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Non-hydrodynamic Contributions to the End Effects in Time of Flight Swarm Experiments

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Abstract

The hydrodynamic part of the distribution function of a swarm is separated from its non-hydrodynamic part using a projection operator, leading to an explicit expression for the time-dependent transport coefficients. These are then related to a time of flight experiment. The contribution from non-hydrodynamic effects to the measured drift velocity is shown to be a power series in $1/d$, where d is the drift length. A calculation based on an exactly soluble Fokker–Planck model shows that the correction to mobility measurements of lithium ions in helium due to non-hydrodynamic effects is of the same order of magnitude as those observed experimentally.

1. Introduction

Investigation of the approach of swarms to the hydrodynamic regime is important for confirming that transport data derived from experiments do in fact correspond to theoretical calculations based on the hydrodynamic assumption. The non-hydrodynamic regime has been explored numerically [by Monte Carlo methods (see e.g. McIntosh 1974) or by numerical solutions to the Boltzmann equation (see e.g. Skullerud 1974, 1977)], and also by taking a continuity equation with time-dependent transport coefficients (see e.g. Tagashira *et al.* 1977). A recent review of this area has been given by Kumar (1984).

This work continues the time-dependent transport coefficient approach. The starting point for this is the work by Kumar (1981), where the connection between non-hydrodynamic behaviour and the spectral properties of the operator $\mathscr{M} \equiv \boldsymbol{a}\,.\,\partial_c + \mathscr{J}$ was established. Here $\boldsymbol{a}$ is the acceleration of the ion due to the electric field, and $\mathscr{J}$ is the collision operator. At large times, the evolution of the swarm will only depend on the smallest eigenvalue of $\mathscr{M}$. This allows us to separate the hydrodynamic terms from the non-hydrodynamic terms by using a projection onto the eigenspace of $\mathscr{M}$ associated with the smallest eigenvalue. This was tried by Kondo (1987) and leads to a distinction, possibly unnatural, between effects due to the relaxation of the initial velocity distribution and those due to the relaxation of the initial spatial distribution.

Instead of working with $\mathscr{M}$, which contains information only about the velocity distribution, we work with the operator $\boldsymbol{c}\,.\,\nabla + \mathscr{M}$, which brings in the effects of spatial gradient. Since $\mathscr{M}$ is independent of $\boldsymbol{r}$, the gradient symbol can be eliminated

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by taking the Fourier transform. Thus, we are lead to using a projection onto the eigenspace of $\mathrm{i}\,\boldsymbol{c}\,.\,\boldsymbol{k}+\mathscr{M}$, corresponding to the lowest eigenvalue of $\mathscr{M}$. This leads to a particularly simple form of the time-dependent transport coefficient.

2. Time-dependent Transport Coefficients

Definitions

The hydrodynamic regime is characterised by a continuity equation for the particle density function $n(\boldsymbol{r}, t)$, with constant coefficients $\omega^{(l)}$,

$$\partial_t n - \sum_{l=0}^{\infty} \omega^{(l)} \odot (-\nabla)^l n = 0 . \tag{1}$$

Here the $\omega^{(l)}$ are rank l tensor coefficients and $\odot$ denotes an l-fold inner product.

The time-dependent transport coefficients are defined by a generalisation of equation (1):

$$\sum_{l=0}^{\infty} \omega^{(l)}(t) \odot (-\nabla)^l n = \partial_t n .$$

Taking the Fourier transform of this equation, and dividing by $\tilde{n}$, the Fourier transform of n, one gets

$$\sum_{l=0}^{\infty} \omega^{(l)}(t) \odot (-\mathrm{i}\,\boldsymbol{k})^l = \partial_t \ln \tilde{n}(\boldsymbol{k}, t) .$$

The individual transport coefficients can be extracted from this power series by taking the lth derivative of this at the origin of $\boldsymbol{k}$-space. Defining the operation

$$\boldsymbol{\Omega}^{(l)} = \lim_{k \to 0} \frac{(\mathrm{i}\,\partial_{\boldsymbol{k}})^l}{l!} ,$$

the transport coefficients can be expressed as

$$\omega^{(l)}(t) = \boldsymbol{\Omega}^{(l)}\, \partial_t \ln \tilde{n}(\boldsymbol{k}, t) . \tag{2}$$

In Kumar *et al.* (1980), these coefficients are identified with the time derivatives of certain correlation functions. In particular, $\omega^{(0)}(t)$ is the logarithmic time derivative of the number of charged particles, and $\omega^{(1)}(t)$ is the velocity of the centroid of the swarm.

