Solution of a generalized Boltzmann's equation for nonequilibrium charged-particle transport via localized and delocalized states

Peter W. Stokes,[*] Bronson Philippa, Daniel Cocks, and Ronald D. White

College of Science, Technology and Engineering, James Cook University, Townsville, QLD 4811, Australia

We present a general phase-space kinetic model for charged-particle transport through combined localized and delocalized states, capable of describing scattering collisions, trapping, detrapping, and losses. The model is described by a generalized Boltzmann equation, for which an analytical solution is found in Fourier-Laplace space. The velocity of the center of mass and the diffusivity about it are determined analytically, together with the flux transport coefficients. Transient negative values of the free particle center-of-mass transport coefficients can be observed due to the trapping to, and detrapping from, localized states. A Chapman-Enskog-type perturbative solution technique is applied, confirming the analytical results and highlighting the emergence of a density gradient representation in the weak-gradient hydrodynamic regime. A generalized diffusion equation with a unique global time operator is shown to arise, reducing to the standard diffusion equation and a Caputo fractional diffusion equation in the normal and dispersive limits. A subordination transformation is used to solve the generalized diffusion equation by mapping from the solution of a corresponding standard diffusion equation.

I. INTRODUCTION

Normal transport, as described by the diffusion equation, has a mean squared displacement that scales linearly with time, t. Dispersive transport, however, is often defined by a mean squared displacement that scales sublinearly, proportional to t^α where $0 < \alpha < 1$ [1]. Physically, this arises due to the presence of traps causing particles to become immobilized (localized states) for extended periods of time and resulting in fundamentally slower transport [2]. A number of physical systems have the potential to exhibit dispersive transport. For example, in organic semiconductors and other disordered media, trapped states arise due to local imperfections or variation in the energetic landscape [2,3]. Electron transport in certain liquids can be influenced by electrons becoming trapped in (localized) bubble states (see, e.g., [4] and [5]), giving rise to dispersive electronic transport in liquid neon [6]. Similar trapping processes occur for positronium in bubbles (see, e.g., [7–9]) and positrons annihilation on induced clusters (see, e.g., [10]).

A consequence of dispersive systems, especially those with long-lived traps, is their dependence on their history. The diffusion equation, which uses a local time operator, is fundamentally incapable of describing such memory effects. Mathematically, an adequate model for dispersive transport requires a global time operator that acts on the entire history of the system. One successful approach to modeling dispersive transport is by replacing the local time derivative in the diffusion equation with a global fractional time derivative of order α [11,12]. This resulting fractional diffusion equation describes memory effects while also satisfying the required sublinear scaling of the mean squared displacement.

However, fractional diffusion equations still share the same spatial operator as the standard diffusion equation, which implies implicitly an assumption of small spatial gradients. At the same time, the memory of the initial condition can cause large spatial gradients to persist for all time. This inconsistency challenges the validity of fractional diffusion equations. This has been addressed by using phase-space kinetic models for dispersive transport that make no such assumptions on the size of spatial gradients [13,14]. Specifically, these have made use of a Boltzmann equation with a generalization of the Bhatnagar-Gross-Krook (BGK) collision operator [15], the standard collision operator in semiconductor physics. In our previous work [14], trapping and detrapping are considered equivalent to a BGK collision scattering event occurring after a delay governed by a trapping time distribution. That study did not consider scattering as a separate process from trapping, thereby limiting the model to situations where trapping dominates over scattering. However, scattering events are key to transport in delocalized states, such as in the conduction band of a semiconductor. The present study builds upon previous work by incorporating a genuine scattering model into a kinetic equation with memory of past trapping events. The new, proposed model also incorporates loss mechanisms such as charged carrier recombination.

In Sec. II, we present a generalized Boltzmann equation with a BGK collision operator to describe transport via delocalized states, a delayed BGK operator to model trapping and detrapping associated with localized (trapped) states, and loss terms corresponding to free and trapped particle recombination. In Sec. III, we determine an analytical Fourier-Laplace-space solution of this model. This analytical solution is used, among other things, to determine analytical expressions for phase-space averaged moments of the generalized Boltzmann equation. Spatial moments provide transport coefficients describing the motion of the center of mass, while velocity moments are used in conjunction to describe the particle flux using flux transport coefficients. In Sec. IV, the model is explored in the weak-gradient hydrodynamic regime, where it is shown to coincide with both a standard diffusion equation and a generalized diffusion equation with history dependence. In Sec. V, the model is also shown to coincide with a Caputo fractional diffusion equation in the particular case where transport is dispersive. In Sec. VI, the solution of the

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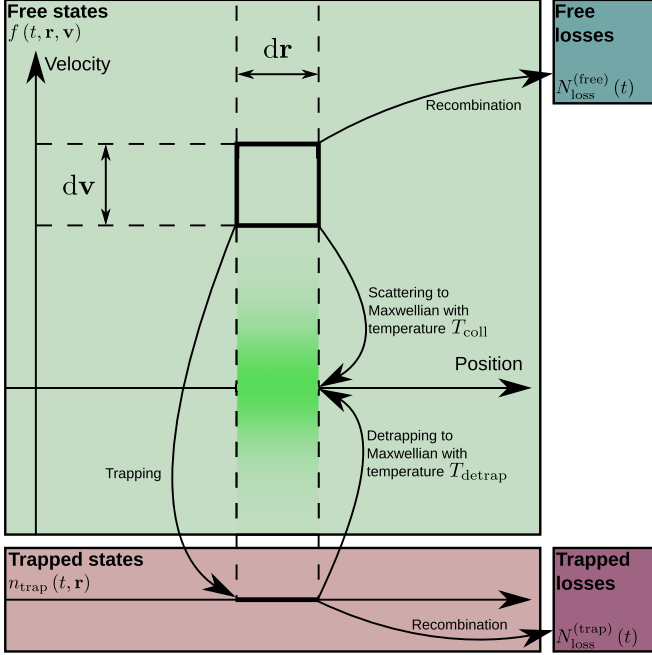[*]peter.stokes@my.jcu.edu.au

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FIG. 1. Phase-space diagram illustrating the collision, trapping, detrapping, and recombination processes considered in the model defined by Eqs. (1)–(8).

generalized diffusion equation is expressed as a subordination transformation of the solution of a corresponding standard diffusion equation. Finally, in Sec. VII, we present conclusions and possible avenues for future work.

II. GENERALIZED BOLTZMANN EQUATION

We consider a generalized phase-space kinetic model describing the transport of free particles undergoing collisions, trapping, detrapping, and recombination as illustrated in Fig. 1. The free particles are described by the phase-space distribution function $f(t,\mathbf{r},\mathbf{v})$, which satisfies the Boltzmann equation

$$
\begin{aligned}
\left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{r}} + \mathbf{a} \cdot \frac{\partial}{\partial \mathbf{v}}\right) & f(t,\mathbf{r},\mathbf{v}) \\
= & -\nu_{\text{coll}}[f(t,\mathbf{r},\mathbf{v}) - n(t,\mathbf{r})w(\alpha_{\text{coll}},v)] \\
& -\nu_{\text{trap}}[f(t,\mathbf{r},\mathbf{v}) - \Phi(t) * n(t,\mathbf{r})w(\alpha_{\text{detrap}},v)] \\
& -\nu_{\text{loss}}^{(\text{free})} f(t,\mathbf{r},\mathbf{v}),
\end{aligned} \tag{1}
$$

where collision, trapping, and free particle loss rates are, respectively, denoted ν_{coll}, ν_{trap}, and $\nu_{\text{loss}}^{(\text{free})}$ and the free particle number density is defined as $n(t,\mathbf{r}) \equiv \int d\mathbf{v} f(t,\mathbf{r},\mathbf{v})$. Collisions are described above by the BGK collision operator [15]. Specifically, free particles are instantaneously scattered to a Maxwellian distribution of velocities of temperature T_{coll}. The Maxwellian velocity distribution is defined as

$$
w(\alpha,v) \equiv \left(\frac{\alpha^2}{2\pi}\right)^{\frac{3}{2}} \exp\left(-\frac{\alpha^2 v^2}{2}\right), \tag{2}
$$

$$
\alpha^2 \equiv \frac{m}{k_B T}, \tag{3}
$$

where m is the free particle mass, k_B is the Boltzmann constant, and T is the temperature of the scattered particles. Similarly, trapping and detrapping processes occur as described by the delayed BGK model [14], according to an effective waiting time distribution $\Phi(t)$, with trapped particles eventually detrapped with a Maxwellian velocity distribution of temperature T_{detrap}. To define this waiting time distribution, consider the simple case of traps of fixed duration τ. Particles enter traps at the rate $\nu_{\text{trap}} n(t,\mathbf{r})$ and so leave traps at this same rate τ units of time in the future. From the present perspective this rate of detrapping is $\nu_{\text{trap}} n(t - \tau,\mathbf{r})$. More generally, for a distribution of trapping times $\phi(t)$, the rate of detrapping is now written as the convolution

$$
\nu_{\text{trap}} \phi(t) * n(t,\mathbf{r}) = \nu_{\text{trap}} \int_0^t d\tau \, \phi(\tau) n(t - \tau,\mathbf{r}). \tag{4}
$$

