum_{i=1}^N \mathbf{A}_i \cdot \left[\int_{V^N} F_e^{(N)} \mathbf{v}_i d\mathbf{r} - D_i \mathbf{A}_i / kT \right] \quad (17)$$

$$= (1/2kT) N^{(\alpha)} \mathbf{A}^{(\alpha)} \cdot (\mathbf{u} - \mathbf{u}_0)$$

Now according to our variation principle, if, in eq. 8, the minimizing function $G^{(N)}$ is replaced by a trial function $\bar{G}^{(N)}$, the resulting value of s will be necessarily greater than the true value (17). We can, of course, still minimize with respect to a λ parameter, but the optimum λ given by (15) will no longer be unity. In place of eq. 16, we thus have the inequality

$$s \leq -(\lambda/2kT) \sum_{i=1}^N D_i \mathbf{A}_i \cdot \int_{V^N} F_e^{(N)} \frac{\partial \bar{G}}{\partial \mathbf{r}_i} d\mathbf{r} \quad (18)$$

or, after application of (15) and (17)

$$\mathbf{A}^{(\alpha)} \cdot (\mathbf{u} - \mathbf{u}_0) \leq \frac{(1/N^{(\alpha)} kT) \left[\sum_{i=1}^N D_i \mathbf{A}_i \cdot \int_{V^N} F_e^{(N)} \frac{\partial \bar{G}^{(N)}}{\partial \mathbf{r}_i} d\mathbf{r} \right]^2}{\sum_{i=1}^N D_i \int_{V^N} F_e^{(N)} \frac{\partial \bar{G}^{(N)}}{\partial \mathbf{r}_i} \cdot \frac{\partial \bar{G}^{(N)}}{\partial \mathbf{r}_i} d\mathbf{r}} \quad (19)$$

This is our key result. With it we can calculate, using only the equilibrium distribution function $F_e^{(N)}$, rigorous upper bounds on the nonequilibrium quantity $\mathbf{A}^{(\alpha)} \cdot (\mathbf{u} - \mathbf{u}_0)$. The precise nature of these bounds will, of course, depend on our choice for the trial function $\bar{G}^{(N)}$. Although only $\bar{G}^{(N)} = G^{(N)}$ will make an equality out of (19), we may nevertheless hope, as in any variational approach, that a trial function

with a sufficient number of adjustable parameters will provide not only a bound, but also an estimate.

The Trial Function

Probably the simplest nontrivial choice for $\bar{G}^{(N)}$ is

$$\bar{G}^{(N)} = \sum_{i=1}^{N^{(\alpha)}} \sum_{j=N^{(\alpha)}+1}^N h(\mathbf{r}_i^{(\alpha)} - \mathbf{r}_j^{(\beta)}) \quad (20)$$

where the double sum extends over all pairs of unlike particles. The function $h(\rho)$ is quite arbitrary, except for the requirement that it vanish as ρ^{-2} or faster in the limit $\rho \rightarrow \infty$ in order for (9) to be satisfied; considerations of symmetry, however, suggest that the optimum h will have the form

$$h(\rho) = q(\rho) \rho \cdot \boldsymbol{\gamma} \quad (21)$$

in which q may be any function of ρ such that $\rho^3 q$ is finite or goes to zero for large ρ , and $\boldsymbol{\gamma}$ is the unit vector in the direction of $\mathbf{A}^{(\alpha)}$.

The gradients of the trial function (20) are

$$\frac{\partial \bar{G}^{(N)}}{\partial \mathbf{r}_i^{(\beta)}} = \sum_{j=N^{(\alpha)}+1}^{N^{(\alpha)}} \mathbf{K}(\mathbf{r}_i^{(\alpha)} - \mathbf{r}_j^{(\beta)}) \quad (22)$$

$$\frac{\partial \bar{G}^{(N)}}{\partial \mathbf{r}_i^{(\alpha)}} = - \sum_{j=1}^{N^{(\alpha)}} \mathbf{K}(\mathbf{r}_j^{(\alpha)} - \mathbf{r}_i^{(\beta)})$$

with

$$\mathbf{K}(\rho) \equiv \frac{\partial h}{\partial \rho} = q(\rho) \boldsymbol{\gamma} + \rho^{-1} \frac{dq}{d\rho} \boldsymbol{\gamma} \cdot \rho \boldsymbol{\rho} \quad (23)$$

