

## Analytically solvable model in fractional kinetic theory

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In this article we give a general prescription for incorporating memory effects in phase space kinetic equation, and consider in particular the generalized “fractional” relaxation time model equation. We solve this for small-signal charge carriers undergoing scattering, trapping, and detrapping in a time-of-flight experimental arrangement in two ways: (i) approximately via the Chapman-Enskog scheme for the weak gradient, hydrodynamic regime, from which the fractional form of Fick’s law and diffusion equation follow; and (ii) exactly, without any limitations on gradients. The latter yields complete and exact expressions in terms of generalized Mittag-Leffler functions for experimentally observable quantities. These expressions enable us to examine in detail the transition from the nonhydrodynamic stage to the hydrodynamic regime, and thereby establish the limits of validity of Fick’s law and the corresponding fractional diffusion equation.

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### I. INTRODUCTION

In recent times there has been much interest in investigating anomalous transport properties exhibited by polymers, amorphous semiconductors, etc., through fractional forms of Fick’s law and of the diffusion equation [1–3]. In these systems scattering is accompanied by trapping and detrapping in localized states, leading to memory effects and long-lived large gradients [4]. On the other hand, it is known that Fick’s law is strictly valid for only small-gradient, hydrodynamic conditions, and that deviations from it are manifest in the context of small-signal charge carriers [5–7]. In treating such systems it is pertinent to ask under what conditions a hydrodynamic description in terms of a diffusion equation is valid when memory effects are involved. We devote the present article to this task and, as in an earlier theoretical investigation of classical transport of ions in a gaseous medium [5], we solve a model problem exactly to provide the benchmark.

At the outset, we emphasize that the most general way of tackling transport problems involving low density, small-signal charge carriers, in either a gaseous [5–7] or condensed matter medium [8], is not *macroscopically* through the diffusion equation, but rather *microscopically* by solving the Boltzmann kinetic equation

$$(\partial_t + \mathbf{v} \cdot \nabla + \mathbf{a} \cdot \partial_{\mathbf{v}})f = C(f) \quad (1)$$

for the particle phase space distribution function  $f(\mathbf{r}, \mathbf{v}, t)$ , from which quantities of physical interest follow as velocity “moments,” e.g., the number density

$$n(\mathbf{r}, t) = \int d\mathbf{v} f(\mathbf{r}, \mathbf{v}, t) \quad (2)$$

and the particle current

$$\mathbf{\Gamma} = \int d\mathbf{v} f(\mathbf{r}, \mathbf{v}, t) \mathbf{v}. \quad (3)$$

In Eq. (1),  $\mathbf{a}$  is the external force per unit mass, and  $C(f)$  denotes the rate of change of  $f$  due to interaction of the particles with the background medium. Ideally, the solution of Eq. (1) should be carried out to the highest degree of accuracy possible, preferably without making any assumptions concerning the magnitude of the respective terms, and otherwise nonperturbatively. Of course, in some circumstances assumptions concerning the nature of the space-time dependence of  $f$  may be possible, and an approximate solution of Eq. (1) can be obtained with relative ease. For example, if (and only if) space and time variations as well as the field  $\mathbf{a}$  are small, Eq. (1) can be solved by the Chapman-Enskog perturbation procedure, as explained in textbooks [9] and in Sec. II C below. This leads to Fick’s law of diffusion at the second level of approximation and thence to the diffusion equation, which one then solves with appropriate boundary and initial conditions for  $n(\mathbf{r}, t)$ . The devolution of the space-time dependence of  $f$  onto macroscopic quantities, such as density, is characteristic of “hydrodynamic” conditions in gases [6,7], and is also the regime of validity of the diffusion equation for hot carriers in amorphous solids.

If, on the other hand, the spatial variations are not weak, then one may have a “nonhydrodynamic” regime, where it makes no sense to use the diffusion equation. In a time-of-flight experiment for a pulse of electrons or ions in a gas, for example, one has both nonhydrodynamic and hydrodynamic regimes, close to and far downstream from the source, respectively [5,7,10]. Significantly, however, the nonhydrodynamic regime is relatively short lived in this case, lasting only a few collision times, and a hydrodynamic regime is quickly established. Similar remarks apply to the classic Haynes-Shockley experiment for crystalline semiconductors [11], where the charge carriers interact with phonons rather than gas molecules or atoms. Such experiments can be satis-

factorily analyzed using the diffusion equation, since hydrodynamic conditions prevail for the predominant part of the transit of the pulse from the source to the detector, a condition which is achieved in practice by increasing either the length of the drift region or the gas pressure [10,12]. For other types of experimental arrangements, however, the elimination of nonhydrodynamic effects may not be possible and the diffusion equation may not be even qualitatively correct. The classic Franck-Hertz experiment is just one example of an inherently nonhydrodynamic system [13]. For amorphous media, where all indications are that large gradients persist to long times [1], it would seem that a nonhydrodynamic description is necessary, and that a full kinetic theory analysis via Eq. (1) is unavoidable. This is the scope of the present article.

So to the outline of this paper: In Sec. II, a kinetic equation of the form of Eq. (1) is solved for a relaxation time model [14] with memory, under initial and boundary conditions appropriate to a time-of-flight experiment. This is done in two ways: first, approximately for weak gradients, from which follow the fractional forms of Fick's law and diffusion equation, and second, analytically and exactly, without any limitations on gradients. In Sec. III exact expressions are obtained for the observables (namely, for the first two spatial moments of the density distribution) in terms of generalized Mittag-Leffler functions [15], while in Sec. IV the limits of validity of the diffusion equation are established. We summarize our results in Sec. V and present in the Appendix a detailed derivation of one of our basic expressions.

