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Hall Coefficient in Solution for a Simple Dynamical Model

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A model Liouville equation is proposed for a system composed of an ion moving in a solvent fluid. Using this model, explicit results are obtained for the Ohmic conductivity L and the Hall conductivity h. These results are then used to calculate the Hall coefficient $R = ehL^{-2}$, which is a measure of the effect of non-Brownian motion, for several charge carriers of interest. Our results are in agreement with earlier findings based on a stochastic model which predict $R > 1$ for H^+(aq). Our results also indicate that $R \approx 1$ for charge carriers such as Na^+, Cl^-, and K^+ which have a mass greater than that of a solvent molecule (here taken as 18 amu).

KEY WORDS: Ion, solvent fluid; applied electrical and magnetic fields; transport coefficients; non-Brownian effects.

1. INTRODUCTION

It is often possible to calculate nonequilibrium properties of liquid systems by considering the motions of the constituent molecules as Brownian, i.e., governed by Langevin's equation (see, e.g., Rice and Gray(1)). This simplified dynamical description gives quite acceptable results for first-order dc transport coefficients;(2) however, the situation with respect to higher-order transport coefficients is not at all clear. One higher-order transport coefficient which is of particular interest in the theory of electrolyte solutions is the Hall conductivity. In a recent paper,(3) Friedman and Ben-Nain have obtained an expression for the Hall conductivity by considering a stochastic model in which the charge carrier (ion) is a "two-state brownon," this being a particle whose motion is governed by Langevin's equation, but whose friction coefficient and mass randomly change between two sets of values. The value of the

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Hall conductivity found using this model can differ appreciably from the pure Brownian-motion value. An index of the effect of non-Brownian motion on the Hall conductivity is the Hall coefficient, $R = ehL^{-2}$ (e the electronic charge, L the Ohmic conductivity, and h the Hall conductivity). This quantity is identically unity when the charge carrier motion is Brownian, and for the two-state Brownian motion, $R > 1$ is found in some cases. Although R is experimentally accessible, there are no data at present since the necessary experiments are quite difficult.(4)

The purpose of this communication is to verify the conclusions of Friedman and Ben-Nain within the context of a dynamical rather than a stochastic model. An exact dynamical description of this problem within the framework of the Liouville equation is of course impossible due to the complexity of the many-body problem which must be considered.(5) We therefore consider as our starting point a model Liouville equation, from which we can obtain explicit results, in terms of two model parameters, for L and h, and thus R. The model which we will use (which is described in Section 2) is similar to other models which have been successfully used in the theory of liquids.(6–8) In addition to supporting the findings of Friedman and Ben-Nain that non-Brownian effects can be appreciable in certain electrolyte systems, our results also allow us to substantiate one of the important assumptions in their theory, which Friedman has independently pointed out required further investigation,(9) namely that heavy ions such as Na^+(aq) or Cl^-(aq), which are not strictly Brownian particles, can be considered as Brownian. These results are derived and discussed in Sections 3 and 4.

2. MODEL LIOUVILLE EQUATION

The system which we will consider is an electrolyte solution at infinite dilution in the presence of externally applied electric and magnetic fields. The system is aged from time $t = -\infty$ until $t = 0$, and then the fields, considered as weak, are turned on. The full statistical mechanical description is then given by Liouville's equation,(5)

$$\begin{aligned} \partial\rho_N/\partial t + H_N{}^0\rho_N &= 0, \qquad -\infty < t \leqslant 0 \\ \partial\rho_N/\partial t + (H_N{}^0 + H')\,\rho_N &= 0, \qquad t > 0 \end{aligned} \tag{1}$$

Here, $\rho_N = \rho_N(\Gamma, t)$ is the probability distribution function at time t which describes the entire system of $N - 1$ solvent particles and single charge carrier, Γ specifies the phase of the system, $H_N{}^0$ is the Hamilton operator for the unperturbed motion of the system, and H' is the Hamilton operator for the perturbing external fields. Formal expressions for the transport coefficients we are interested in can be found by solving (1);(5) however, these results are not very useful since they depend on the solution of the N-body problem. This of course is a familar problem in the non-equilibrium theory of liquids, and a myriad of approximating techniques have been devised for its circumvention. Many of these are covered in a recent review article by Berne and Harp.(10)