Substituting (22) into (19), we have, in the numerator

$$(1/N^{(\alpha)}) \sum_{i=1}^N D_i \mathbf{A}_i \cdot \int_{V^N} F_e^{(N)} \frac{\partial \bar{G}^{(N)}}{\partial \mathbf{r}_i} d\mathbf{r} = (1/N^{(\alpha)}) (D^{(\alpha)} \mathbf{A}^{(\alpha)} - D^{(\beta)} \mathbf{A}^{(\beta)}) \cdot \sum_{i=1}^{N^{(\alpha)}} \sum_{j=N^{(\alpha)}+1}^N \int_{V^N} F_e^{(N)} \mathbf{K}(\mathbf{r}_i^{(\alpha)} - \mathbf{r}_j^{(\beta)}) d\mathbf{r} = \mathbf{A}^{(\alpha)} \cdot (D^{(\alpha)} c^{(\beta)} + D^{(\beta)} c^{(\alpha)}) \int f^{(\alpha\beta)}(\rho) \mathbf{K}(\rho) d\rho \quad (24)$$

where the last step is achieved by invoking eq. 2 and introducing the bulk concentrations $c^{(\alpha)} \equiv N^{(\alpha)}/V$ and $c^{(\beta)} \equiv N^{(\beta)}/V$, together with the equilibrium two-particle distribution function $f^{(\alpha\beta)}(\rho)$ for an $\alpha\beta$ pair in the absence of external forces; the normalization of $f^{(\alpha\beta)}$ has been chosen so that it approaches unity as ρ becomes large. The denominator in (19) can be treated in similar fashion, to give

$$(1/N^{(\alpha)}) \sum_{i=1}^N D_i \int_{V^N} F_e^{(N)} \frac{\partial \bar{G}^{(N)}}{\partial \mathbf{r}_i} \cdot \frac{\partial \bar{G}^{(N)}}{\partial \mathbf{r}_i} d\mathbf{r} = (1/N^{(\alpha)}) \left[(D^{(\alpha)} + D^{(\beta)}) \sum_{i=1}^{N^{(\alpha)}} \sum_{j=N^{(\alpha)}+1}^N \int_{V^N} F_e^{(N)} \mathbf{K}(\mathbf{r}_i^{(\alpha)} - \mathbf{r}_j^{(\beta)}) \cdot \mathbf{K}(\mathbf{r}_i^{(\alpha)} - \mathbf{r}_j^{(\beta)}) d\mathbf{r} + 2D^{(\alpha)} \sum_{i=1}^{N^{(\alpha)}} \sum_{j=N^{(\alpha)}+1}^{j-1} \int_{V^N} F_e^{(N)} \mathbf{K}(\mathbf{r}_i^{(\alpha)} - \mathbf{r}_j^{(\alpha)}) \cdot \mathbf{K}(\mathbf{r}_i^{(\alpha)} - \mathbf{r}_j^{(\alpha)}) d\mathbf{r} + 2D^{(\beta)} \sum_{i=N^{(\alpha)}+1}^N \sum_{j=1}^{N^{(\alpha)}} \sum_{l=1}^{j-1} \int_{V^N} F_e^{(N)} \mathbf{K}(\mathbf{r}_j^{(\alpha)} - \mathbf{r}_l^{(\beta)}) \cdot \mathbf{K}(\mathbf{r}_i^{(\alpha)} - \mathbf{r}_l^{(\beta)}) d\mathbf{r} \right] =$$