## II. SOLUTIONS OF THE KINETIC EQUATION

### A. General comments

First a note of warning concerning terminology: In statistical mechanics the terms “kinetic theory” and “kinetic equations” strictly apply to density distributions in *phase space* ( $\mathbf{r}, \mathbf{v}$ ), whereas the field of “fractional kinetics” focuses mostly (but not exclusively) on density distributions in *configuration space*. The “Fokker-Planck” equation, for example, has quite a different connotation in the respective literatures. At all times, it should be understood that irrespective of terminology and notation, our main task is to connect the two areas, by starting with a phase space kinetic equation, and proceeding, through approximations which are to be quantified, to the familiar descriptions in configuration space.

A few general remarks are also in order about the strategy to be followed before we embark on our task.

(i) The first step is to adapt Eq. (1) to include both scattering and trapping, generalizing the prescription of Scher and Montroll [16] to velocity space, in a manner similar to that proposed by Barkai and Silbey [17], that is, making the transformation

$$C(f) \Rightarrow \phi(t) * C(f(t)) \equiv \int_0^t dt' \phi(t-t') C(f(t')), \quad (4)$$

where  $*$  denotes a convolution. In this work as elsewhere [2], we incorporate trapping and memory effects through a phe-

nomenological “relaxation function” of the form

$$\phi(t) = t_0^{-1} (t_0/t)^\gamma, \quad (5)$$

where  $t_0$  denotes some representative time scale for trapping, and  $\gamma$  is a fractional exponent, taken to lie in the range  $0 < \gamma < 1$ . As we shall see, this prescription in phase space ultimately leads to the familiar form of the fractional diffusion equation in configuration space.

(ii) Convolutions with  $\phi(t)$  can be written as fractional derivatives when it is convenient to do so. Since by definition [1]

$${}_0\partial_t^{\gamma-1} f(t) = \frac{1}{\Gamma(1-\gamma)} \int_0^t dt' (t-t')^{-\gamma} f(t'), \quad (6)$$

the *fundamental fractional kinetic equation* is therefore

$$(\partial_t + \mathbf{v} \cdot \nabla + \mathbf{a} \cdot \partial_{\mathbf{v}}) f = \phi(t) * C(f) = {}_0\partial_t^{\gamma-1} C_\gamma(f(t)), \quad (7)$$

where  $C_\gamma(f) \equiv t_0^{\gamma-1} \Gamma(1-\gamma) C(f)$ .

(iii) An exact, analytic solution is found for the kinetic equation (7), by taking a relaxation time scattering operator, and applying boundary and initial conditions appropriate to the classic Haynes-Shockley or time-of-flight experiment [11].

(iv) The focus of the calculations is ultimately on the density and particle flux, Eqs. (2) and (3), respectively. They are related by the equation of continuity

$$\partial_t n + \nabla \cdot \Gamma = 0, \quad (8)$$

which is exact, and obtained by integrating Eq. (1) over all velocities and using the fact that for *any* particle-conserving collision operator  $\int d\mathbf{v} C(f) \equiv 0$  holds.

(v) In this way we obtain an exact expression for the density and subsequently for its first two spatial moments, the quantities effectively measured in experiment.

(vi) Comparison is then made with the corresponding expressions obtained from the solution of the diffusion equation, whose limits of validity are thereby established.

### B. The fractional Bhatnagar-Gross-Krook kinetic equation

In its simplest form the Bhatnagar-Gross-Krook (BGK) [14] relaxation time collision model is

$$C_{\text{BGK}}(f) = -\nu [f - n w(\alpha, v)], \quad (9)$$

where  $\nu$  denotes a representative, constant collision frequency,  $\alpha^2 = m/kT$ , and

$$w(\alpha, v) = (\alpha^2/2\pi)^{3/2} \exp\left(-\frac{1}{2}\alpha^2 v^2\right) \quad (10)$$

is a Maxwellian distribution at the temperature  $T$  of the background medium. Although Eq. (9) can be readily justified for resonant charge exchange collisions of ions in their parent gas [7], the model is more widely used in both gaseous and condensed matter physics in a semiquantitative way, in order to simplify the mathematics and thereby elucidate the underlying physics. This is also the spirit in which the present article is written.

The explicit form of the BGK kinetic equation with memory is thus

$$\begin{aligned} & (\partial_t + \mathbf{v} \cdot \nabla + \mathbf{a} \cdot \partial_{\mathbf{v}})f(\mathbf{r}, \mathbf{v}, t) \\ &= -\nu \phi(t) * [f(\mathbf{r}, \mathbf{v}, t) - w(\alpha, \nu)n(\mathbf{r}, t)] \\ &= -\nu_\gamma {}_0\partial_t^{\gamma-1} [f(\mathbf{r}, \mathbf{v}, t) - w(\alpha, \nu)n(\mathbf{r}, t)], \end{aligned} \quad (11)$$

where

$$\nu_\gamma = \nu t_0^{\gamma-1} \Gamma(1-\gamma). \quad (12)$$

In what follows both approximate and exact solutions of Eq. (11) will be obtained.

### C. Weak gradient solutions and the diffusion equation

#### 1. Chapman-Enskog procedure

In the Chapman-Enskog solution procedure, the entire left-hand side of Eq. (11) is regarded as being small, and an iterative scheme of successive approximations to  $f(\mathbf{r}, \mathbf{v}, t)$  is established, starting with the Maxwellian  $f^{(1)} = w(\alpha, \nu)n(\mathbf{r}, t)$  as the first approximation. This is substituted in the left-hand side of Eq. (11) to obtain the equation for the second approximation  $f^{(2)}$ , and so on [9]. Without going into the details, it can be shown that at the level of the second Chapman-Enskog approximation the particle flux is given by

$$\phi * \Gamma = n\mathbf{v}_d - D \nabla n, \quad (13)$$

where

$$\mathbf{v}_d \equiv \mathbf{a}/\nu \text{ and } D \equiv \frac{kT}{m\nu} \quad (14)$$

denote the drift velocity and the diffusion coefficient, respectively. Together with the equation of continuity Eq. (8), this yields the diffusion equation

$$\phi * \partial_t n + \mathbf{v}_d \cdot \nabla n - D \nabla^2 n = 0 \quad (15a)$$

or, equivalently, using Eq. (6),

$${}_0\partial_t^\gamma n + \mathbf{v}_{d,\gamma} \cdot \nabla n - D_\gamma \nabla^2 n = 0, \quad (15b)$$

where

$$\mathbf{v}_{d,\gamma} \equiv \mathbf{a}/\nu_\gamma \text{ and } D_\gamma \equiv \frac{kT}{m\nu_\gamma}. \quad (16)$$

Equation (15b) is the fractional diffusion equation, which appears frequently in the modern literature [1], and Eq. (13) is just Fick's law of diffusion.