The method we propose to follow here is to replace (1) by a model which, although it retains the physical content of the full Liouville equation, is tractable with respect to the concomitant dynamical problem. The model we consider treats the charge carrier as interacting with a single solvent particle which in turn interacts with the rest of the solvent fluid. The carrier–solvent interparticle potential is assumed to be harmonic, and the solvent particle–solvent interaction is described by a simple relaxational form. The statistical description (1) is then replaced by

$$\begin{aligned} \partial\rho/\partial t + H_2{}^0\rho &= (\rho^0 - \rho)/\tau, \qquad -\infty < t \leqslant 0 \\ \partial\rho/\partial t + (H_2{}^0 + H')\,\rho &= (\rho^0 - \rho)/\tau, \qquad t > 0 \end{aligned} \tag{2}$$

with $\rho = \rho(\mathbf{q}, \mathbf{p}, \mathbf{Q}, \mathbf{P}, t) = \rho(\gamma, t)$ the probability distribution function at time t which describes the charge carrier and interacting solvent particle. The r.h.s. of (2) takes into account the effect of the rest of the solvent fluid, which in effect acts as a reservoir. When no external fields are present, the effect of the reservoir is to bring ρ to the canonical form ρ^0, which it does with a characteristic time τ, the solvent relaxation time. The phase of the charge carrier is denoted by $(\mathbf{q}, \mathbf{p})$ and that of the interacting solvent particle by $(\mathbf{Q}, \mathbf{P})$. The Hamilton operators which appear in (2) are

$$\begin{aligned} H_2{}^0 &= (\mathbf{p}/m)\cdot(\partial/\partial\mathbf{q}) + (\mathbf{P}/M)\cdot(\partial/\partial\mathbf{Q}) \\ &\quad - (\partial U/\partial\mathbf{q})\cdot(\partial/\partial\mathbf{p}) - (\partial U/\partial\mathbf{Q})\cdot(\partial/\partial\mathbf{P}) \equiv H^0 \\ H' &= e\mathbf{E}\cdot(\partial/\partial\mathbf{p}) + (e/m)\,\mathbf{p}\wedge\mathbf{H}\cdot(\partial/\partial\mathbf{p}) \end{aligned} \tag{3}$$

with $U = \frac{1}{2}\omega_0(\mathbf{Q} - \mathbf{q})^2$. It should be noted that the above model has at least two adjustable parameters,[2] τ and ω_0. The solvent particle mass M could also be treated as an adjustable parameter if we wished to consider the charge carrier as interacting with a neighboring mass of solvent fluid rather than a single molecule, and although this is probably preferable, we will be sufficiently pressed to determine only two parameters, so that we will not adopt this embellishment at present. We believe that the model given by (2) and (3) gives a reasonable description of the physical problem being considered, and is certainly justified for carrying out exploratory calculations of the type we have in mind. In further justification of its use, we mention that our model is identical to the itinerant-oscillator model of simple liquids proposed by Damle *et al.*(7) when the time-dependent friction coefficient which appears in their model is choosen in a particular way. These authors also use a harmonic potential. Further, Gray(6) has used a model quite similar to (2) (with a Lennard-Jones potential) to also study simple liquids. In both cases, the models used were capable of producing results in substantial agreement with available data for liquid argon (see, e.g., Berne *et al.*(11) and Gray(6)). Finally, it should be mentioned that our model can be considered as a simplified version of a model introduced by Lebowitz and Rubin.(8) In their model, the ρ^0 term on the r.h.s. of (2) becomes replaced by $f(\mathbf{q}, \mathbf{p}, t)\, P^0(\mathbf{q}, \mathbf{p}/\mathbf{Q}, \mathbf{P})$, where f is the charge carrier distribution function, and P^0 the equilibrium value of the conditional distribution function.

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[2] Most models of liquid systems (see below) contain parameters to be determined. By way of comparison, the stochastic model of Friedman and Ben-Nain contains six such parameters.