Here, the quantity $dP \equiv \phi(\tau)d\tau$ can be interpreted as an infinitesimal probability that particles will remain trapped for duration τ. Note that this expression does not take into account the possibility that particles may undergo trap-based losses instead of detrapping. As trapped particles are being lost exponentially at the rate $\nu_{\text{loss}}^{(\text{trap})}$, the probability of detrapping decays correspondingly, $dP = e^{-\nu_{\text{loss}}^{(\text{trap})}\tau}\phi(\tau)d\tau$. That is, we now have the effective waiting time distribution

$$
\Phi(t) \equiv e^{-\nu_{\text{loss}}^{(\text{trap})}t}\phi(t). \tag{5}
$$

As the trapped particles are localized in configuration space, we describe them with the number density $n_{\text{trap}}(t,\mathbf{r})$, which satisfies the continuity equation

$$
\frac{\partial}{\partial t} n_{\text{trap}}(t,\mathbf{r}) = \nu_{\text{trap}}(1 - \Phi*)n(t,\mathbf{r}) - \nu_{\text{loss}}^{(\text{trap})} n_{\text{trap}}(t,\mathbf{r}), \tag{6}
$$

where $\nu_{\text{loss}}^{(\text{trap})}$ is the loss rate of trapped particles. Although the loss processes of the free and trapped particles can occur through various mechanisms (e.g., recombination, attachment), for simplicity we refer to all losses as being due to recombination processes. The numbers of free and trapped particles that undergo recombination, $N_{\text{loss}}^{(\text{free})}(t)$ and $N_{\text{loss}}^{(\text{trap})}(t)$, can be counted accordingly,

$$
\frac{d}{dt} N_{\text{loss}}^{(\text{free})}(t) = \nu_{\text{loss}}^{(\text{free})} N(t), \tag{7}
$$

$$
\frac{d}{dt} N_{\text{loss}}^{(\text{trap})}(t) = \nu_{\text{loss}}^{(\text{trap})} N_{\text{trap}}(t), \tag{8}
$$

in terms of the number of free and trapped particles, defined by $N(t) \equiv \int d\mathbf{r} \, n(t,\mathbf{r})$ and $N_{\text{trap}}(t) \equiv \int d\mathbf{r} \, n_{\text{trap}}(t,\mathbf{r})$.

The physical origin of the differences in the functional form of the waiting time distribution is dependent on the mechanism for trapping. For example, for amorphous/organic materials, trapping is into existing trapped states, and the waiting time distribution is calculated from the density of trapped states (see, e.g., [14]). For dense gases/liquids, the trapped states are formed by the electron itself, and hence the waiting time distribution is dependent on the scattering, fluctuation profiles, and subsequent fluid bubble evolution (see, e.g., [16]).

III. ANALYTICAL SOLUTION OF THE GENERALIZED BOLTZMANN EQUATION

A. Solution in Fourier-Laplace-transformed phase space

The Boltzmann equation with the BGK collision operator has been solved analytically in Fourier-Laplace space [17]. This same solution technique can be applied to the generalized Boltzmann equation, (1), with the additional processes of trapping, detrapping, and recombination. Applying the Laplace transform in time, $t \to p$, and the Fourier transform in phase space, $(\mathbf{r}, \mathbf{v}) \to (\mathbf{k}, \mathbf{s})$, Eq. (1) transforms to

$$\left(\tilde{p} + \tilde{v} + \iota \frac{\partial}{\partial \mathbf{s}} \cdot \iota \mathbf{k} + \mathbf{a} \cdot \iota \mathbf{s} \right) f(p, \mathbf{k}, \mathbf{s})$$
$$= f(t = 0, \mathbf{k}, \mathbf{s}) + \nu_{\text{coll}} n(p, \mathbf{k}) w(\alpha_{\text{coll}}, s)$$
$$+ \nu_{\text{trap}} \Phi(p) n(p, \mathbf{k}) w(\alpha_{\text{detrap}}, s), \quad (9)$$

where the Fourier-Laplace-transformed phase-space distribution function is

$$f(p, \mathbf{k}, \mathbf{s}) \equiv \int_0^\infty \mathrm{d}t \int \mathrm{d}\mathbf{r} \int \mathrm{d}\mathbf{v} e^{-(pt + \iota \mathbf{k} \cdot \mathbf{r} + \iota \mathbf{s} \cdot \mathbf{v})} f(t, \mathbf{r}, \mathbf{v}), \quad (10)$$

the Fourier-transformed Maxwellian velocity distribution is

$$w(\alpha, s) \equiv \exp\left(-\frac{s^2}{2\alpha^2} \right), \quad (11)$$

and the following frequencies have been defined:

$$\tilde{p} \equiv p + \nu_{\text{trap}}[1 - \Phi(p)] + \nu_{\text{loss}}^{(\text{free})}, \quad (12)$$

$$\tilde{v} \equiv \nu_{\text{coll}} + \nu_{\text{trap}} \Phi(p). \quad (13)$$

By writing all vectors in terms of components parallel and perpendicular to the unit vector $\hat{\mathbf{k}} \equiv \mathbf{k}/k$,

$$\mathbf{s}_\parallel = (\mathbf{s} \cdot \hat{\mathbf{k}})\hat{\mathbf{k}}, \quad (14)$$

$$\mathbf{a}_\parallel = (\mathbf{a} \cdot \hat{\mathbf{k}})\hat{\mathbf{k}}, \quad (15)$$

$$\mathbf{s}_\perp = \mathbf{s} - \mathbf{s}_\parallel, \quad (16)$$

$$\mathbf{a}_\perp = \mathbf{a} - \mathbf{a}_\parallel, \quad (17)$$

the Fourier-Laplace-transformed Boltzmann equation, (9), can be restated as a single first-order differential equation in the Fourier velocity-space variable $s_\parallel$

$$\left[\frac{\partial}{\partial s_\parallel} - \frac{1}{k}(\tilde{p} + \tilde{v} + a_\parallel \iota s_\parallel + \mathbf{a}_\perp \cdot \iota \mathbf{s}_\perp) \right] f(p, \mathbf{k}, \mathbf{s})$$
$$= -\frac{f(t = 0, \mathbf{k}, \mathbf{s})}{k} - \frac{\nu_{\text{coll}}}{k} n(p, \mathbf{k}) w(\alpha_{\text{coll}}, s)$$
$$- \frac{\nu_{\text{trap}} \Phi(p)}{k} n(p, \mathbf{k}) w(\alpha_{\text{detrap}}, s). \quad (18)$$

Finally, solving Eq. (18) provides the Fourier-Laplace-transformed solution of the generalized Boltzmann equation, (1),

$$f(p, \mathbf{k}, \mathbf{s}) = -\frac{1}{k \mu(s_\parallel)} \int_{-\infty}^{s_\parallel} \mathrm{d}\sigma \, \mu(\sigma) \{ f(t = 0, \mathbf{k}, \sigma, \mathbf{s}_\perp)$$
$$+ n(p, \mathbf{k})[\nu_{\text{coll}} w(\alpha_{\text{coll}}, \sigma, \mathbf{s}_\perp)$$
$$+ \nu_{\text{trap}} \Phi(p) w(\alpha_{\text{detrap}}, \sigma, \mathbf{s}_\perp)]\}, \quad (19)$$

written in terms of the integrating factor

$$\mu(s_\parallel) \equiv \exp\left[-\frac{s_\parallel}{k} \left(\tilde{p} + \tilde{v} + \frac{1}{2} a_\parallel \iota s_\parallel + \mathbf{a}_\perp \cdot \iota \mathbf{s}_\perp \right) \right]. \quad (20)$$

We use the analytical expression, (19), to evaluate relevant spatial and velocity moments to obtain the macroscopic transport properties.