#### 2. Weak gradient, arbitrary field

We now relax any assumption about the magnitude of the field, and consider only the first two terms on the left-hand side of Eq. (11) to be small. Again an iterative solution is followed, generalizing the procedure established for ions and electrons in gases [7]. To first order in  $\nabla n$  it is found that Fick's law generalizes to

$$\phi * \phi * \phi * \Gamma = \phi * \phi * n\mathbf{v}_d - [ID\phi * \phi * + \mathbf{v}_d \mathbf{v}_d / \nu] \cdot \nabla n, \quad (17)$$

where  $I$  is the unit tensor. The generalized diffusion equation then follows with Eq. (8):

$$\begin{aligned} & \phi * \phi * \phi * \partial_t n + \phi * \phi * \mathbf{v}_d \cdot \nabla n - [ID\phi * \phi * \\ & + \mathbf{v}_d \mathbf{v}_d / \nu] : \nabla \nabla n = 0, \end{aligned} \quad (18a)$$

or, equivalently, in fractional derivative form with Eq. (6):

$${}_0\partial_t^\gamma n + \mathbf{v}_{d,\gamma} \cdot \nabla n - \left( ID_\gamma + \frac{\mathbf{v}_{d,\gamma} \mathbf{v}_{d,\gamma}}{\nu_\gamma} {}_0\partial_t^{2(1-\gamma)} \right) : \nabla \nabla n = 0. \quad (18b)$$

We note that the tensor nature of diffusion has long been recognized in gaseous and semiconductor physics [6,7,17], and that Eqs. (18) merely extend this to the fractional domain, albeit for the particular case of the BGK collision model. In fact, we could consider even more general tensorial collision operators, by extending well-established methods in gaseous electronics [7], but this is beyond the scope of the present paper.

### 3. Solution of diffusion equation

The solution of the diffusion equation corresponding to the time-of-flight experiment in an infinite medium can be readily obtained through Laplace and Fourier transformations in time and in configuration space, respectively. For an initial sharp pulse released at the origin, i.e., for

$$n(\mathbf{r}, t=0) = n_0 \delta(\mathbf{r}), \quad (19)$$

the transformed density is found to be

$$\begin{aligned} \hat{n}_p^{(\text{DE})}(\mathbf{k}) &\equiv \int_0^\infty dt \int_{-\infty}^\infty d\mathbf{r} n(\mathbf{r}, t) \exp\{-pt - i\mathbf{k} \cdot \mathbf{r}\} \\ &= \frac{n_0}{p + i\mathbf{k} \cdot \mathbf{v}_{d,\gamma}/p^{1-\gamma} + \mathbf{k}\mathbf{k} : [ID_\gamma + \mathbf{v}_{d,\gamma} \mathbf{v}_{d,\gamma} / \nu_\gamma p^{2(1-\gamma)}]}, \end{aligned} \quad (20)$$

where the superscript ‘‘DE’’ has been added for future reference to indicate that this is the solution of the diffusion equation. We now obtained the corresponding expression directly from the kinetic equation (11), without relying upon the approximations associated with the diffusion equation.

### D. Exact solution of the kinetic equation

The first step in the exact solution of Eq. (11) is to take the Laplace transform in time, giving

$$[p + \mathbf{v} \cdot \nabla + \mathbf{a} \cdot \partial_{\mathbf{v}}] \bar{f}_p = \bar{\phi}_p C(\bar{f}_p) + f(\mathbf{r}, \mathbf{v}, t=0),$$

where  $\bar{f}_p = \int_0^\infty e^{-pt} f(\mathbf{r}, \mathbf{v}, t) dt$ . Assuming that a total of  $n_0$  particles of mass  $m$  are released from the origin of coordinates at time  $t=0$ , with a Maxwellian velocity distribution at an arbitrary temperature  $T'$ , the initial condition may be written as

$$f(\mathbf{r}, \mathbf{v}, t=0) = n_0 w(\alpha', c) \delta(\mathbf{r}), \quad (21)$$

with  $(\alpha')^2 = m/kT'$ . [Note that this is consistent with the initial condition Eq. (19) used in solving the diffusion equation, as an integration of Eq. (21) over all velocities  $\mathbf{v}$  shows.] The solution proceeds further through Fourier transformation in *phase space*, with boundary conditions  $f(\mathbf{r}, \mathbf{v}, t) \rightarrow 0$  as  $\mathbf{r} \rightarrow \infty$ ,  $\mathbf{v} \rightarrow \infty$ ; thus the transformed distribution function is found to be:

$$\begin{aligned} \tilde{f}_p(\mathbf{k}, \mathbf{s}) &= \int_0^t dt \int_{-\infty}^{\infty} d\mathbf{v} \int_{-\infty}^{\infty} d\mathbf{r} f(\mathbf{r}, \mathbf{v}, t) \exp\{-[i(\mathbf{k} \cdot \mathbf{r} + \mathbf{s} \cdot \mathbf{v}) + pt]\} \\ &= -\exp\left\{\frac{is_{\parallel}}{k} \left(\frac{1}{2}s_{\parallel}a_{\parallel} + \mathbf{s}_{\perp} \cdot \mathbf{a}_{\perp} - \Omega\right)\right\} \int_{-\infty}^{s_{\parallel}} d\sigma \frac{1}{k} \\ &\quad \times \left[ \left\{ \nu \bar{\phi}_p \hat{n}_p(\mathbf{k}) \exp\left(-\frac{\sigma^2 + s_{\perp}^2}{2\alpha'^2}\right) + f_0(\mathbf{k}, \sigma, \mathbf{s}_{\perp}) \right\} \right. \\ &\quad \left. \times \exp\left(-\frac{i\sigma\left(\frac{1}{2}\sigma a_{\parallel} + \mathbf{s}_{\perp} \cdot \mathbf{a}_{\perp} - \Omega\right)}{k}\right) \right], \quad (22) \end{aligned}$$

where the Fourier transform of the initial condition (21) is

$$\begin{aligned} f_0(\mathbf{k}, \mathbf{s}) &= \int d\mathbf{r} \int d\mathbf{v} f(\mathbf{r}, \mathbf{v}, t=0) \exp\{-i(\mathbf{k} \cdot \mathbf{r} + \mathbf{s} \cdot \mathbf{v})\} \\ &= n_0 \exp\left\{\frac{-s^2}{2(\alpha')^2}\right\}, \quad (23) \end{aligned}$$

$$\begin{aligned} \mathbf{s}_{\parallel} &= \frac{(\mathbf{s} \cdot \mathbf{k})\mathbf{k}}{k^2}, \quad \mathbf{s}_{\perp} = \mathbf{s} - \mathbf{s}_{\parallel}, \\ \mathbf{a}_{\parallel} &= \frac{(\mathbf{a} \cdot \mathbf{k})\mathbf{k}}{k^2}, \quad \mathbf{a}_{\perp} = \mathbf{a} - \mathbf{a}_{\parallel}, \quad (24) \end{aligned}$$

and

$$\Omega = i(p + \nu \bar{\phi}_p).$$

It is important to note that the transformed particle density and the initial distribution function are related by

$$\hat{n}_p(\mathbf{k}) = \int dt \int d\mathbf{r} n(\mathbf{r}, t) \exp\{-pt - i\mathbf{k} \cdot \mathbf{r}\} = \tilde{f}_p(\mathbf{k}, \mathbf{s} = \mathbf{0}). \quad (25)$$

Equations (22) and (25) together furnish the transformed number density (see the Appendix for details):

$$\hat{n}_p(\mathbf{k}) = n_0 \frac{(\beta'/i\sqrt{2k})Z(\zeta')}{1 + \nu \bar{\phi}_p(i\beta'/\sqrt{2k})Z(\zeta)}, \quad (26)$$

where  $Z(\zeta)$  is the plasma dispersion function [18], defined by

$$Z(\zeta) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} dx \frac{e^{-x^2}}{x - \zeta} \quad (27a)$$

for  $\text{Im}(\zeta) \geq 0$ , and its analytic continuation for  $\text{Im}(\zeta) < 0$ , while

$$\beta^{-2} \equiv \alpha^{-2} + \frac{i\mathbf{a} \cdot \mathbf{k}}{k^2}$$

and

$$\zeta \equiv \frac{\Omega\beta}{\sqrt{2k}}, \quad (27b)$$

with  $\beta'$  and  $\zeta'$  being similarly defined in terms of  $\alpha'$ . Equation (26) could now be substituted back into Eq. (22) to obtain the complete and exact expression for the transformed phase space distribution function, if desired. We can therefore say that the problem has been solved exactly, to the extent that Eqs. (22) and (26) effectively contain all the information about the (transformed) phase space distribution function and number density, respectively.

Notice that the exact expression Eq. (26) for the transformed density appears to be markedly different from Eq. (20), obtained from the diffusion equation: reconciliation is obviously required, and this will be dealt with separately in Sec. IV.

If the full, explicit expression for  $n(\mathbf{r}, t)$  were desired, it would be necessary to carry out the Fourier-Laplace inversion of Eq. (26), a difficult task. Instead, we shall concentrate on finding  $n(\mathbf{r}, t)$  in various limits, and also upon obtaining its spatial moments. In this context it is useful to note that the inversion of the Laplace transform only leads to the Fourier-transformed number density,

$$\tilde{n}(\mathbf{k}, t) \equiv \int_{-\infty}^{\infty} d\mathbf{r} e^{-i\mathbf{k} \cdot \mathbf{r}} n(\mathbf{r}, t) = \frac{1}{2\pi i} \int_C dp e^{pt} \hat{n}_p(\mathbf{k}), \quad (28)$$

which in turn provides all the information necessary to compare with experiment, as explained below. The contour  $C$  in the familiar Bromwich integral lies to the right of the singularities of  $\hat{n}_p(\mathbf{k})$ , which from Eq. (26) may be seen to include the zero  $p_k$  of

$$1 + \nu \bar{\phi}_p \frac{i\beta}{\sqrt{2k}} Z(\zeta) = 0, \quad (29)$$

and this dispersion relation plays a central role in determining transport properties.

