

LETTERS TO THE EDITOR

The Letters to the Editor section is divided into three categories entitled Notes, Comments, and Errata. Letters to the Editor are limited to one and three-fourths journal pages as described in the Announcement in the 1 January 1999 issue.

NOTES

Third-order transport coefficients of ions in electrostatic fields

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(Received 21 August 1998; accepted 5 November 1998)

[S0021-9606(99)52006-0]

High-order diffusional motion for ions moving in low-density gases under the action of a homogeneous electrostatic field has been at the reach of molecular-dynamics simulation of the ion motion by now. Calculations of certain components of the third-order transport coefficients, \mathbf{Q} , have already been performed in the cases of K^+ in $\text{Ar}^{1,2}$ and Na^+ in Ar^{3} . However, since the ion transport in traditional drift tube experiments does not depend significantly on high-order transport properties, coefficients \mathbf{Q} have not been measured so far. Similarly, an analytic procedure that has also been developed for the calculation of \mathbf{Q} based on kinetic theory⁴ has not been applied to real systems. A recently developed method, however, based on generalized relations between high-order transport coefficients^{5,6} is promising to provide coefficients \mathbf{Q} for ions in gases at the level of accuracy of such relations. In this work it is stressed that the definition of \mathbf{Q} should involve three independent components which seems to be in variance to our calculation of only two such components.² To elucidate this difference, we study the symmetry of our expressions and show in the following that the coefficient which we have considered corresponds to the symmetrical form of the third-order transport coefficient.

The diffusional motion of ions in low-density neutral gases under the action of an electrostatic field can be expanded in terms of high-order gradients of the ion number density as follows:

$$\mathbf{J}_d = -\mathbf{D} \cdot \nabla n + \mathbf{Q} : \nabla \nabla n + \dots, \quad (1)$$

where n is the ion density and \mathbf{D} , \mathbf{Q} etc. are diffusion and high-order transport coefficients represented by tensors of second, third, etc. rank. Terms of the form $\nabla n \nabla n$ etc. are excluded since they are small, not affecting measurements in drift tube experiments. The evolution of the ion density in space can then be obtained from the continuity equation, which involves the total ion flux due to drift and diffusional motion

$$\frac{dn}{dt} = -n \nabla \cdot \mathbf{v}_d + \mathbf{D} : \nabla \nabla n - \mathbf{Q} : \nabla \nabla \nabla n + \dots, \quad (2)$$

with \mathbf{v}_d the ion drift velocity.

Macroscopic considerations about the cylindrical symmetry and the invariance of \mathbf{J}_d on the permutation of gradient operators in Eq. (1) show that \mathbf{D} has at most two independent components, \mathbf{Q} has three components etc.^{4,6} However, in our recent attempt to calculate coefficients \mathbf{Q}^2 from a molecular-dynamics simulation method we produced only two components through the use of

$$\mathbf{Q} = \left(\frac{1}{3!} \right) \frac{1}{t} \langle \Delta \mathbf{r} \Delta \mathbf{r} \Delta \mathbf{r} \rangle, \quad (3)$$

where $\Delta \mathbf{r} = \mathbf{r}(t) - \langle \mathbf{r}(t) \rangle$ is the spatial displacements of a tagged ion with t approaching infinity and the brackets represent steady-state ensemble average.

The apparent contradiction related to the number of independent components of \mathbf{Q} led S. B. Vrhovac *et al.*⁶ to conclude that our \mathbf{Q} is not identical to the coefficient defined through Eq. (1). However, they comment that in the case of low fields the number of the components of \mathbf{Q} may reduce to two as in our case.