B. Particle number and the existence of a steady state

Integration of the Boltzmann equation, (1), throughout all phase space provides the equation for the free particle number, $N(t)$:

$$\left[\frac{\mathrm{d}}{\mathrm{d}t} + \nu_{\text{trap}}(1 - \Phi*) + \nu_{\text{loss}}^{(\text{free})} \right] N(t) = 0. \quad (21)$$

Similarly, integration over configuration space for the trapped continuity equation, (6), provides an equation for the trapped particle number, $N_{\text{trap}}(t)$:

$$\left[\frac{\mathrm{d}}{\mathrm{d}t} + \nu_{\text{loss}}^{(\text{trap})} \right] N_{\text{trap}}(t) = \nu_{\text{trap}}(1 - \Phi(t)*) N(t). \quad (22)$$

In conjunction with Eqs. (7) and (8) for the respective number of recombined free and trapped particles, each particle number can be written explicitly in Laplace space,

$$N(p) = \frac{N(0)}{p + \nu_{\text{trap}}[1 - \Phi(p)] + \nu_{\text{loss}}^{(\text{free})}}, \quad (23)$$

$$N_{\text{trap}}(p) = \frac{\nu_{\text{trap}}[1 - \Phi(p)]}{p + \nu_{\text{loss}}^{(\text{trap})}} N(p), \quad (24)$$

$$N_{\text{loss}}^{(\text{free})}(p) = \frac{\nu_{\text{loss}}^{(\text{free})}}{p} N(p), \quad (25)$$

$$N_{\text{loss}}^{(\text{trap})}(p) = \frac{\nu_{\text{loss}}^{(\text{trap})}}{p} N_{\text{trap}}(p), \quad (26)$$

allowing for steady-state values to be determined using the final value theorem, $\lim_{t \to \infty} N(t) = \lim_{p \to 0} p N(p)$. Two possible situations arise in the long-time limit. In the case of no recombination, $\nu_{\text{loss}}^{(\text{free})} = \nu_{\text{loss}}^{(\text{trap})} = 0$, an equilibrium steady state is reached between the free and the trapped particle numbers,

$$\lim_{t \to \infty} \frac{N(t)}{N(0)} = \frac{\nu_{\text{detrap}}}{\nu_{\text{detrap}} + \nu_{\text{trap}}}, \quad (27)$$

$$\lim_{t \to \infty} \frac{N_{\text{trap}}(t)}{N(0)} = \frac{\nu_{\text{trap}}}{\nu_{\text{detrap}} + \nu_{\text{trap}}}, \quad (28)$$

where the detrapping rate has been defined as

$$\nu_{\text{detrap}}^{-1} \equiv \int_0^\infty \mathrm{d}t \, \phi(t) t. \quad (29)$$

Figure 2 plots the number of free and trapped particles, $N(t)$ and $N_{\text{trap}}(t)$, and their respective steady-state values, (27) and (28), for an exponential waiting time distribution $\phi(t) = \nu_{\text{detrap}} e^{-\nu_{\text{detrap}} t}$.
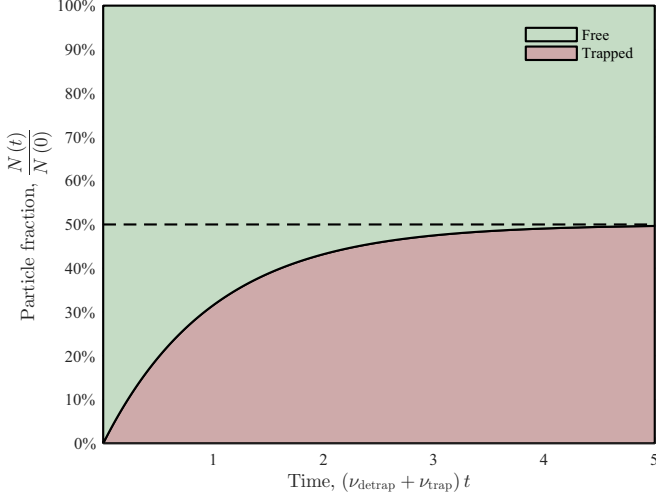
FIG. 2. Free and trapped particle numbers for the exponential waiting time distribution $\phi(t) = \nu_{\text{detrap}} e^{-\nu_{\text{detrap}} t}$. As no recombination is present, $\nu_{\text{loss}}^{(\text{free})} = \nu_{\text{loss}}^{(\text{trap})} = 0$, an equilibrium steady state is reached between the particles as described by Eqs. (27) and (28). Here, the detrapping and trapping rates are set equal, $\nu_{\text{detrap}} = \nu_{\text{trap}}$, resulting in the same number of free and trapped particles in the steady state.

In the case of *any* recombination, $\nu_{\text{loss}}^{(\text{free})} > 0$ or $\nu_{\text{loss}}^{(\text{trap})} > 0$, no free particle steady state is reached, as all free and trapped particles are eventually lost in the proportions

$$\lim_{t \to \infty} \frac{N_{\text{loss}}^{(\text{free})}(t)}{N(0)} = \frac{\nu_{\text{loss}}^{(\text{free})}}{\nu_{\text{loss}}^{(\text{free})} + \nu_{\text{trap}} P_{\text{loss}}}, \qquad (30)$$

$$\lim_{t \to \infty} \frac{N_{\text{loss}}^{(\text{trap})}(t)}{N(0)} = \frac{\nu_{\text{trap}} P_{\text{loss}}}{\nu_{\text{loss}}^{(\text{free})} + \nu_{\text{trap}} P_{\text{loss}}}, \qquad (31)$$

where the probability that a trapped particle undergoes recombination instead of detrapping is

$$P_{\text{loss}} \equiv 1 - \int_0^\infty dt\, \Phi(t). \qquad (32)$$

Figure 3 plots the number of free, trapped, and recombined particles in this case, where recombination is present for the same exponential waiting time distribution used in Fig. 2. It can be seen that, although there is an initial increase in the number of trapped particles, all free and trapped particles are eventually lost to recombination in the respective proportions (30) and (31).
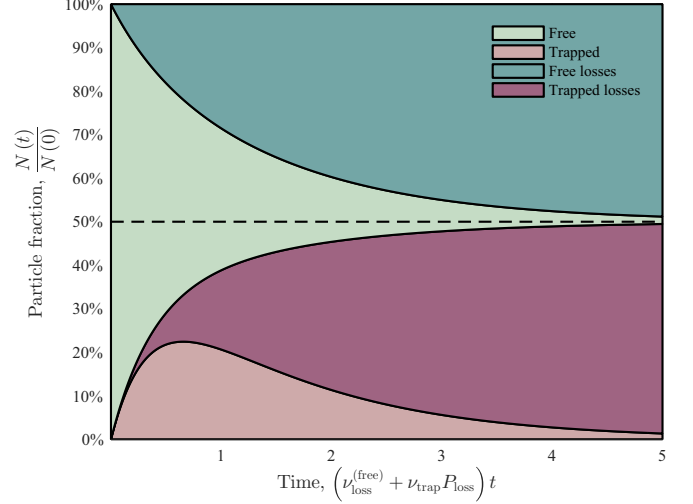

FIG. 3. Free, trapped, and recombined particle numbers for the exponential waiting time distribution $\phi(t) = \nu_{\text{detrap}} e^{-\nu_{\text{detrap}} t}$. As recombination is present, all free and trapped particles are eventually lost in the proportions given by Eqs. (30) and (31). Transiently, however, there is an initial increase in the number of trapped particles. Here, we set equal the free particle recombination rate and the product of the trapping rate with the trapped particle recombination probability, $\nu_{\text{loss}}^{(\text{free})} = \nu_{\text{trap}} P_{\text{loss}}$. For this exponential distribution of waiting times this probability is $P_{\text{loss}} = \nu_{\text{loss}}^{(\text{trap})} / (\nu_{\text{detrap}} + \nu_{\text{loss}}^{(\text{trap})})$. By making the aforementioned quantities equal, the numbers of recombined free and trapped particles also become equal in the long-time limit. In this case, the detrapping and trapping rates are set to $\nu_{\text{detrap}} = \nu_{\text{trap}} = \nu_{\text{loss}}^{(\text{free})} + \nu_{\text{trap}} P_{\text{loss}}$, which consequently specifies the trapped particle recombination rate $\nu_{\text{loss}}^{(\text{trap})} = \nu_{\text{loss}}^{(\text{free})} + \nu_{\text{trap}} P_{\text{loss}}$.