### E. Asymptotic expressions

If  $k$  is sufficiently small, then from Eq. (27)

$$|\zeta| \equiv \left| \frac{\Omega\beta}{\sqrt{2k}} \right| \gg 1 \quad (30)$$

and the asymptotic representation of the plasma dispersion function is [18]

$$Z \approx -\frac{1}{\zeta} \left( 1 + \frac{1}{2}\zeta^{-2} + \frac{3}{4}\zeta^{-4} + \dots \right), \quad (31)$$

we can show that the left-hand side of Eq. (29) becomes

$$1 + \nu \bar{\phi}_p \frac{i\beta}{\sqrt{2k}} Z(\zeta) \approx \frac{ip}{\Omega} \left\{ 1 - \frac{\nu \bar{\phi}_p}{p\Omega^2} \left( \frac{k^2}{\alpha^2} + i\mathbf{a} \cdot \mathbf{k} - \frac{3(\mathbf{a} \cdot \mathbf{k})^2}{\Omega^2} \right) \right\} + O(k^3). \quad (32)$$

Hence by Eq. (26)

$$\begin{aligned} \frac{\hat{n}_p(\mathbf{k})}{n_0} &= \frac{(i\beta'/\sqrt{2k})Z(\zeta')}{1 + \nu \bar{\phi}_p (i\beta'/\sqrt{2k})Z(\zeta)} \\ &\approx \frac{1}{p} \left\{ 1 + \frac{i\mathbf{a} \cdot \mathbf{k}}{\Omega^2} \left[ 1 + \frac{\nu \bar{\phi}_p}{p} \right] + \frac{k^2}{\Omega^2} \left[ \frac{\nu \bar{\phi}_p}{\alpha^2 p} + \frac{1}{(\alpha')^2} \right] \right. \\ &\quad \left. - \frac{(\mathbf{a} \cdot \mathbf{k})^2}{\Omega^4} \left[ \frac{(\nu \bar{\phi}_p)^2}{p^2} + \frac{4\nu \bar{\phi}_p}{p} + 3 \right] \right\} + O(k^3), \quad (33) \end{aligned}$$

we obtain immediately and *exactly*

$$\frac{i}{n_0} \left\{ \frac{\partial \hat{n}_p(\mathbf{k})}{\partial \mathbf{k}} \right\}_{\mathbf{k}=\mathbf{0}} = \frac{\mathbf{a}}{p^2(p + \nu \bar{\phi}_p)} \quad (34)$$

and

$$\begin{aligned} -\frac{1}{n_0} \left\{ \frac{\partial^2 \hat{n}_p(\mathbf{k})}{\partial \mathbf{k} \partial \mathbf{k}} \right\}_{\mathbf{k}=\mathbf{0}} &= \frac{2\mathbf{1}}{p(p + \nu \bar{\phi}_p)^2} \left[ \frac{1}{(\alpha')^2} + \frac{\nu \bar{\phi}_p}{\alpha^2 p} \right] \\ &\quad + \frac{2\mathbf{a}\mathbf{a}}{(p + \nu \bar{\phi}_p)^3} \left[ \frac{\nu \bar{\phi}_p}{p^3} + \frac{3}{p^2} \right]. \quad (35) \end{aligned}$$

Note that the classical expressions may be regained immediately at any stage, since in that case,  $\phi(t) = \delta(t)$  and  $\bar{\phi}_p = 1$ . Exact expressions for the macroscopically observable quantities  $\langle \mathbf{r} \rangle$  and  $\langle \mathbf{r}\mathbf{r} \rangle$  follow from Eqs. (34) and (35) after inverting the Laplace transforms, as explained in the next section.

### III. MACROSCOPICALLY OBSERVABLE QUANTITIES

#### A. General expressions in terms of Mittag-Leffler functions

The quantities inferred in the time-of-flight experiment are not normally the full density distribution  $n(\mathbf{r}, t)$  as such, but rather spatial moments, such as the position of the centroid

$$\langle \mathbf{r} \rangle = \frac{1}{n_0} \int d\mathbf{r} \mathbf{r} n(\mathbf{r}, t) \quad (36a)$$

and the dispersion about the centroid

$$\langle \mathbf{R}\mathbf{R} \rangle = \frac{1}{n_0} \int d\mathbf{r} \mathbf{R}\mathbf{R} n(\mathbf{r}, t) \equiv \langle \mathbf{r}\mathbf{r} \rangle - \langle \mathbf{r} \rangle \langle \mathbf{r} \rangle, \quad (36b)$$

where

$$\mathbf{R} \equiv \mathbf{r} - \langle \mathbf{r} \rangle.$$

These quantities may be obtained directly from Eq. (28) by differentiation,

$$\langle \mathbf{r} \rangle = \frac{i}{n_0} \left\{ \frac{\partial \tilde{n}(\mathbf{k}, t)}{\partial \mathbf{k}} \right\}_{\mathbf{k}=\mathbf{0}} \quad (37)$$

and

$$\langle \mathbf{r}\mathbf{r} \rangle = -\frac{1}{n_0} \left\{ \frac{\partial^2 \tilde{n}(\mathbf{k}, t)}{\partial \mathbf{k} \partial \mathbf{k}} \right\}_{\mathbf{k}=\mathbf{0}}. \quad (38)$$

After taking the inverse Laplace transforms of Eqs. (34) and (35) and substituting in the right hand sides of Eqs. (37) and (38), respectively, we obtain

$$\langle \mathbf{r} \rangle = \mathbf{a} t^2 E_{2-\gamma, 3}(-\nu_\gamma t^{2-\gamma}) \quad (39)$$

and

$$\begin{aligned} \langle \mathbf{r}\mathbf{r} \rangle &= \mathbf{1} \left[ \frac{2t^2}{(\alpha')^2} E_{2-\gamma, 1+\gamma}^{(1)}(-\nu_\gamma t^{2-\gamma}) + \frac{2\nu_\gamma t^{4-\gamma}}{\alpha^2} E_{2-\gamma, 3}^{(1)} \right. \\ &\quad \left. \times (-\nu_\gamma t^{2-\gamma}) \right] + \mathbf{a}\mathbf{a} \left[ \nu_\gamma t^{6-\gamma} E_{2-\gamma, 3+\gamma}^{(2)}(-\nu_\gamma t^{2-\gamma}) \right. \\ &\quad \left. + 3t^4 E_{2-\gamma, 2\gamma+1}^{(2)}(-\nu_\gamma t^{2-\gamma}) \right], \quad (40) \end{aligned}$$

where

$$E_{\alpha, \beta}(z) \equiv \sum_{k=0}^{\infty} \frac{z^k}{\Gamma(\alpha k + \beta)} \quad (41)$$

is the generalized Mittag-Leffler function [15] and  $E_{\alpha, \beta}^{(n)}(z) \equiv (d/dz)^n E_{\alpha, \beta}(z)$ . In obtaining these expressions from Eqs. (34) and (35) we have made use of the Laplace transform relationship

$$\int_0^{\infty} dt e^{-pt} \frac{t^{\alpha k + \beta - 1}}{n!} E_{\alpha, \beta}^{(n)}(-bt^\alpha) = \frac{p^{\alpha - \beta}}{(p^\alpha + b)^{n+1}}. \quad (42)$$

Although we now have a complete and exact description of the time evolution of the centroid and of the width of the pulse in Eqs. (30) and (31), respectively, it is interesting to examine how the expressions simplify in appropriate limits.