To reconcile the situation one has to study the definition of \mathbf{Q} , Eq. (3), and the symmetry of its parts. Explicit consideration of the symmetry properties of the averaged product $\langle \Delta \mathbf{r} \Delta \mathbf{r} \Delta \mathbf{r} \rangle$ ⁶ has shown that this term is more symmetric under permutation of space coordinates than \mathbf{Q} defined through Eq. (1). However, in our case this product was related to \mathbf{Q}^1 through the use of the continuity Eq. (2), in which \mathbf{Q} as participating in a threefold scalar product, can be set also in symmetrical form. Thus, the transport coefficient defined through Eq. (3) should be identified as the symmetrical form of \mathbf{Q} defined through Eq. (1), which is consistent with the continuity Eq. (2). By comparing the components we have considered, Q_{\parallel} and Q_{\perp} ($Q_{\parallel} = Q_{zzz}$ with the field in the z direction and Q_{\perp} representing all remaining and equal to one another components of symmetrical \mathbf{Q}), to the exact components, we infer that

$$\begin{aligned} Q_{\parallel} &= Q_{zzz} \\ Q_{\perp} &= \frac{1}{3}(Q_{xxz} + Q_{xzx} + Q_{zxx}) = \frac{1}{3}(Q_{yyz} + Q_{yzy} + Q_{zyy}). \end{aligned} \quad (4)$$

Since, in general $Q_{xxz} = Q_{xzx}$ and similarly with y in the position of x , on the right hand side we have three independent components. In this form the symmetric property under permutation of space coordinates of Q_{\parallel} and Q_{\perp} becomes apparent. Further, these components can be expressed in terms of the three independent components, Q_1 , Q_2 , and Q_3 , defined by Wealton and Mason⁴ through

$$Q_{\parallel} = Q_1 + Q_2 + 2Q_3 \quad \text{and} \quad Q_{\perp} = \frac{1}{3}(Q_2 + 2Q_3). \quad (5)$$

A direct approach to obtain the above relations can be based on the Fourier transformed conditional probability of a tagged ion,^{2,7}

$$P(\mathbf{k}, t) = \langle e^{i\mathbf{k}\Delta\mathbf{r}} \rangle, \quad (6)$$

which produces

$$\frac{\partial^3 P}{\partial k_l \partial k_m \partial k_n} = \langle \Delta r_n \Delta r_m \Delta r_l \rangle, \quad (7)$$

in the limit of \mathbf{k} approaching zero. Here indices $\{l, m, k\}$ represent space coordinates. A similar application to the hydrodynamic analog of $P(\mathbf{k}, t)$, [Eq. (8) of Ref. 1], and comparison to the above equation produces

$$\langle \Delta r_n \Delta r_m \Delta r_l \rangle = t \sum_{\{lmn\}} Q_{lmn}, \quad (8)$$

with the summation involving all six permutations of $\{l, m, n\}$ indices. Comparing this result with Eq. (3) we obtain again Eqs. (4) and (5).

The above considerations are in conformity to the results of Kumar *et al.*⁸ which have already presented as equivalent expression embedded in a kinetic theory analysis. Their expression connecting \mathbf{Q} to $\langle \Delta\mathbf{r}\Delta\mathbf{r}\Delta\mathbf{r} \rangle$ involves time derivative in the place of division by time of Eq. (3)

$$\mathbf{Q} = \left(\frac{1}{3!} \right) \frac{d}{dt} \langle \Delta\mathbf{r}\Delta\mathbf{r}\Delta\mathbf{r} \rangle, \quad (9)$$

These transport coefficients have been set in symmetrical form and emerge as constant quantities at long times. The latter requires the average of the triple $\Delta\mathbf{r}$ product to be linear in time and thus both differentiation (as in Kumar *et al.*⁸) and time division (as in our procedure) produce identical coefficients \mathbf{Q} . Actually, the above expression can be obtained also from our procedure if two relevant differential forms of the conditional probability of the ions [Eq. (6) differentiated by time and first of Eq. (8) both of Ref. 1] are compared term by term.

A final comment refers to the case of small fields where the number of independent Q components may be reduced to two.⁶ In this case, since $Q_{zxx} = Q_{xzx} = Q_{xxz}$, and similarly for y in the position of x , Eq. (4) show that Q_{\parallel} and Q_{\perp} can be associated to the independent components of \mathbf{Q} . As the field strength diminishes, the two remaining components approach each other and gradually vanish since odd order transport coefficients are excluded at equilibrium.

The author wishes to thank Professor L. A. Viehland for helpful discussions as well as his colleagues for providing their manuscript prior to publication. This work was supported by a grant from the Ministry of Industry and Development of Greece, No. 95EA/364.

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