Projection Operator

We assume that the operator $\mathrm{i}\,\boldsymbol{c}\,.\,\boldsymbol{k}+\mathscr{M}$ and its adjoint admit a complete set of biorthogonal eigenfunctions

$$(\mathrm{i}\,\boldsymbol{c}\,.\,\boldsymbol{k}+\mathscr{M})\,\Psi_\alpha(\boldsymbol{c}, \boldsymbol{k}) = -\omega_\alpha(\mathrm{i}\,\boldsymbol{k})\,\Psi_\alpha(\boldsymbol{c}, \boldsymbol{k}) , \tag{3a}$$

$$(\mathrm{i}\,\boldsymbol{c}\,.\,\boldsymbol{k}+\tilde{\mathscr{M}})\,\Phi_\alpha(\boldsymbol{c}, \boldsymbol{k}) = -\omega_\alpha(\mathrm{i}\,\boldsymbol{k})\,\Phi_\alpha(\boldsymbol{c}, \boldsymbol{k}) , \tag{3b}$$

$$\int \Psi_\alpha(\boldsymbol{c}, \boldsymbol{k})\,\Phi_\beta(\boldsymbol{c}, \boldsymbol{k})\,\mathrm{d}\boldsymbol{c} = \delta_{\alpha\beta} . \tag{3c}$$

The eigenfunctions and eigenvalues of $\mathscr{M}$ and $\tilde{\mathscr{M}}$, $\Psi_\alpha^{(0)}(c) = \Psi_\alpha(c,0)$, $\Phi_\alpha^{(0)}(c) = \Phi_\alpha(c,0)$ and $\omega_\alpha^{(0)} = \omega_\alpha(0)$, will also have these properties as a special case. Furthermore, we suppose that there is an eigenvalue $-\omega_0^{(0)}$ such that $\omega_0^{(0)} = \mathrm{Re}(\omega_0^{(0)}) > \mathrm{Re}(\omega_\alpha^{(0)})$ for any other α. Then, we define a projection operator P_k, which projects out the hydrodynamic (long time) part of the Fourier transform of a phase space distribution $\tilde{f}(c, k, t)$ by

$$P_k \tilde{f}(c, k, t) = \Psi_0(c, k) \int \Phi_0(c', k) \tilde{f}(c', k, t)\, \mathrm{d}c' . \tag{4}$$

The k-space density function can now be split into a hydrodynamic part

$$\tilde{n}_0(k, t) = \int P_k \tilde{f}(c, k, t)\, \mathrm{d}c , \tag{5}$$

and a non-hydrodynamic part

$$x(k, t) = \frac{\tilde{n}(k, t) - \tilde{n}_0(k, t)}{\tilde{n}_0(k, t)} . \tag{6}$$

The Taylor series coefficients of $x(k, t)$ are denoted by

$$x^{(l)}(t) = \boldsymbol{\Omega}^{(l)}\, x(k, t) . \tag{7}$$

Substituting $\tilde{n} = \tilde{n}_0(1+x)$ into (2), the time-dependent transport coefficients become

$$\begin{aligned} \omega^{(l)}(t) &= \boldsymbol{\Omega}^{(l)}\, \partial_t \{\ln \tilde{n}_0 + \ln(1+x)\} \\ &= \boldsymbol{\Omega}^{(l)} \{ \partial_t \ln \tilde{n}_0 + \partial_t x(1 - x + x^2 - \ldots)\} . \end{aligned} \tag{8}$$

Formal Solution of the Boltzmann Equation

The Boltzmann equation describing the evolution of a swarm of particles from an initial distribution $f_i(c, r)$ is

$$(\partial_t + c \, . \, \nabla + \mathscr{M}) f(c, r, t) = \delta(t) f_i(c, r) . \tag{9}$$

The Fourier transform of this is

$$(\partial_t + \mathrm{i}\, c \, . \, k + \mathscr{M}) \tilde{f}(c, k, t) = \delta(t) \tilde{f}_i(c, k) , \tag{10}$$

and has the formal solution

$$\tilde{f}(c, k, t) = \Theta(t) \exp\{ -(\mathrm{i}\, c \, . \, k + \mathscr{M}) t \} \tilde{f}_i(c, k) , \tag{11}$$

where $\Theta(t)$ is the Heaviside step function; $\Theta(t<0) = 0$ and $\Theta(t \geqslant 0) = 1$.

Equation (11) can be expressed in terms of the complete basis defined by equations (3) as

$$\tilde{f}(c, k, t) = \Theta(t) \sum_\alpha \exp\{ \omega_\alpha(\mathrm{i}\, k) t \}\; \Psi_\alpha(c, k) \int \Phi_\alpha(c', k) \tilde{f}_i(c', k)\, \mathrm{d}c' .$$

familiar from quantum mechanics:

$$\left\{\partial_g^2 - g^2 + 3 + \left(- \frac{2\omega_a(\boldsymbol{k})}{\nu_1} - \frac{2k^2\nu_2}{\nu_1^3} - \frac{2\mathrm{i}\,\boldsymbol{a}\,.\,\boldsymbol{k}}{\nu_1^3} - 6 + \frac{2\nu_0}{\nu_1}\right)\right\} \Xi_a(g) = 0\,. \quad (20)$$