#### B. Limiting cases

##### 1. Short time behavior

At short times,  $\nu_\gamma t^{2-\gamma} \ll 1$ , the position of the centroid is found from Eq. (39) and the small-argument approximation

$$E_{\alpha, \beta}(z) = \frac{1}{\Gamma(\beta)} + \frac{z}{\Gamma(\alpha + \beta)} + \dots$$

leads to

$$\langle \mathbf{r} \rangle = \mathbf{a} t^2 \left\{ \frac{1}{\Gamma(3)} + O(t^{2-\gamma}) \right\} = \frac{1}{2} \mathbf{a} t^2 + O(t^{4-\gamma}), \quad (43)$$

corresponding to the expected ballistic expression for charged particles accelerated freely from rest by a constant electric field.



## 2. Asymptotic behavior in time

On the other hand, at long times  $\nu_\gamma t^{2-\gamma} \gg 1$ , or, equivalently, for

$$t \gg t_0 \left( \frac{1}{\nu t_0} \right)^{1/(2-\gamma)} \quad (44)$$

we have, using the asymptotic relation

$$E_{\alpha,\beta}^{(n)}(-bt^\alpha) \sim n! \frac{t^{-(n+1)\alpha}}{b^{n+1}\Gamma(\beta-\alpha)} \quad (45)$$

and retaining only leading terms, that

$$\begin{aligned} \langle \mathbf{r} \rangle &\sim \frac{\mathbf{a}t^\gamma}{\nu_\gamma \Gamma(1+\gamma)}, \\ \langle \mathbf{r}\mathbf{r} \rangle &\sim \frac{2\mathbf{a}\mathbf{a}t^{2\gamma}}{\nu_\gamma^2 \Gamma(2\gamma+1)}, \end{aligned} \quad (46)$$

and

$$\langle \mathbf{R}\mathbf{R} \rangle \sim \frac{\mathbf{a}\mathbf{a}t^{2\gamma}}{\nu_\gamma^2} \left\{ \frac{2}{\Gamma(2\gamma+1)} - \frac{1}{\Gamma(1+\gamma)^2} \right\}.$$

Equation (44) may be considered as a *necessary* condition for the *hydrodynamic regime* in the presence of trapping, and Eqs. (46) give the corresponding expressions for measurable quantities. Notice that the factor  $\alpha'$  does not appear in these averaged properties, and no memory remains of the initial conditions. Notice also that the time dependence of *both* the centroid *and* the dispersion about the centroid goes as  $t^\gamma$ , implying, in contrast to the classical case, and as expected [1,4], that there is no well-defined pulse *per se*.

## C. Classical transport

The classical, nontrapping limit can be obtained from the general framework above by setting  $\bar{\phi}_p=1$ , or more directly from the particular expressions (39) and (40) via the mathematical device  $\gamma \rightarrow 1$ ,  $\nu_\gamma \rightarrow \nu$ , and using properties of the Mittag-Leffler functions [15]:

$$\langle \mathbf{r} \rangle = \mathbf{a}\nu^{-1}t - \mathbf{a}\nu^{-2} + \mathbf{a}\nu^{-2}e^{-\nu t}$$

and

$$\begin{aligned} \langle \mathbf{r}\mathbf{r} \rangle = 2l \left\{ \frac{1}{(\alpha'\nu)^2} [1 - (1+\nu t)e^{-\nu t}] + \frac{1}{(\alpha\nu)^2} [\nu t - 2 \right. \\ \left. + (2+\nu t)e^{-\nu t}] \right\} + \frac{\mathbf{a}\mathbf{a}}{\nu^4} \{ \nu^2 t^2 - 6 + 2(\nu^2 t^2 + 3\nu t + 3)e^{-\nu t} \}. \end{aligned}$$

These expressions agree with results obtained previously [5]. At short times  $\nu t < 1$ , nonhydrodynamic conditions prevail, and the centroid behaves ballistically,  $\langle \mathbf{r} \rangle \approx \frac{1}{2}\mathbf{a}t^2$ . The hydrodynamic regime is, however, quickly attained after a few collision times,  $\nu t > 1$ , and then the above expressions yield

$$\langle \mathbf{r} \rangle \approx \mathbf{v}_d t$$

and

$$\langle \mathbf{R}\mathbf{R} \rangle \approx 2Dt$$

where

$$\mathbf{v}_d = \frac{\mathbf{a}}{\nu} \quad \text{and} \quad \mathbf{D} = \nu^{-1}(l\alpha^{-2} + \mathbf{v}_d \mathbf{v}_d)$$

denote the classical drift velocity and the diffusion tensor, respectively. Since the dispersion about the centroid goes as  $t^{1/2}$  in this classical case, while the position of the centroid itself goes as  $t$ , the pulse spreads slowly relative to the centroid's position, and therefore retains a well-defined identity as it moves through the medium. In contrast, Eqs. (46) illustrate the well-known result [4] that there is no such separation of time dependence when trapping occurs, and therefore no well-defined pulse.

So much for moments of the density, and we now move on to a discussion of  $n(\mathbf{r}, t)$  itself.