As we have mentioned above, the reason for introducing (2) is that it obviates the problem of having to solve the N-body problem. Instead of having to treat the N-body streaming operators $\exp(tH_N{}^0)$, we have only the much simpler operators $\exp(tH_2{}^0)$ to consider. Explicit results can be obtained for these latter operators, e.g., in our calculation of the Ohmic and Hall conductivities the quantity $\exp(tH_2{}^0)\,\mathbf{p}$ appears, and as may be directly verified

$$[\exp(tH_2{}^0)]\,\mathbf{p} = \mathbf{p} + m^*\{[(\mathbf{P} - (\mathbf{p}/m)](1 - \cos\omega t) + \omega(\mathbf{Q} - \mathbf{q})\sin\omega t\} \tag{4}$$

where we have set $M = 1$ for convenience, and m^*, the reduced mass, and ω are defined as

$$m^* = m/(1 + m)$$

$$\omega = \omega_0[1 + (1/m)]^{1/2}$$

3. OHMIC AND HALL CONDUCTIVITIES

The response of an aged system to an external, weak perturbation which is turned on at $t = 0$ is easily calculated (at least formally) by using the so-called direct Kubo method. The full current which flows at $t > 0$ in response to the external fields is

$$\mathbf{j}(t) = (e/m)\int d\gamma\,\rho(\gamma, t)\,\mathbf{p} \tag{5}$$

Substituting for $\rho(\gamma, t)$ in (5) by noting that a formal solution to (2) for $t > 0$ is

$$\begin{aligned}\rho(\gamma, t) = {} & [\exp(-tH^0)]\,\rho(\gamma, 0) \\ & - \int_0^t dt_1\{\exp[-(t - t_1)(H^0 + H' + 1/\tau)]\}\,H'\rho(\gamma, 0)\end{aligned} \tag{6}$$

we find, after some simple manipulation, that the steady-state current $\mathbf{j}_s$ is

$$\mathbf{j}_s \equiv \lim_{t\to\infty}\mathbf{j}(t) = \beta(e^2/m^2)\,\mathbf{E}\cdot\tilde{\underline{\underline{\phi}}}(0) \tag{7}$$

where $\beta = 1/kT$, and $\tilde{\underline{\underline{\phi}}}(S)$ is the Laplace transform of the model momentum autocorrelation function,

$$\underline{\underline{\phi}}(t) = \int d\gamma\,\rho^0(\gamma)\,\mathbf{p}\{\exp[t(H^0 + H' - 1/\tau)]\}\,\mathbf{p} \tag{8}$$

Equations (7) and (8) can be expanded in powers of $|\mathbf{E}|$ and $|\mathbf{H}|$, and the coefficient of $|\mathbf{E}|^x\,|\mathbf{H}|^y$ in (7) will be a transport coefficient of order $x + y$ which is given by a term of order $x + y - 1$ in the expansion of $\underline{\underline{\phi}}$. If we call $\underline{\underline{\phi}}^{(n)}$ that part of $\underline{\underline{\phi}}$ which is of order n in H', then the usual Kubo formula for the linear response, i.e., the Ohmic current $\mathbf{j}_O$, can be written as $\mathbf{j}_O = L\mathbf{E}$, where the Ohmic conductivity L is

$$L = (e^2/m)\,\beta\tilde{\underline{\underline{\phi}}}^{(0)}(0) \tag{9}$$

Expanding the exponential operator in (8) to obtain $\underline{\underline{\phi}}^{(0)}$, which, with (5), can be explicity calculated, we then find

$$L = (e^2/m)\,\tau(1 - (m^*/m) + (m^*/m)\{1/[1 + (\omega\tau)^2]\}) \tag{10}$$

Continuing, we turn now to the second-order response to H', which is the Hall current $\mathbf{j}_H$. This quantity is not generally a simple functional of $\underline{\underline{\phi}}^{(0)}$, but instead has the following more complicated form[(5)]:

$$\begin{aligned}\mathbf{j}_H &= \beta(e^2/m^2)\,\mathbf{E}\cdot\underline{\underline{\phi}}^{(1)}(0)\\ &= \beta(e^2/m^2)\,\mathbf{E}\cdot\int_0^\infty dt\int_0^t dt_1\int d\gamma\,\rho^0(\gamma)\\ &\quad\times\mathbf{p}\{\exp[(t-t_1)(H^0-1/\tau)]\}\,H'\{\exp[t_1(H^0-1/\tau)]\}\,\mathbf{p}\end{aligned} \tag{11}$$