C. Moments and transport coefficients

In this and later sections we are predominantly interested in steady-state quantities, independent of the choice of initial conditions. For simplicity, we assume that there are initially $N(0)$ free particles centered at the origin, with a Maxwellian distribution of velocities of temperature $T_0 \equiv m/k_B \alpha_0^2$,

$$f(t = 0, \mathbf{r}, \mathbf{v}) \equiv N(0)\delta(\mathbf{r})w(\alpha_0, v). \qquad (33)$$

Velocity integration of the generalized Boltzmann equation, (1), provides the continuity equation for the free particle number density:

$$\left[\frac{\partial}{\partial t} + \nu_{\text{trap}}(1 - \Phi(t)*) + \nu_{\text{loss}}^{(\text{free})} \right] n(t,\mathbf{r}) + \frac{\partial}{\partial \mathbf{r}} \cdot [n(t,\mathbf{r})\langle \mathbf{v} \rangle(t,\mathbf{r})] = 0. \qquad (34)$$

This can be solved analytically using the generalized Boltzmann equation solution, (19), yielding

$$n(p,\mathbf{k}) = \frac{N(0)\zeta_0(\mathbf{k})Z[-(\tilde{p} + \tilde{\nu})\zeta_0(\mathbf{k})]}{1 - \nu_{\text{coll}}\zeta_{\text{coll}}(\mathbf{k})Z[-(\tilde{p} + \tilde{\nu})\zeta_{\text{coll}}(\mathbf{k})] - \nu_{\text{trap}}\Phi(p)\zeta_{\text{detrap}}(\mathbf{k})Z[-(\tilde{p} + \tilde{\nu})\zeta_{\text{detrap}}(\mathbf{k})]}, \qquad (35)$$

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

$$Z(\xi) \equiv \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} dx \frac{e^{-x^2}}{x - \xi}, \qquad (36)$$

and each Maxwellian yields a term of the form

$$\zeta(\mathbf{k}) \equiv \left[2\iota\mathbf{k}\cdot\left(\frac{\iota\mathbf{k}}{\alpha^2}-\mathbf{a}\right)\right]^{-\frac{1}{2}}. \tag{37}$$

From this analytical solution, phase-space averaged moments of the generalized Boltzmann equation can be found exactly for all times. For example, we have the spatial moments

$$\mathcal{L}\left\{\frac{N(t)}{N(0)}\langle\mathbf{r}\rangle(t)\right\} = \frac{\mathbf{a}}{\tilde{p}^2(\tilde{p}+\tilde{\nu})},$$

$$\mathcal{L}\left\{\frac{N(t)}{N(0)}\langle\mathbf{rr}\rangle(t)\right\} = \frac{2\mathbf{I}}{\tilde{p}^2(\tilde{p}+\tilde{\nu})^2}\left[\frac{\tilde{p}}{\alpha_0^2}+\frac{\nu_{\text{coll}}}{\alpha_{\text{coll}}^2}+\frac{\nu_{\text{trap}}\Phi(p)}{\alpha_{\text{detrap}}^2}\right]$$

$$+\frac{2\mathbf{aa}}{\tilde{p}^2(\tilde{p}+\tilde{\nu})^2}\left(\frac{1}{\tilde{p}}+\frac{2}{\tilde{p}+\tilde{\nu}}\right), \tag{38}$$

where the Laplace transform operator is explicitly denoted $\mathcal{L}$. From these moments, the motion of the center of mass (CM) can be described. The CM velocity is defined as the time rate of change of its position,

$$\mathbf{W}_{\text{CM}}(t) \equiv \frac{\mathrm{d}}{\mathrm{d}t}\langle\mathbf{r}\rangle(t), \tag{39}$$

while the CM diffusivity is defined as being proportional to the rate of change of the particle dispersion about it:

$$\mathbf{D}_{\text{CM}}(t) \equiv \frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}t}[\langle\mathbf{rr}\rangle(t)-\langle\mathbf{r}\rangle(t)\langle\mathbf{r}\rangle(t)]. \tag{40}$$

CM transport coefficients can be defined for the free, trapped, and total particles. Although trapped particles are localized in space their CM still moves due to repeated detrapping and trapping.

The movement of the free particles can also be described by looking directly at the velocity moments of the generalized Boltzmann equation, (1),

$$\mathcal{L}\left\{\frac{N(t)}{N(0)}\langle\mathbf{v}\rangle(t)\right\} = \frac{\mathbf{a}}{\tilde{p}(\tilde{p}+\tilde{\nu})}, \tag{41}$$

$$\mathcal{L}\left\{\frac{N(t)}{N(0)}\langle\mathbf{rv}\rangle(t)\right\} = \frac{\mathbf{I}}{\tilde{p}(\tilde{p}+\tilde{\nu})^2}\left[\frac{\tilde{p}}{\alpha_0^2}+\frac{\nu_{\text{coll}}}{\alpha_{\text{coll}}^2}+\frac{\nu_{\text{trap}}\Phi(p)}{\alpha_{\text{detrap}}^2}\right]$$

$$+\frac{\mathbf{aa}}{\tilde{p}(\tilde{p}+\tilde{\nu})^2}\left(\frac{1}{\tilde{p}}+\frac{2}{\tilde{p}+\tilde{\nu}}\right), \tag{42}$$

from which we define the average velocity

$$\mathbf{W}(t) \equiv \langle\mathbf{v}\rangle(t) \tag{43}$$

and average diffusivity

$$\mathbf{D}(t) \equiv \langle\mathbf{rv}\rangle(t)-\langle\mathbf{r}\rangle(t)\langle\mathbf{v}\rangle(t). \tag{44}$$

Figure 4 plots the CM velocity $\mathbf{W}_{\text{CM}}(t)$ for the free, trapped, and total particles alongside the average velocity $\mathbf{W}(t)$ for the free particles. We can see that all measures of velocity begin at 0 due to the Maxwellian initial condition, (33), being spherically symmetric in velocity space. All velocities then increase due to the applied field, with the free particle CM velocity $\mathbf{W}_{\text{CM}}^{(\text{free})}(t)$ and average velocity $\mathbf{W}(t)$ coinciding linearly at early times:

$$\mathbf{W}(t) \approx \mathbf{W}_{\text{CM}}^{(\text{free})}(t) \approx \mathbf{a}t. \tag{45}$$
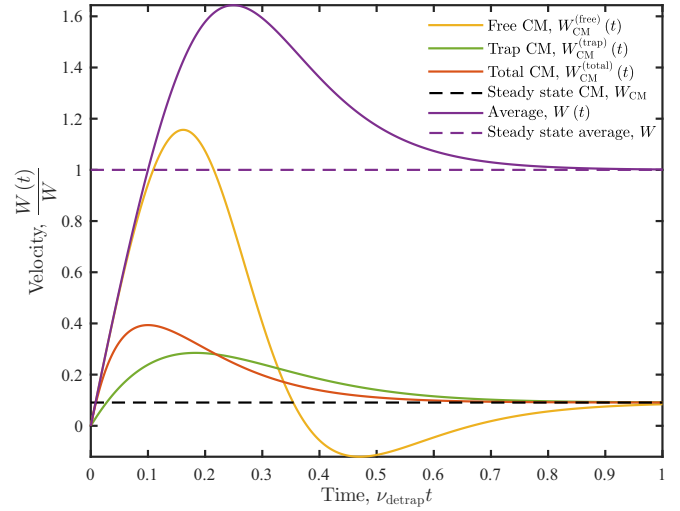

FIG. 4. Plot of the center-of-mass (CM) velocities for free, trapped, and total particles—$\mathbf{W}_{\text{CM}}^{(\text{free})}(t)$, $\mathbf{W}_{\text{CM}}^{(\text{trap})}(t)$, and $\mathbf{W}_{\text{CM}}^{(\text{total})}(t)$—as well as the actual average velocity for the free particles, $\mathbf{W}(t)$, for the exponential waiting time distribution $\phi(t) = \nu_{\text{detrap}}e^{-\nu_{\text{detrap}}t}$. The free particle CM velocity $\mathbf{W}_{\text{CM}}^{(\text{free})}(t)$ and average velocity $\mathbf{W}(t)$ coincide linearly at early times according to Eq. (45). The free particle CM velocity $\mathbf{W}_{\text{CM}}(t)$ is seen to transiently become negative due to particles trapped early near the origin leaving their traps. In this case, there is no recombination present, $\nu_{\text{loss}}^{(\text{free})} = \nu_{\text{loss}}^{(\text{trap})} = 0$, the collision frequency is set to $\nu_{\text{coll}}/\nu_{\text{detrap}} = 1$, and the trapping rate is made sufficiently high so that the transient negative velocity manifests, $\nu_{\text{trap}}/\nu_{\text{detrap}} = 10$. An additional consequence of this relatively high trapping rate is that almost all free particles become trapped early on, allowing the velocities to almost reach their steady-state values after only a single trapping time $\nu_{\text{detrap}}t = 1$.