## IV. RECONCILIATION OF THE DIFFUSION EQUATION WITH THE EXACT SOLUTION

We have considered how the general expressions simplify for small  $k$  in Sec. II E, and we now additionally consider the small- $p$  limit, in the sense that

$$p \ll \nu \bar{\phi}_p, \quad (47)$$

for which it follows from Eq. (26) that

$$\frac{\hat{n}_p(\mathbf{k})}{n_0} = \frac{(i\beta'/\sqrt{2k})/Z(\zeta')}{1 + \nu \bar{\phi}_p (i\beta'/\sqrt{2k})Z(\zeta)} \approx \frac{F_p(\mathbf{k})}{p + p_{\mathbf{k}}^{(0)}} \equiv \frac{\hat{n}_p^{(\infty)}(\mathbf{k})}{n_0}, \quad (48)$$

which is accurate to  $O(k^2)$ , where

$$F_p(\mathbf{k}) \equiv 1 + \frac{i\mathbf{a} \cdot \mathbf{k}}{(\nu \bar{\phi}_p)^2} + \frac{3(\mathbf{a} \cdot \mathbf{k})^2}{(\nu \bar{\phi}_p)^4} - \frac{k^2}{(\nu \bar{\phi}_p)^2 (\alpha')^2} \quad (49)$$

is a factor of the order of unity, and

$$\begin{aligned} p_{\mathbf{k}}^{(0)} &\equiv \frac{1}{\bar{\phi}_p} [i\mathbf{v}_d \cdot \mathbf{k} + \nu^{-1}(l\alpha^{-2} + \mathbf{v}_d \mathbf{v}_d / \bar{\phi}_p^2) : \mathbf{k}\mathbf{k}] \\ &= i\mathbf{k} \cdot \frac{\mathbf{v}_{d,\gamma}}{p^{1-\gamma}} + \mathbf{k}\mathbf{k} : \left( lD_\gamma + \frac{\mathbf{v}_{d,\gamma} \mathbf{v}_{d,\gamma}}{\nu_\gamma p^{2(1-\gamma)}} \right). \end{aligned} \quad (50)$$

Comparison of Eq. (20) with Eq. (48) shows that the asymptotic and diffusion equation solutions are related by

$$\hat{n}_p^{(\infty)}(\mathbf{k}) = F_p(\mathbf{k}) \hat{n}_p^{(\text{DE})}(\mathbf{k}) + O(k^3). \quad (51)$$

Since  $F_p(\mathbf{k}) \rightarrow 1$  as  $p \rightarrow 0$ , it is clear that the exact expression for the small- $k$  form of the Fourier transform of density approaches the diffusion equation result asymptotically at long times, i.e., that

$$\hat{n}(\mathbf{k}, t) \sim \hat{n}^{(\text{DE})}(\mathbf{k}, t) + O(k^3), \quad (52)$$

and it follows that the spatial moments  $\langle \mathbf{r} \rangle$  and  $\langle \mathbf{r}\mathbf{r} \rangle$  of  $n^{(\text{DE})}(\mathbf{r}, t)$  must be also given by the asymptotic expressions for the exact quantities, Eqs. (46).

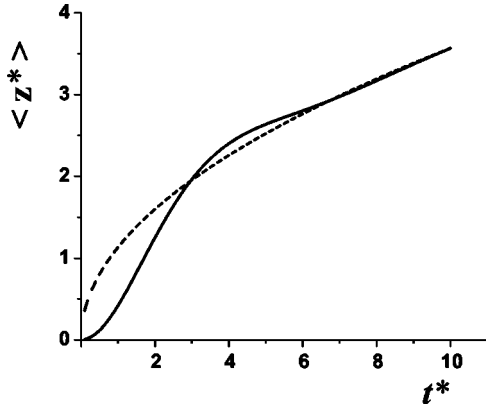


FIG. 1. Centroid position of pulse as a function of time ( $z^* = zv^2/a, t^* = vt$ ) obtained from the exact (solid line) and approximate expressions (dashed line), Eqs. (39) and (46), respectively.

The situation is illustrated in Figs. 1 and 2 for the centroid position and mean square displacement along the field direction ( $z$  axis), respectively, for the case where  $\alpha' = \alpha$ ,  $(vt_0)^{1-\gamma} = \Gamma(1-\gamma)$ ,  $(v/a\alpha)^2 = 0.1$ , and  $\gamma = 0.5$ . These calculations confirm the observation that while the diffusion equation is inadequate for dealing with the short-time, nonhydrodynamic regime, it generates accurate moments in the asymptotic limit.

As for the density distribution itself, Eq. (52), it is to be interpreted as saying that the actual density approaches the solution of the diffusion equation asymptotically,

$$n(\mathbf{r}, t) \sim n^{(\text{DE})}(\mathbf{r}, t) \quad (53)$$

for sufficiently long times [the small- $p$  condition Eq. (47) is equivalent to the long-time condition Eq. (44)] and for distances sufficiently far downstream from the source (the “far field” region), according to Eq. (44) and to

$$r > \frac{1}{\alpha v_\gamma t^{1-\gamma}}, \quad (54)$$

respectively. This last condition follows heuristically from Eq. (30) with  $p \sim t^{-1}$ ,  $k \sim r^{-1}$ . Clearly, the domain of validity of the hydrodynamic regime and of the diffusion equation

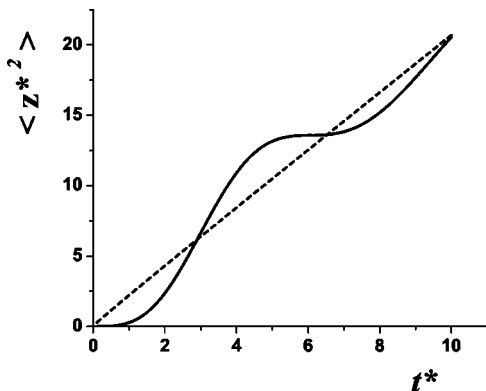


FIG. 2. Mean square displacement in the field direction, calculated exactly (solid line) and approximately (dashed line) from Eqs. (40) and (46), respectively.

increases in the course of time, i.e., Eq. (18b) applies ever closer to the source as  $t$  increases.