$$c^{(\beta)} \left[(D^{(\alpha)} + D^{(\beta)}) \int f^{(\alpha\beta)}(\rho) \mathbf{K}(\boldsymbol{\rho}) \cdot \mathbf{K}(\boldsymbol{\rho}) d\boldsymbol{\rho} + \right. \\ \left. D^{(\alpha)} c^{(\beta)} \int f^{(\alpha\beta\beta)}(\boldsymbol{\rho}, \boldsymbol{\rho}') \mathbf{K}(\boldsymbol{\rho}) \cdot \mathbf{K}(\boldsymbol{\rho}') d\boldsymbol{\rho} d\boldsymbol{\rho}' + \right. \\ \left. D^{(\beta)} c^{(\alpha)} \int f^{(\alpha\alpha\beta)}(\boldsymbol{\rho}, \boldsymbol{\rho}') \mathbf{K}(\boldsymbol{\rho}) \cdot \mathbf{K}(\boldsymbol{\rho}') d\boldsymbol{\rho} d\boldsymbol{\rho}' \right] \quad (25)$$

The functions $f^{(\alpha\beta\beta)}(\boldsymbol{\rho}, \boldsymbol{\rho}')$ and $f^{(\alpha\alpha\beta)}(\boldsymbol{\rho}, \boldsymbol{\rho}')$ in (25) are the equilibrium three-particle distributions for an $\alpha\beta\beta$ - and an $\alpha\alpha\beta$ -group of particles, respectively, and have been normalized so as to approach unity as ρ, ρ' , and $|\boldsymbol{\rho} - \boldsymbol{\rho}'|$ go to infinity.

Symmetry considerations demand that the vectors $\mathbf{A}^{(\alpha)}$, \mathbf{u} , \mathbf{u}_0 , and $\int f^{(\alpha\beta)}(\rho) \mathbf{K}(\boldsymbol{\rho}) d\boldsymbol{\rho}$ all be colinear. The result of substituting (24) and (25) into (19) may therefore be written⁶

$$\frac{\mathbf{u} - \mathbf{u}_0}{A^{(\alpha)} c^{(\alpha)}} < - \frac{(D^{(\alpha)} c^{(\beta)} + D^{(\beta)} c^{(\alpha)})}{kT c^{(\alpha)} c^{(\beta)}} \times \\ \left\{ \int f^{(\alpha\beta)}(\rho) \mathbf{K}(\boldsymbol{\rho}) d\boldsymbol{\rho} \cdot \int f^{(\alpha\beta)}(\rho) \mathbf{K}(\boldsymbol{\rho}) d\boldsymbol{\rho} \right\} \times \\ \left\{ (D^{(\alpha)} + D^{(\beta)}) \int f^{(\alpha\beta)}(\rho) K^2(\boldsymbol{\rho}) d\boldsymbol{\rho} + \int (D^{(\alpha)} c^{(\beta)} f^{(\alpha\beta\beta)}(\boldsymbol{\rho}, \boldsymbol{\rho}') + \right. \\ \left. D^{(\beta)} c^{(\alpha)} f^{(\alpha\alpha\beta)}(\boldsymbol{\rho}, \boldsymbol{\rho}') \mathbf{K}(\boldsymbol{\rho}) \cdot \mathbf{K}(\boldsymbol{\rho}') d\boldsymbol{\rho} d\boldsymbol{\rho}' \right\}^{-1} \quad (26)$$

For any $\mathbf{K}(\boldsymbol{\rho})$ of the form (23), the inequality (26) supplies a rigorous upper bound on u in terms of equilibrium two- and three-particle distribution functions. The lowest upper bound is obtained when $\mathbf{K}(\boldsymbol{\rho})$ is the gradient of a function $h(\boldsymbol{\rho})$ which satisfies the Euler-Lagrange equation