In the corresponding expression for $\mathbf{j}_H$ based on the solution of (1), the Hamilton operators $H_N{}^0$ appear in place of $(H^0 - 1/\tau)$, and explicit calculations cannot be carried out. In the present case, however, this expression can be evaluated, and we find $\mathbf{j}_H = h\mathbf{E} \wedge \mathbf{H}$, where the Hall conductivity h is given as

$$h = \frac{e^3}{m^2}\tau^2\left[1 - 2\frac{m^*}{m}\frac{(\omega\tau)^2}{1+(\omega\tau)^2} + \left(\frac{m^*}{m}\right)^2\left(1 - \frac{3}{2}\frac{1}{1+(\omega\tau)^2} + \frac{1}{2}\frac{1-(\omega\tau)^2}{[1+(\omega\tau)^2]^2}\right)\right] \tag{12}$$

Equations (10) and (12) are the results which we will utilize to calculate the Hall coefficient. As these results now stand, however, they are quite useless unless some method can be devised for obtaining meaningful values of ω and τ for systems of interest. If molecular dynamics results were available, e.g., momentum autocorrelation function data, for a foreign particle moving in a host solvent fluid, then standard methods could be applied to evaluate ω and τ.[(11)] We expect such data will become available soon;[(12)] however, for the present, we will have to be content with the more *ad hoc* methods described in the following section.

4. CALCULATION OF THE HALL COEFFICIENT

In this section, we restrict ourselves to systems in which the host solvent fluid is water (in part 4.1, the restriction is only that the solvent molecules have a mass of 18 amu). We will distinguish between two cases, (1) charge carrier mass $>$ 18 amu, and (2) charge carrier mass $<$ 18 amu.

4.1. Heavy Charge Carriers ($M/m < 1$)

It can be shown that the Brownian-motion description is embedded in the exact statistical mechanical description in a particular limit in which $M/m \to 0$.[(3)] Friedman and Ben-Nain, on the other hand, have considered the motion of $\mathrm{Cl^-(aq)}$ as being strictly Brownian; subsequently, Friedman[(9)] has indicated that this particular assumption in the FB-N theory calls for further examination. In order to utilize the results of the last section to estimate the non-Brownian effects of heavy, but not strictly Brownian charge carriers, we must first determine a procedure for assigning values to ω and τ. Limiting Ohmic conductivity data for ions in water are readily available;(14) however, no other reliable independent data are presently in the literature. Thus, we will have to resort to some *ad hoc* procedure in choosing one of our parameters. Fortunately, the solvent fluid relaxation time τ can be estimated with a reasonable amount of accuracy, and so the procedure we will adopt is to make an educated guess of its value, and then use the conductivity data with (10) to evaluate ω.

In the limit $m^*/m \to 0$ (strict Brownian motion) $\tau \to \tau_B$, where τ_B is the Brownian-motion relaxation time. This latter quantity is related to L through the Einstein relationship $L = \tau_B(e^2/m)$, which defines τ_B for arbitrary m^*/m, so that from (10) we have, for arbitrary m^*/m

$$0 \leqslant (\omega\tau)^2 = [(m/m^*)(\tau_B/\tau) + 1 - (m/m^*)]^{-1} - 1 \tag{13}$$