A similar short-time expansion can be written for the free particle diffusivities:

$$\mathbf{D}(t) \approx \mathbf{D}_{\text{CM}}^{(\text{free})}(t) \approx \frac{\mathbf{I}}{\alpha_0^2}t + \frac{\mathbf{aa}}{12}\big[\nu_{\text{coll}} + 6\big(\nu_{\text{loss}}^{(\text{free})} + \nu_{\text{trap}}\big)\big]t^4. \tag{46}$$

This coincidence between the free particle CM and the average velocities only lasts temporarily before the CM velocity decreases, becoming negative prior to reaching its positive steady-state value. This movement of the free particle CM against the field is due to the processes of trapping and detrapping. Specifically, as all particles are initially untrapped, an unusually large "pulse" of particles is trapped near the origin, which is later released, causing a bias of the distribution and shifting the CM towards the origin. Similarly, as the diffusivity of particles trapped early is initially small, the free particle CM diffusivity $\mathbf{D}_{\text{CM}}^{(\text{free})}(t)$ can also become transiently negative, as the distribution appears to "bunch up" near the origin as the initial pulse is released. Finally, we can see that all CM velocities approach the same steady-state value, while the free particle average velocity approaches a separate steady state. Specifically, the CM transport coefficients, $\mathbf{W}_{\text{CM}}(t)$ and $\mathbf{D}_{\text{CM}}(t)$, approach the values given by Eqs. (83) and (84), while the average transport coefficients, $\mathbf{W}(t)$ and $\mathbf{D}(t)$, approach Eqs. (60) and (76).

IV. HYDRODYNAMIC REGIME AND THE GENERALIZED DIFFUSION EQUATION

A. Chapman-Enskog perturbative solution

The Chapman-Enskog perturbative solution technique [19] assumes that certain terms in the Boltzmann equation are small relative to others, allowing the solution to be written in the form of a Maclaurin series expansion. Traditionally, the Chapman-Enskog expansion assumes that both the explicit and the implicit time derivatives in the Boltzmann equation are small. An implication of this is that the perturbative solution is valid only when the applied field is small. We relax this condition and instead use a generalization of the Chapman-Enskog expansion that only considers small explicit time and space derivatives, known as the hydrodynamic expansion. We expect the resulting solution to be most accurate in the long-distance steady state. Note, however, that in Sec. III B we determined that a steady state is not always attainable for our generalized Boltzmann equation, (1). Specifically, if there is *any* recombination present, all free and trapped particles are eventually lost. To enforce that a steady state is always reached, we introduce the scaled phase-space distribution function of constant particle number $N(0)$:

$$F(t,\mathbf{r},\mathbf{v}) \equiv \frac{N(0)}{N(t)} f(t,\mathbf{r},\mathbf{v}). \quad (47)$$

Substitution into the generalized Boltzmann equation, (1), provides a corresponding generalized Boltzmann equation for this scaled distribution,

$$\left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{r}} + \mathbf{a} \cdot \frac{\partial}{\partial \mathbf{v}}\right) F(t,\mathbf{r},\mathbf{v})$$
$$= -\nu_{\text{coll}}[F(t,\mathbf{r},\mathbf{v}) - n_F(t,\mathbf{r})w(\alpha_{\text{coll}},v)]$$
$$- \nu_{\text{trap}}[R(t)F(t,\mathbf{r},\mathbf{v}) - R(t,\mathbf{r})n_F(t,\mathbf{r})w(\alpha_{\text{detrap}},v)], \quad (48)$$

where $n_F(t,\mathbf{r}) \equiv \int d\mathbf{v} F(t,\mathbf{r},\mathbf{v})$ and we have introduced the ratio of detrapping and trapping rates,

$$R(t,\mathbf{r}) \equiv \frac{\Phi(t) * n(t,\mathbf{r})}{n(t,\mathbf{r})}, \quad (49)$$

and its spatially homogeneous form,

$$R(t) \equiv \frac{\Phi(t) * N(t)}{N(t)}. \quad (50)$$

For the terms we wish to denote as small, we temporarily introduce a multiplicative parameter, δ,

$$\delta\left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{r}}\right) F_\delta(t,\mathbf{r},\mathbf{v}) + \mathbf{a} \cdot \frac{\partial}{\partial \mathbf{v}} F_\delta(t,\mathbf{r},\mathbf{v})$$
$$= -\nu_{\text{coll}}[F_\delta(t,\mathbf{r},\mathbf{v}) - n_F(t,\mathbf{r})w(\alpha_{\text{coll}},v)]$$
$$- \nu_{\text{trap}}[R(t)F_\delta(t,\mathbf{r},\mathbf{v}) - R(t,\mathbf{r})n_F(t,\mathbf{r})w(\alpha_{\text{detrap}},v)], \quad (51)$$

through which we can expand the solution in a power series:

$$F_\delta(t,\mathbf{r},\mathbf{v}) = \sum_{n \geqslant 0} F^{(n)}(t,\mathbf{r},\mathbf{v})\delta^n. \quad (52)$$

This allows the actual solution to be recovered by setting $\delta = 1$ in the above series expansion:

$$F(t,\mathbf{r},\mathbf{v}) = \sum_{n \geqslant 0} F^{(n)}(t,\mathbf{r},\mathbf{v}). \quad (53)$$

The terms in this series solution can be found recursively by substituting the δ expansion, (52), for $F_\delta(t,\mathbf{r},\mathbf{v})$ into the generalized Boltzmann equation, (51), and equating powers of δ:

$$\left[\nu_{\text{coll}} + \nu_{\text{trap}}R(t) + \mathbf{a} \cdot \frac{\partial}{\partial \mathbf{v}}\right] F^{(n)}(t,\mathbf{r},\mathbf{v})$$
$$= -\left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{r}}\right) F^{(n-1)}(t,\mathbf{r},\mathbf{v}). \quad (54)$$

This recurrence relationship is valid for $n \geqslant 1$, with the initial term given separately as

$$\left[1 + \langle\mathbf{v}\rangle^{(0)}(t) \cdot \frac{\partial}{\partial \mathbf{v}}\right] F^{(0)}(t,\mathbf{r},\mathbf{v})$$
$$= \frac{\nu_{\text{coll}}w(\alpha_{\text{coll}},v) + \nu_{\text{trap}}R(t,\mathbf{r})w(\alpha_{\text{detrap}},v)}{\nu_{\text{coll}} + \nu_{\text{trap}}R(t,\mathbf{r})} n_F(t,\mathbf{r}), \quad (55)$$

in terms of its average velocity

$$\langle\mathbf{v}\rangle^{(0)}(t) \equiv \frac{\mathbf{a}}{\nu_{\text{coll}} + \nu_{\text{trap}}R(t)}. \quad (56)$$

Note that here we have enforced the normalization condition

$$\int d\mathbf{v} F^{(0)}(t,\mathbf{r},\mathbf{v}) \equiv n_F(t,\mathbf{r}). \quad (57)$$

In Fourier-transformed velocity space we can write this initial term explicitly,

$$F^{(0)}(t,\mathbf{r},\mathbf{s}) = \tilde{w}(t,\mathbf{r},\mathbf{s})n_F(t,\mathbf{r}), \quad (58)$$

where

$$\tilde{w}(t,\mathbf{r},\mathbf{s}) \equiv \frac{1}{1 + \langle\mathbf{v}\rangle^{(0)}(t) \cdot \iota\mathbf{s}}$$
$$\times \frac{\nu_{\text{coll}}w(\alpha_{\text{coll}},s) + \nu_{\text{trap}}R(t,\mathbf{r})w(\alpha_{\text{detrap}},s)}{\nu_{\text{coll}} + \nu_{\text{trap}}R(t,\mathbf{r})}. \quad (59)$$