$$\frac{\partial}{\partial \boldsymbol{\rho}} \cdot \left[(D^{(\alpha)} + D^{(\beta)}) f^{(\alpha\beta)}(\rho) \frac{\partial h(\boldsymbol{\rho})}{\partial \boldsymbol{\rho}} + \right. \\ \left. \int [D^{(\alpha)} c^{(\beta)} f^{(\alpha\beta\beta)}(\boldsymbol{\rho}, \boldsymbol{\rho}') + D^{(\beta)} c^{(\alpha)} f^{(\alpha\alpha\beta)}(\boldsymbol{\rho}, \boldsymbol{\rho}')] \frac{\partial h(\boldsymbol{\rho}')}{\partial \boldsymbol{\rho}'} d\boldsymbol{\rho}' \right] = \\ \Gamma \cdot \frac{\partial f^{(\alpha\beta)}(\rho)}{\partial \boldsymbol{\rho}} \quad (27)$$

in which Γ is a constant vector in the direction of the external forces; the magnitude of Γ is irrelevant, since it enters into $h(\boldsymbol{\rho})$ only as a constant multiplier, and so cannot affect the right-hand side of (26). The boundary condition on eq. 27 is that $h(\boldsymbol{\rho})$ must vanish for large ρ .

An Example

The greatest obstacle to the application of (26) is, of course, the difficulty of obtaining the required distribution functions $f^{(\alpha\beta)}$, $f^{(\alpha\beta\beta)}$, and $f^{(\alpha\alpha\beta)}$. This is a problem in equilibrium statistical mechanics which has so far resisted all attempts at solution, except in the most trivial cases. It is for one of these that we shall now illustrate the use of (26).

Let us suppose that the β -particles do not interact with each other at all, and that the α -particles are present in such exceedingly low concentration that $\alpha\alpha$ -interactions can also be ignored. This leaves us with only $\alpha\beta$ -interactions to consider, and if we assume that these are pairwise additive, the pair distribution $f^{(\alpha\beta)}$ becomes simply

$$f^{(\alpha\beta)}(\rho) = \exp(-\phi(\rho)/kT) \quad (28)$$

(6) We wish to take this opportunity to point out an error in ref. 4: in eq. 6 of that note, $c^{(\alpha)}$ and $c^{(\beta)}$ were inadvertently interchanged. Equation 26 gives the correct result.

where ϕ is the interaction potential between an α - and a β -particle. Furthermore, since the β -particles are, by assumption, completely independent of one another, the three-particle distribution function $f^{(\alpha\beta\beta)}$ can be factored to give

$$f^{(\alpha\beta\beta)}(\boldsymbol{\rho}, \boldsymbol{\rho}') = f^{(\alpha\beta)}(\rho) f^{(\alpha\beta)}(\rho') \quad (29)$$

The simplicity of equilibrium statistical mechanics for this system does not, however, extend to irreversible phenomena: the calculation of u remains very much a nontrivial problem. We can, nevertheless, obtain the upper bound (26). In the limit $c^{(\alpha)} \rightarrow 0$, the term in $f^{(\alpha\alpha\beta)}$ on the right-hand side can be neglected, and the relation (29) allows us to write

$$\int \int f^{(\alpha\beta\beta)}(\boldsymbol{\rho}, \boldsymbol{\rho}') \mathbf{K}(\boldsymbol{\rho}) \cdot \mathbf{K}(\boldsymbol{\rho}') d\boldsymbol{\rho} d\boldsymbol{\rho}' = \\ \int f^{(\alpha\beta)}(\rho) \mathbf{K}(\boldsymbol{\rho}) d\boldsymbol{\rho} \cdot \int f^{(\alpha\beta)}(\rho') \mathbf{K}(\boldsymbol{\rho}') d\boldsymbol{\rho}' \quad (30)$$

The inequality (26) thus reduces to

$$(\mathbf{u} - \mathbf{u}_0)/D^{(\alpha)} A^{(\alpha)} < -(1/kT) D^{(\alpha)} c^{(\beta)} / \\ [(D^{(\alpha)} + D^{(\beta)}) \Xi + D^{(\alpha)} c^{(\beta)}] \quad (31)$$

with Ξ given by

$$\Xi = \frac{\int f^{(\alpha\beta)}(\rho) K^2(\boldsymbol{\rho}) d\boldsymbol{\rho}}{\int f^{(\alpha\beta)}(\rho) \mathbf{K}(\boldsymbol{\rho}) d\boldsymbol{\rho} \cdot \int f^{(\alpha\beta)}(\rho) \mathbf{K}(\boldsymbol{\rho}) d\boldsymbol{\rho}} \quad (32)$$