Near the source and for short times, nonhydrodynamic conditions prevail, and the diffusion equation is of no use: a complete expression for  $n(\mathbf{r}, t)$  can only be found from the full Boltzmann equation solution, which for the present situation means inverting Eq. (26) numerically, without further approximation. Given that this is a model calculation, and that in any case the observable quantities, the spatial moments of  $n(\mathbf{r}, t)$ , have been determined exactly in Sec. III for both nonhydrodynamic and hydrodynamic circumstances, we have not attempted such a program.

## V. DISCUSSION AND CONCLUDING REMARKS

Here we have shown that Eq. (15), the diffusion equation underpinning fractional kinetics, follows from the solution of the Boltzmann kinetic equation with memory for the phase space distribution function  $f(\mathbf{r}, \mathbf{v}, t)$  at the level of the second Chapman-Enskog approximation, i.e., that it is valid in the weak gradient, weak field hydrodynamic regime only, where the space-time dependence of  $f(\mathbf{r}, \mathbf{v}, t)$  can be projected out onto the number density  $n(\mathbf{r}, t)$ . We have relaxed the weak field restriction to obtain a new generalized fractional diffusion equation (18). In general, however, the space-time dependence cannot be simplified in this way, and the diffusion equation must yield to a full solution of Boltzmann’s equation, without approximation, in nonhydrodynamic situations.

The Boltzmann kinetic equation with a BGK relaxation time scattering term has been solved analytically, for a pulse of small-signal charge carriers under conditions corresponding to the time-of-flight experiment, to obtain the exact Eq. (26) for the Fourier-Laplace transform of the number density. The exact analytic expressions Eqs. (39) and (40) were then obtained for the centroid of the pulse and for the dispersion, respectively, valid under both hydrodynamic and nonhydrodynamic conditions. The diffusion equation is thus shown to be valid for describing the time-of-flight experiment only in the asymptotic long-time limit, Eq. (44), at distances sufficiently far downstream from the source, Eq. (54). At short times, close enough to the source, nonhydrodynamic conditions prevail and only a solution of the Boltzmann equation will suffice.

Since the solution of Boltzmann’s equation for the pulsed time-of-flight experiment effectively yields the Green’s function, other experimental situations can (at least formally) be dealt with in the usual way, by appropriate integration over space and/or time. The hydrodynamic Fick’s law and diffusion equation regime can also be identified in these cases, but one should not expect that it should be the same as for the time-of-flight-experiment. The situation where charge carriers are emitted from an infinite plane source at a steady rate into an infinite medium, such that a steady state is eventually achieved at long times, is a case in point: it is straightforward to show that the diffusion equation does not yield physically tenable results anywhere, except trivially at infinity. There one has an inherently nonhydrodynamic situation and there seems to be no alternative but to solve the phase space kinetic equation without approximation, a task that is under-

taken nowadays on a regular basis by researchers in transport in gaseous media [13,19]. An investigation of the relevance to condensed matter transport is clearly of interest.

In summary, we suggest that the fractional diffusion equation be employed with great care, whatever the context.

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#### APPENDIX: DERIVATION OF THE EXACT EXPRESSION FOR $\hat{n}_p(\mathbf{k})$ , Eq. (25)

From Eqs. (22), (23), and (25) there follows

$$\hat{n}_p(\mathbf{k}) = - \int_{-\infty}^0 d\sigma \frac{1}{k} \left[ \nu \bar{\phi}_p \hat{n}_p(\mathbf{k}) \exp\left(-\frac{\sigma^2}{2\alpha^2}\right) + f_0(\mathbf{k}, \sigma, \mathbf{0}) \right] \times \exp\left(-\frac{i\sigma\left(\frac{1}{2}\sigma a_{\parallel} - \Omega\right)}{k}\right). \quad (\text{A1})$$

Substituting the Fourier transform of the Gaussian initial condition, Eq. (21), namely,

$$f_0(\mathbf{k}, \sigma, \mathbf{0}) = n_0 \exp\left\{-\frac{\sigma^2}{2(\alpha')^2}\right\} \quad (\text{A2})$$

into Eq. (A1), there follows

$$\hat{n}_p(\mathbf{k}) = - \int_{-\infty}^0 d\sigma \frac{1}{k} \left\{ \nu \bar{\phi}_p \hat{n}_p(\mathbf{k}) \exp\left(-\frac{\sigma^2}{2\beta^2}\right) + n_0 \exp\left(\frac{i\sigma\Omega}{k} - \frac{\sigma^2}{2(\beta')^2}\right) \right\}, \quad (\text{A3})$$

where  $\beta$  and  $\beta'$  are defined by

$$\beta^{-2} \equiv \alpha^{-2} + \frac{\mathbf{ia} \cdot \mathbf{k}}{k^2} \quad (\text{A4})$$

and

$$\beta'^{-2} \equiv \alpha'^{-2} + \frac{\mathbf{ia} \cdot \mathbf{k}}{k^2}. \quad (\text{A5})$$

The integral over  $\sigma$  may be carried out with the help of the identity

$$\int_{-\infty}^0 d\sigma \exp\left(\frac{i\sigma\Omega}{k} - \frac{\sigma^2}{2\beta^2}\right) = \frac{i\beta}{\sqrt{2}} Z(\zeta), \quad (\text{A6})$$

where the plasma dispersion function  $Z(\zeta)$  and  $\zeta$  are defined by Eqs. (27a) and (27b)). The solution of Eq. (A3) then gives Eq. (25) immediately.

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