We can confirm that this approximate hydrodynamic solution is most accurate in the steady state by noting that its average velocity coincides with the actual average velocity, (43), at late times, $\lim_{t\to\infty} \langle\mathbf{v}\rangle^{(0)}(t) = \lim_{t\to\infty} \langle\mathbf{v}\rangle(t)$. We denote this shared steady-state velocity as

$$\mathbf{W} \equiv \frac{\mathbf{a}}{\nu_{\text{eff}}}, \quad (60)$$

where the separate collision and trapping processes contribute to the effective frequency

$$\nu_{\text{eff}} \equiv \nu_{\text{coll}} + R\nu_{\text{trap}}, \quad (61)$$

defined in terms of the spatially averaged limiting ratio of detrapping and trapping rates,

$$R \equiv \lim_{t\to\infty} R(t). \quad (62)$$

This limit can be evaluated implicitly as satisfying

$$R \equiv \int_0^\infty dt\, \Phi(t) e^{[\nu_{\text{loss}}^{(\text{free})} + \nu_{\text{trap}}(1-R)]t}. \quad (63)$$

Specific expressions for R for various choices of the waiting time distribution $\phi(t)$ are listed in Table I (Appendix A). In terms of this velocity, $\mathbf{W}$, we can write the steady-state limit

of Eq. (59) as

$$\tilde{w}(\mathbf{r},\mathbf{s}) = \frac{1}{1 + \mathbf{W} \cdot \iota \mathbf{s}} \frac{\nu_{\text{coll}} w(\alpha_{\text{coll}},s) + \nu_{\text{trap}} R(\mathbf{r}) w(\alpha_{\text{detrap}},s)}{\nu_{\text{coll}} + \nu_{\text{trap}} R(\mathbf{r})}, \tag{64}$$

where the limiting ratio of detrapping and trapping rates is

$$R(\mathbf{r}) \equiv \lim_{t \to \infty} R(t,\mathbf{r}). \tag{65}$$

In direct analogy with the implicit definition, (63), of R we have the following implicit definition of $R(\mathbf{r})$:

$$R(\mathbf{r}) \equiv \int_0^\infty dt\, \Phi(t) \exp\left\{ \left[\nu_{\text{loss}}^{(\text{free})} + \nu_{\text{trap}}(1 - R(\mathbf{r})) \right. \right. \\ \left. \left. + \frac{1}{n}\frac{\partial}{\partial \mathbf{r}} \cdot n\langle \mathbf{v}\rangle \right] t \right\}. \tag{66}$$

Finally, we can explore the spatial dependence of $\tilde{w}(\mathbf{r},\mathbf{s})$ by considering a perturbation from its spatially averaged state:

$$\tilde{w}(\mathbf{s}) = \frac{\nu_{\text{coll}} w(\alpha_{\text{coll}},s) + \nu_{\text{trap}} R w(\alpha_{\text{detrap}},s)}{\nu_{\text{coll}} + \nu_{\text{trap}} R + \mathbf{a} \cdot \iota \mathbf{s}}. \tag{67}$$

To spatially perturb $\tilde{w}(\mathbf{s})$, we must first spatially perturb R using the definition, (66), of $R(\mathbf{r})$. Introducing the first-order spatial perturbation δR and using the asymptotic velocity in the hydrodynamic regime, $\langle \mathbf{v}\rangle \sim \mathbf{W}$, provides the expression

$$R + \delta R = R\left\langle \exp\left[\left(\frac{1}{n}\frac{\partial n}{\partial \mathbf{r}} \cdot \mathbf{W} - \nu_{\text{trap}} \delta R \right) t \right] \right\rangle, \tag{68}$$

in terms of the time average defined by

$$\langle \eta(t)\rangle \equiv \frac{1}{R}\int_0^\infty dt\, \Phi(t) e^{[\nu_{\text{loss}}^{(\text{free})} + \nu_{\text{trap}}(1-R)]t} \eta(t). \tag{69}$$

Performing a power-series expansion and truncating beyond first order gives the solution $R(\mathbf{r}) = R + \delta R$ as a density gradient expansion up to first order,

$$R(\mathbf{r}) = R + \mathbf{R}^{(1)} \cdot \frac{1}{n}\frac{\partial n}{\partial \mathbf{r}}, \tag{70}$$

in terms of the vector coefficient

$$\mathbf{R}^{(1)} \equiv \frac{R\langle t\rangle}{1 + \nu_{\text{trap}}\langle t\rangle}\mathbf{W}. \tag{71}$$

Now the spatially averaged steady-state velocity distribution $\tilde{w}(\mathbf{s})$ can be spatially perturbed using the density gradient expansion, (70), resulting in, to first spatial order,

$$F^{(0)}(t,\mathbf{r},\mathbf{s}) = \tilde{w}(\mathbf{s}) n_F(t,\mathbf{r}) \\ + \frac{w(\alpha_{\text{detrap}},s) - \tilde{w}(\mathbf{s})}{\nu_{\text{coll}} + \nu_{\text{trap}} R + \mathbf{a} \cdot \iota \mathbf{s}} \nu_{\text{trap}} \mathbf{R}^{(1)} \cdot \frac{\partial}{\partial \mathbf{r}} n_F(t,\mathbf{r}). \tag{72}$$

Using the recurrence relationship, (54), and the continuity equation, (34), to evaluate the explicit time derivative provides the next term, also to first spatial order:

$$F^{(1)}(t,\mathbf{r},\mathbf{s}) = \frac{\mathbf{W}\tilde{w}(\mathbf{s}) - \iota\frac{\partial}{\partial \mathbf{s}}\tilde{w}(\mathbf{s})}{\nu_{\text{coll}} + \nu_{\text{trap}} R + \mathbf{a} \cdot \iota \mathbf{s}} \cdot \frac{\partial}{\partial \mathbf{r}} n_F(t,\mathbf{r}). \tag{73}$$

Similarly, $F^{(2)}(t,\mathbf{r},\mathbf{v})$ can be found and shown to be of minimum second order in spatial gradients. In general, $F^{(n)}(t,\mathbf{r},\mathbf{v})$ is described by a full density gradient expansion of minimum spatial order n. Including all zeroth- and first-order contributions, the generalized Boltzmann equation solution is

$$f(t,\mathbf{r},\mathbf{s}) = \tilde{w}(\mathbf{s})n(t,\mathbf{r}) + \frac{\left[\mathbf{W} - \nu_{\text{trap}}\mathbf{R}^{(1)} - \iota\frac{\partial}{\partial \mathbf{s}}\right]\tilde{w}(\mathbf{s}) + \nu_{\text{trap}}\mathbf{R}^{(1)} w(\alpha_{\text{detrap}},s)}{\nu_{\text{coll}} + \nu_{\text{trap}} R + \mathbf{a} \cdot \iota \mathbf{s}} \cdot \frac{\partial}{\partial \mathbf{r}} n(t,\mathbf{r}). \tag{74}$$

Velocity integration provides Fick's law for the free particle flux,

$$n\langle \mathbf{v}\rangle = \mathbf{W}n - \mathbf{D} \cdot \frac{\partial n}{\partial \mathbf{r}}, \tag{75}$$

which implies that $\mathbf{W}$ is the flux drift velocity and defines the flux diffusion coefficient as

$$\mathbf{D} \equiv \frac{1}{\nu_{\text{eff}}}\left[\frac{\mathbf{I}}{\alpha_{\text{eff}}^2} + (\mathbf{W} + \nu_{\text{trap}}\mathbf{R}^{(1)})\mathbf{W} \right], \tag{76}$$

written in terms of the effective frequency, (61), and the effective temperature,

$$T_{\text{eff}} \equiv \frac{\nu_{\text{coll}}}{\nu_{\text{coll}} + R\nu_{\text{trap}}}T_{\text{coll}} + \frac{R\nu_{\text{trap}}}{\nu_{\text{coll}} + R\nu_{\text{trap}}}T_{\text{detrap}}. \tag{77}$$

Similarly to the flux drift velocity $\mathbf{W}$, the flux diffusion coefficient $\mathbf{D}$ could also have been derived as the long-time limit of the average diffusivity, (44):

$$\mathbf{D} \equiv \lim_{t \to \infty} [\langle \mathbf{rv}\rangle(t) - \langle \mathbf{r}\rangle(t)\langle \mathbf{v}\rangle(t)]. \tag{78}$$

The flux diffusion coefficient derived here differs slightly from what was derived in [14] for a similar phase-space

kinetic model utilizing the same operator for trapping and detrapping. It is likely that they did not consider the spatial dependence in Eq. (49) for the ratio of detrapping and trapping rates $R(t,\mathbf{r})$, as their diffusion coefficient lacked the additional anisotropic component $\frac{\nu_{\text{trap}}}{\nu_{\text{eff}}}\mathbf{R}^{(1)}\mathbf{W}$. Subsequently, their diffusion coefficient is only valid in the isotropic case without an applied field, where $\mathbf{W} = 0$, or in the limit of instantaneous detrapping, where $\mathbf{R}^{(1)} = \mathbf{0}$.