For a given value of $c^{(\beta)}$, minimizing the upper bound (31) on u is equivalent to minimizing Ξ . The Euler-Lagrange equation (27) for the function $h(\boldsymbol{\rho})$ can therefore be replaced by

$$\frac{\partial}{\partial \boldsymbol{\rho}} \cdot \left(f^{(\alpha\beta)}(\rho) \frac{\partial h}{\partial \boldsymbol{\rho}} \right) = \Gamma \cdot \frac{\partial f^{(\alpha\beta)}(\rho)}{\partial \boldsymbol{\rho}} \quad (33)$$

The boundary condition remains $h(\boldsymbol{\rho}) \rightarrow 0$ as ρ becomes large. Equation 33 is just the steady-state diffusion equation for the concentration distribution $c(\boldsymbol{\rho}) \equiv c^{(\alpha)} f^{(\alpha\beta)}(\rho) (1 + h(\boldsymbol{\rho}))$ of α -species around an isolated β -particle fixed at the origin, if the α -particles are subjected to a weak external force $kT\Gamma$.

It appears, therefore, that when $c^{(\beta)}$ is small (though still large compared to $c^{(\alpha)}$), the trial function (20) represents the true state of affairs, provided h satisfies eq. 33. The right-hand side of (31) then gives, not just an upper bound, but the actual value of $u - u_0$, and we have, remembering that in this case $u_0 = D^{(\alpha)} A^{(\alpha)} / kT$

$$\epsilon \equiv \lim_{c^{(\beta)} \rightarrow 0} (u_0 - u) / u_0 c^{(\beta)} = \\ D^{(\alpha)} / [(D^{(\alpha)} + D^{(\beta)}) \Xi] \quad (34)$$

From (32) and (33), however, we see that Ξ is independent of $c^{(\beta)}$, so that the inequality (31) becomes, after some rearrangement

$$u < u_0 / (1 + \epsilon c^{(\beta)}) \quad (35)$$

a result which is valid at any concentration of β .⁷

It is interesting to note that, according to (35), u must go to zero in the limit of very high $c^{(\beta)}$, even though $\phi(\rho)$ may be everywhere finite. This is not so surprising as it may seem at first glance: the deviation of u from u_0 is determined essentially by the fluctua-

(7) A special case of this result has been published by H. L. Weissberg, *J. Appl. Phys.*, **34**, 2639 (1963).

tions in the potential energy of an α -particle as it moves from one point to another, and these increase without limit as $c^{(b)}$ becomes large.

Further Development

There are several questions which arise in connection with the results of this paper. First of all, if the α - and β -species are solutes in a liquid solvent, then hydrodynamic interactions between diffusing particles (the electrophoretic effect in electrolyte conduction) must not be ignored. Such interactions can be fitted into the variational treatment, but lead, inevitably, to more complicated expressions for the upper bound on $u - u_0$, expressions which involve four-particle distribution functions. We shall treat this point in a separate publication.

Next, we may ask whether it is possible to bound $u - u_0$ from below as well as from above. Such bounds have been derived in related problems⁸ and can also

(8) Z. Hashin and S. Shtrikman, *J. Appl. Phys.*, **33**, 3125 (1962); J. L. Jackson and S. R. Coriell, *J. Chem. Phys.*, **38**, 959 (1963); D. M. Schrader and S. Prager, *ibid.*, **37**, 1456 (1962); S. Prager and J. O. Hirschfelder, *ibid.*, **39**, 3289 (1963).

be obtained here. Once again, however, the calculations turn out to involve four-particle distribution functions or worse. Moreover, when the interparticle potentials can become infinite, which is all too likely in view of the short range repulsive forces that are usually present, the lower bound on u simply vanishes, leaving us with a rather trivial result.