This equation is separable in the cartesian coordinates g_1, g_2, g_3, and has solutions in terms of Hermite polynomials (Abramowitz and Stegun 1965, 22.6.20):

$$\Xi_a(g) = \mathrm{e}^{-g^2/2}\, H_{a_1}(g_1)\, H_{a_2}(g_2)\, H_{a_3}(g_3)\,, \quad (21)$$

$$\omega_a(\mathrm{i}\,\boldsymbol{k}) = -\nu_1(3+\alpha_1+\alpha_2+\alpha_3) + \nu_0 - \frac{\mathrm{i}\,\boldsymbol{a}\,.\,\boldsymbol{k}}{\nu_1} - \frac{\nu_2}{\nu_1^2}\,k^2\,. \quad (22)$$

These solutions can also be expressed in spherical coordinates by means of Burnett functions (Kumar 1980). The non-reactive case is specified by setting $\omega_0^{(0)} = \nu_0 - 3\nu_1 = 0$, which provides an expression for ν_0.

To use this model to calculate $\boldsymbol{x}^{(1)}(0)$, we need to make some assumptions about the initial phase space distribution. The swarm is collected in a potential well formed by the electric shutter, before being released into the drift tube. For calculational simplicity, we assume that the initial velocity distribution is a gaussian. Thus, we have

$$\tilde{f}_i(c, \boldsymbol{k}) = (\sigma/\pi)^{\frac{3}{2}} \exp(-\sigma c^2)\,. \quad (23)$$

Substituting this into (5), we get

$$\tilde{n}_0(\boldsymbol{k},0) = \exp\left\{+\frac{\nu_2\,k^2}{2\nu_1^3}\left(3 - \frac{\nu_1}{2\nu_2\,\sigma}\right) + \frac{\mathrm{i}\,\boldsymbol{a}\,.\,\boldsymbol{k}}{\nu_1^2}\right\}, \quad (24)$$

$$\boldsymbol{x}^{(1)}(0) = \boldsymbol{\Omega}^{(1)}\left(\frac{1-\tilde{n}_0(\boldsymbol{k},0)}{\tilde{n}_0(\boldsymbol{k},0)}\right) = +\frac{\boldsymbol{a}}{\nu_1^2} = +\frac{\boldsymbol{v}_{\mathrm{dr}}}{\nu_1}\,. \quad (25)$$

England and Elford (1987) have measured the mobility of Li^+ ions in helium at various distances, and fitted the experimental data to equation (14), truncating the series at α_2. Their fitted values for α_1 ranged from 0·5 to 2 mm, as a function of electric field strength. It is of interest to compare this value of α_1, which is the combined error due to all end effects, with the numerical value for $\boldsymbol{x}^{(1)}(0)$ obtained by substituting the experimental parameters into equation (25). Even though this Fokker–Planck model is not really applicable to lithium in helium, where the ions and neutrals have nearly the same mass, the result should indicate whether non-hydrodynamic effects are a significant proportion of the total end effect.

The experiment was performed with a neutral gas pressure of 50 Pa and a temperature of 300 K. Using the ideal gas equation of state, this corresponds to a number density of 10^{22} particles per m^3. The measured drift velocity was $4\times10^3\ \mathrm{m\,s^{-1}}$. From Viehland (1982), the cross section at this kinetic energy ($\frac{1}{2}m_{\mathrm{Li}}\,v_{\mathrm{dr}}^2$) is about $20a_0^2 = 5\times10^{-20}\ \mathrm{m}^2$, where a_0 is the Bohr radius. This figure is very similar to $4\pi a_0^2$ obtained by considering the collision of two rigid spheres of radius a_0. From this, we can conclude that the collision frequency will be of the order of $500\,v_{\mathrm{dr}}$, or $\nu_1 \approx 870\,v_{\mathrm{dr}}$. Substituting this into equation (25), the value of $\boldsymbol{x}^{(1)}(0)$ will be of the order of 1 mm.

While experimental corrections must include other end effects, as discussed by England and Elford (1987), we can conclude that non-hydrodynamic effects are a significant contribution to experimental end effects.

5. Conclusions

In this paper, I have calculated the form of the error due to non-hydrodynamic effects in mobility measurements. This error has the same dependence on drift length as the combined end effects observed by England and Elford (1987). A calculation based on a very simple model indicates that the errors contribute significantly to the experimentally observed end effects. Using a more sophisticated model, the contribution of non-hydrodynamic effects can be calculated more accurately. It is possible that experimental data on end effects can become a source of information constraining model calculations of potentials, and of the ion production. However, to extract out that part of the end effect due to non-hydrodynamic phenomena would require a detailed study of the other end effects, most notably the effect that absorption of ions at boundaries have on the swarm distribution, and the problem of fields leaking into the drift tube.

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