B. Analytical correspondence of transport coefficients

1. Diffusion equations in the hydrodynamic regime

In the previous subsection we have considered a perturbative solution of the generalized Boltzmann equation, (1), written in the hydrodynamic regime as the density gradient expansion, (74). This solution directly provides the flux transport coefficients of velocity, (60), and diffusion, (76). In this subsection, we look to reconcile these results analytically using Eq. (35) for the number density. We can describe the asymptotics of the number density by looking at its poles in

Laplace space, given by solving the dispersion relation [17]:

$$1 - \nu_{\text{coll}}\zeta_{\text{coll}}(\mathbf{k})Z[-(\tilde{p} + \tilde{\nu})\zeta_{\text{coll}}(\mathbf{k})]$$
$$- \nu_{\text{trap}}\Phi(p)\zeta_{\text{detrap}}(\mathbf{k})Z[-(\tilde{p} + \tilde{\nu})\zeta_{\text{detrap}}(\mathbf{k})] = 0. \quad (79)$$

Using the asymptotic-series representation of the plasma dispersion function [18],

$$Z(\xi) = -\frac{1}{\xi}\sum_{n \geqslant 0}\frac{(2n-1)!!}{2^n}\xi^{-2n}$$
$$= -\frac{1}{\xi}\left(1 + \frac{1}{2}\xi^{-2} + \frac{3}{4}\xi^{-4} + \cdots\right), \quad (80)$$

we perform a small-$\mathbf{k}$ expansion and find the root of the dispersion relation to second spatial order,

$$p = -\nu_{\text{trap}}(1 - R) - \nu_{\text{loss}}^{(\text{free})} - \mathbf{W}_{\text{CM}} \cdot \iota\mathbf{k} + \mathbf{D}_{\text{CM}} : \iota\mathbf{k}\iota\mathbf{k}, \quad (81)$$

which corresponds to the diffusion equation

$$\left[\frac{\partial}{\partial t} + \nu_{\text{trap}}(1 - R) + \nu_{\text{loss}}^{(\text{free})}\right.$$
$$\left. + \mathbf{W}_{\text{CM}} \cdot \frac{\partial}{\partial \mathbf{r}} - \mathbf{D}_{\text{CM}} : \frac{\partial^2}{\partial\mathbf{r}\partial\mathbf{r}}\right]n(t,\mathbf{r}) = 0. \quad (82)$$

Here the steady-state CM transport coefficients are defined,

$$\mathbf{W}_{\text{CM}} \equiv \frac{\mathbf{R}^{(1)}}{R\langle t\rangle}, \quad (83)$$

$$\mathbf{D}_{\text{CM}} \equiv \frac{\langle t^2\rangle}{2\langle t\rangle}\mathbf{W}_{\text{CM}}\mathbf{W}_{\text{CM}} - \frac{\mathbf{R}^{(2)}}{R\langle t\rangle}, \quad (84)$$

using the density gradient expansion of $R(\mathbf{r})$,

$$R(\mathbf{r}) = R + \mathbf{R}^{(1)} \cdot \frac{1}{n}\frac{\partial n}{\partial \mathbf{r}} + \mathbf{R}^{(2)} : \frac{1}{n}\frac{\partial^2 n}{\partial\mathbf{r}\partial\mathbf{r}}, \quad (85)$$

now written to second order using the flux diffusion coefficient $\mathbf{D}$,

$$\mathbf{R}^{(2)} \equiv \frac{R\langle t^2\rangle}{2(1 + \nu_{\text{trap}}R\langle t\rangle)^3}\mathbf{W}\mathbf{W} - \frac{R\langle t\rangle}{1 + \nu_{\text{trap}}R\langle t\rangle}\mathbf{D}, \quad (86)$$

where time averages are defined by Eq. (69). Substitution of the root of the dispersion relation into the time operator of the continuity equation yields, to second spatial order,

$$p + \nu_{\text{trap}}[1 - \Phi(p)] + \nu_{\text{loss}}^{(\text{free})} = -\mathbf{W} \cdot \iota\mathbf{k} + \mathbf{D} : \iota\mathbf{k}\iota\mathbf{k}, \quad (87)$$

which corresponds to the generalized diffusion equation

$$\left[\frac{\partial}{\partial t} + \nu_{\text{trap}}(1 - \Phi(t)*) + \nu_{\text{loss}}^{(\text{free})}\right.$$
$$\left. + \mathbf{W} \cdot \frac{\partial}{\partial \mathbf{r}} - \mathbf{D} : \frac{\partial^2}{\partial\mathbf{r}\partial\mathbf{r}}\right]n(t,\mathbf{r}) = 0, \quad (88)$$

in terms of the flux transport coefficients $\mathbf{W}$ and $\mathbf{D}$. This could, alternatively, have been derived by approximating the flux in the continuity equation directly using its density gradient expansion (Fick's law) given by Eq. (75).

2. Approaching the steady state

So far we have considered the continuity equation in both the steady state and the nearly spatially homogeneous state. Using the analytical solution, it is possible to relax this steady-state assumption. We can write the flux exactly by rearranging the continuity equation, (34), in Fourier-Laplace space:

$$\iota\mathbf{k} \cdot \mathcal{L}\{n(t,\mathbf{k})\langle\mathbf{v}\rangle(t)\} = \left[\frac{N(0)}{n(p,\mathbf{k})} - \tilde{p}\right]n(p,\mathbf{k}). \quad (89)$$

Performing a small-$\mathbf{k}$ expansion of the above coefficient of $n(p,\mathbf{k})$ gives an approximate continuity equation valid for large distances or nearly spatially homogeneous states,

$$\left[p + \nu_{\text{trap}}(1 - \Phi(p)) + \nu_{\text{loss}}^{(\text{free})}\right.$$
$$\left. + \mathfrak{W}(p) \cdot \iota\mathbf{k} - \mathfrak{D}(p) : \iota\mathbf{k}\iota\mathbf{k}\right]n(p,\mathbf{k}) = N(0), \quad (90)$$

where the p-dependent velocity and diffusivity are defined in Laplace space,

$$\mathfrak{W}(p) \equiv \frac{\mathbf{a}}{\tilde{p} + \tilde{\nu}}, \quad (91)$$

$$\mathfrak{D}(p) \equiv \frac{\mathbf{I}}{(\tilde{p} + \tilde{\nu})^2}\left[\frac{\tilde{p}}{\alpha_0^2} + \frac{\nu_{\text{coll}}}{\alpha_{\text{coll}}^2} + \frac{\nu_{\text{trap}}\Phi(p)}{\alpha_{\text{detrap}}^2}\right] + \frac{2\mathbf{a}\mathbf{a}}{(\tilde{p} + \tilde{\nu})^3}, \quad (92)$$

although in the time domain $\mathfrak{W}(t)$ and $\mathfrak{D}(t)$ have units of length and area, respectively. Performing the inverse Fourier-Laplace transform yields

$$\left[\frac{\partial}{\partial t} + \nu_{\text{trap}}(1 - \Phi(t)*) + \nu_{\text{loss}}^{(\text{free})} + \mathfrak{W}(t) * \cdot\frac{\partial}{\partial \mathbf{r}}\right.$$
$$\left. - \mathfrak{D}(t)* : \frac{\partial^2}{\partial\mathbf{r}\partial\mathbf{r}}\right]n(t,\mathbf{r}) = 0, \quad (93)$$

which is of a form similar to that of the generalized diffusion equation, but now the "transport coefficients" are time convolved with the number density. It should be noted that, as the flux has been written to second spatial order, the first- and second-order spatial moments of this approximate continuity equation are exact for all times.