Finally, it is evident that the variational approach is not restricted to the interdiffusion problem of the present paper. For example, a similar treatment can be developed for the viscosity of solutions in which the solute particles interact with one another.⁹ A rather different type of situation involving the Brownian movement of interacting particles is offered by a diffusion-controlled reaction; here it is possible to obtain bounds on the reaction rate, and some work along these lines has been published.¹⁰

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(9) S. Prager, *Physica*, **29**, 129 (1963).

(10) S. Prager, *Chem. Eng. Sci.*, **18**, 227 (1963).

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A Correction to the Poisson-Boltzmann Equation for Unsymmetrical Electrolytes

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The lowest order correction term to the Poisson-Boltzmann equation for unsymmetrical electrolytes is computed; the logical symmetry of the distribution functions obviates any need to consider greater sets than pairs of ions for this purpose. The dominant part of the correction is proportional to the first power of the concentration, with a coefficient which depends only on the Coulomb interaction. The effect may be interpreted as a scale-dependent activity correction to the effective ionic strength.

Debye and Hückel¹ computed the mutual shielding of Coulomb forces between the ions in solution on the assumption that the concentration $n_{ji}(r)$ of species i near species j is given according to the Boltzmann principle by the charge e_j of the former and the average potential $\psi_j(r)$ near the latter

$$n_{ji}(r) = n_i \exp(-e_i\psi_j(r)/kT) \quad (1)$$

This combined with the Poisson relations

$$\begin{aligned} \Delta^2\psi_j &= -(4\pi/D)\rho_j \\ &= -(4\pi/D)\sum e_i n_{ji}(r) \\ &\quad (r > a) \end{aligned} \quad (2)$$

$$a^2\psi_j'(a) = -e_j/D \quad (3)$$

to obtain the Poisson-Boltzmann equation

$$\Delta^2\psi_j = -(4\pi/D)\sum n_i e_i \exp(-e_i\psi_j/kT) \quad (4)$$

The solution of (4) with the boundary condition (3) yields the potential $\psi_j(e_j, a)$ at the ion as a function of the charge e_j and of the concentrations and charges of other ions, and the electrostatic contributions to the free energy can be computed as the work involved in an idealized charging process.

On general principles, such idealization is quite legitimate, and if the potentials described were known ac-

curately, one should obtain the same result whether the ions are charged one at a time² or together in proportion.³ However, these two methods yield somewhat different results when applied to the solutions of the Poisson-Boltzmann equation. Consistent results are obtained when the linear approximation

$$n_{ji}(r) \approx n_i(1 - (e_i\psi_j/kT)) \quad (5)$$

is substituted for the Boltzmann formula, whence

$$\Delta^2\psi = \kappa^2\psi \quad (6)$$

$$\kappa^2 = \left(\frac{4\pi}{DkT}\right) \sum_i n_i e_i^2$$

Discrepancies appear as soon as any additional terms are retained in the power series of the exponential function in eq. 1

$$\Delta^2\psi_j - \kappa^2\psi_j = -\kappa^2(n_i/2kT)\psi_j^2 + O(\psi_j^3) \quad (7)$$

$$\eta_2 = \sum n_i e_i^3 / \sum n_i e_i^2$$

for electrolytes of unsymmetrical valence type, and

$$\Delta^2\psi_j - \kappa^2\psi_j = (n_2/6(kT)^2)\psi_j^3 + O(\psi_j^5) \quad (8)$$

$$\eta_2 = \sum n_i e_i^4 / \sum n_i e_i^2$$

for binary electrolytes or mixtures of any symmetric type.

(2) H. Mueller, *ibid.*, **38**, 324 (1927); **39**, 78 (1928).

(3) T. R. Gronwall, K. Sandved, and V. K. La Mer, *ibid.*, **39**, 358 (1928).

(1) P. Debye and E. Hückel, *Physik. Z.*, **24**, 185 (1923).