from which it follows that

$$1 - (m^*/m) \leqslant \tau_B/\tau \leqslant 1 \tag{14}$$

This result is suggested by the detailed and rigorous study of Resebois *et al.*,(15) who have shown for a weakly coupled system that the actual fluid relaxation time is of the same order and greater than the relaxation time associated with a Markovian description of the system. For heavy ion carriers, $0 \leqslant m^*/m \leqslant \frac{1}{2}$, and (14) gives us a reasonable bound on the value of τ. In order to ensure that τ is choosen in a consistent manner as m^*/m varies, it seems reasonable in the absence of any other information to use the mean values given by (14). A particular advantage of this method of choosing τ is that it obviates the need for Ohmic conductivity data in computing R, since τ is given directly in terms of τ_B, and thus the results which are obtained are for arbitrary solvent conditions. We have carried out calculations for the Hall coefficient $R = ehL^{-2}$ for Na^+, Cl^-, and K^+, and the results are $R = 1.00$, 0.95, 0.95, respectively. (See Table I for the corresponding values of $\omega\tau$, τ/τ_B, and a representative value of τ_B.) The first is an example of a decidedly non-Brownian particle, the second and third are considerably more Brownian. For heavier charge carriers, one finds $R \approx 1$. Thus, our results indicate, in accord with the assumption

Table I. Summary of Results[a]

Ion	R	τ/τ_B	$(\omega\tau)^2$	τ_B, sec
Na^+	1.00	1.28	1.00	1.26×10^{-14}
Cl^-	0.95	1.20	1.00	2.85×10^{-14}
K^+	0.95	1.19	1.00	3.08×10^{-14}
H^+	7.28	$10^{-13}/\tau_B$	25.6	3.75×10^{-15}
H^+	22.4	$5 \times 10^{-13}/\tau_B$	133	3.75×10^{-15}

[a] τ_B calculated in H_2O at 25°C.(14)

of Friedman and Ben-Nain, that non-Brownian effects are not significant for heavy charge carriers.

4.2. Light Charge Carriers (H^+)

We now turn our attention to the most important of the light charge carriers, H^+. Here, it no longer seems justifiable to consider τ in terms of its deviation from the Brownian relaxation time, the situation being markedly non-Brownian in this case. A reasonable guess can be made, however, as to a lower bound for τ. This would be the time required for a solvent molecule to move an appreciable distance,[3] which is of the order of 10^{-1} psec (10^{-13} sec). Using this value for τ, and the experimental data for L,(14) we find for $H^+(aq)$ at 25° that $R = 7.28$. Further, for τ chosen as 5×10^{-1} psec, and under the same conditions, $R = 22.4$, and for τ increasing, R also increases (see Table I). Thus, despite the uncertainty in determining τ, our results still strongly indicate that non-Brownian effects are significant, and can thus be considered as independent evidence in support of the conclusions of Friedman and Ben-Nain.

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REFERENCES

1. S. A. Rice and P. Gray, *The Statistical Mechanics of Simple Liquids*, Interscience, New York, 1965.
2. R. Zwanzig, in *Lectures in Theoretical Physics*, Vol. 3, W. E. Brittin, W. B. Downs, and J. Downs, eds., Interscience, New York, 1962.
3. H. L. Friedman and A. Ben-Nain, *J. Chem. Phys.* **48**:120 (1968).
4. J. M. Ziman, *Phil. Mag.* **7**:865 (1962).
5. S. Harris and H. L. Friedman, *J. Chem. Phys.* **50**:765 (1965).
6. P. Gray, *Mol. Phys.* **7**:235 (1964).
7. P. S. Damle, A. Sjolander, and K. S. Swingi, *Phys. Rev.* **165**:277 (1968).
8. J. L. Lebowitz and E. Rubin, *Phys. Rev.* **131**:2381 (1963).
9. H. L. Friedman, *J. Chim. Phys.* (Numero Speciale), p. 75 (1969).
10. B. J. Berne and G. D. Harp, On the calculation of time correlation functions," *Advan. Chem. Phys.*, to appear.
11. B. J. Berne, J. P. Boon, and S. A. Rice, *J. Chem. Phys.* **45**:1086 (1966).
12. A. Raman, private communication.
13. P. Mazur and I. Oppenheim, *J. Phys. Soc. Japan (Suppl.)* **26**:35 (1969).
14. R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, Butterworths, London, 1955.
15. P. Resebois, J. Brocas, and G. Decan, *J. Math. Phys.* **10**:1964 (1969).

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[3] By appreciable, we mean a microscopic distance which could conceivably give a measurable effect in a suitable experiment. This criterion implies a separation of the two microscopic time scales which appear in the model, ω^{-1} and τ, and from Table I it is seen that this self-consistency requirement is met.