V. CONNECTION WITH FRACTIONAL TRANSPORT

Dispersive transport is physically characterized by long-lived traps [2]. For the right choice of parameters, the generalized Boltzmann equation, (1), is capable of modeling such trapped states. A necessary condition for dispersive transport is a waiting time distribution with a divergent mean. One choice is a waiting time distribution with a heavy tail of the power-law form,

$$\phi(t) \sim t^{-(1+\alpha)}, \quad (94)$$

where $0 < \alpha < 1$. This takes the small-p form in Laplace space:

$$\phi(p) \approx 1 - r_\alpha p^\alpha. \quad (95)$$

Additionally, we must enforce that no trap-based recombination occurs, $\nu_{\text{loss}}^{(\text{trap})} = 0$, as this has the effect of prematurely shortening the trapping time so that the mean trapping time

no longer diverges. In this case, the effective waiting time distribution, (5), is no longer weighted by an exponential decay term, $\Phi(t) \rightarrow \phi(t)$, and the continuity equation, (34), becomes

$$\left[\frac{\partial}{\partial t} + \nu_{\text{trap}}(1 - \phi(t)*) + \nu_{\text{loss}}^{\text{(free)}} \right] n(t,\mathbf{r})$$
$$+ \frac{\partial}{\partial \mathbf{r}} \cdot [n(t,\mathbf{r})\langle \mathbf{v}\rangle(t,\mathbf{r})] = 0. \quad (96)$$

We can separate the power-law tail from the waiting time distribution,

$$\phi(t) * n(t,\mathbf{r}) = \psi(t) * n(t,\mathbf{r})$$
$$- r_\alpha \left[{}_0^{\text{C}}\mathcal{D}_t^\alpha n(t,\mathbf{r}) + \frac{t^{-\alpha}}{\Gamma(1-\alpha)} n(0,\mathbf{r}) \right], \quad (97)$$

where the moments of $\psi(t)$ are well defined and the operator of Caputo fractional differentiation of order α is defined as

$$ {}_0^{\text{C}}\mathcal{D}_t^\alpha n(t,\mathbf{r}) \equiv \frac{1}{\Gamma(1-\alpha)} \int_0^t \mathrm{d}\tau (t - \tau)^{-\alpha} \frac{\partial}{\partial \tau} n(\tau,\mathbf{r}). \quad (98)$$

The continuity equation can now be written exactly as

$$\left[\frac{\partial}{\partial t} + r_\alpha \nu_{\text{trap}} {}_0^{\text{C}}\mathcal{D}_t^\alpha + \nu_{\text{trap}}(1 - \psi(t)*) + \nu_{\text{loss}}^{\text{(free)}} \right] n(t,\mathbf{r})$$
$$+ \frac{\partial}{\partial \mathbf{r}} \cdot [n(t,\mathbf{r})\langle \mathbf{v}\rangle(t,\mathbf{r})] = -\frac{r_\alpha \nu_{\text{trap}}}{t^\alpha \Gamma(1-\alpha)} n(0,\mathbf{r}). \quad (99)$$

Truncating the small-p expansion in Laplace space yields a form of the continuity equation valid for long times,

$$\left({}_0^{\text{C}}\mathcal{D}_t^\alpha + \frac{\nu_{\text{loss}}^{\text{(free)}}}{r_\alpha \nu_{\text{trap}}} \right) n(t,\mathbf{r}) + \frac{\partial}{\partial \mathbf{r}} \cdot \left[n(t,\mathbf{r})\frac{\langle \mathbf{v}\rangle(t,\mathbf{r})}{r_\alpha \nu_{\text{trap}}} \right]$$
$$= \left[\delta(r_\alpha \nu_{\text{trap}} t) - \frac{t^{-\alpha}}{\Gamma(1-\alpha)} \right] n(0,\mathbf{r}), \quad (100)$$

now written solely in terms of the time operator of fractional differentiation. Finally, performing a small-$\mathbf{k}$ approximation in Fourier space provides the Captuo time-fractional advection-diffusion equation,

$$\left({}_0^{\text{C}}\mathcal{D}_t^\alpha + \frac{\nu_{\text{loss}}^{\text{(free)}}}{r_\alpha \nu_{\text{trap}}} + \mathbf{W}_\alpha \cdot \frac{\partial}{\partial \mathbf{r}} - \mathbf{D}_\alpha \cdot \frac{\partial^2}{\partial \mathbf{r}\partial \mathbf{r}} \right) n(t,\mathbf{r})$$
$$= \left[\delta(r_\alpha \nu_{\text{trap}} t) - \frac{t^{-\alpha}}{\Gamma(1-\alpha)} \right] n(0,\mathbf{r}), \quad (101)$$

with the fractional transport coefficients defined as

$$\mathbf{W}_\alpha \equiv \frac{\mathbf{W}}{\nu_{\text{trap}} r_\alpha}, \quad (102)$$

$$\mathbf{D}_\alpha \equiv \frac{\mathbf{D}}{\nu_{\text{trap}} r_\alpha}, \quad (103)$$

in terms of the flux drift velocity, (60), and diffusion coefficient, (76), respectively. Note that, as the waiting time distribution $\phi(t)$ has a divergent mean, the flux diffusion coefficient takes the particular form

$$\mathbf{D} \equiv \frac{1}{\nu_{\text{eff}}} \left(\frac{\mathbf{I}}{\alpha_{\text{eff}}^2} + 2\mathbf{WW} \right). \quad (104)$$

There exist generalizations of the time-fractional diffusion equations, like Eq. (101), where spatial derivatives are also taken to be of noninteger order [20]. Physically, these fractional space derivatives arise when particles undergo long jumps in space [21]. This is analogous to the above situation where a time-fractional diffusion equation arose from particles experiencing traps of a long duration. As our model currently allows only for variation in the trapping time, we conclude that to similarly derive a space-fractional diffusion equation would require adjustments to the kinetic theory.

Importantly, we should also note that a similar asymptotic approximation of the generalized Boltzmann equation, (1), does not result in a fractional time operator that acts on the phase-space distribution function. That is, it does not seem possible to derive a similar "fractional Boltzmann equation" from our model. This conclusion differs from that in [13], where a similar kinetic model was used to successfully derive a fractional Boltzmann equation. However, their model was inconsistent, as it simultaneously modeled trapping while also maintaining a constant number of free particles.

VI. SUBORDINATION TRANSFORMATION

As shown in the previous section, the generalized diffusion equation is capable of describing dispersive transport in the same way that the Caputo fractional diffusion equation does. A general feature shared by both of these diffusion equations is the history dependence of their solutions. This is physically due to the existence of trapped states and delayed detrapping. Mathematically, this manifests as a global time operator, be it a fractional derivative or, in the case of the generalized diffusion equation, (88), a convolution with the effective waiting time distribution $\Phi(t)$.

Due to their nature, global operators introduce additional complexity when it comes to solving problems numerically. For example, in finite-difference schemes the computation time generally scales linearly with the number of time steps chosen. The exception is when a global time operator is present, causing the computation time to scale *quadratically* with the number of time steps. Although this increased computational complexity is inherent to these systems, a number of techniques have been suggested to improve upon it for fractional differential equations [22–25]. One approach involves first solving a standard diffusion equation and then performing a subordination integral transformation [11,25] to find the desired solution of a fractional diffusion equation. We generalize this approach to solve the generalized diffusion equation for the free particle number density $n(t,\mathbf{r})$.

Replacing the time operator in the generalized diffusion equation with an explicit time derivative yields a standard diffusion equation with the same linear spatial operator:

$$\left(\frac{\partial}{\partial \tau} + \mathbf{W} \cdot \frac{\partial}{\partial \mathbf{r}} - \mathbf{D} : \frac{\partial^2}{\partial \mathbf{r}\partial \mathbf{r}} \right) u(\tau,\mathbf{r}) = 0. \quad (105)$$

For the same initial conditions, $u(0,\mathbf{r}) \equiv n(0,\mathbf{r})$, we can relate both solutions directly in Laplace space,

$$n(p,\mathbf{r}) = u\big(p + \nu_{\text{loss}}^{\text{(free)}} + \nu_{\text{trap}}[1 - \Phi(p)],\mathbf{r} \big), \quad (106)$$

which, in the time domain, corresponds to the subordination integral transform

$$n(t,\mathbf{r}) \equiv \mathcal{A}u(t,\mathbf{r})$$

$$\equiv \int_0^t \mathrm{d}\tau\, A(\tau, t - \tau) u(\tau, \mathbf{r}), \qquad (107)$$

where the kernel is defined in terms of the inverse Laplace transform $\mathcal{L}^{-1}$,

$$A(\tau, t) \equiv e^{-(\nu_{\mathrm{loss}}^{(\mathrm{free})} + \nu_{\mathrm{trap}})\tau} e^{-\nu_{\mathrm{loss}}^{(\mathrm{trap})} t} \mathcal{L}^{-1}\{e^{\nu_{\mathrm{trap}}\phi(p)\tau}\}. \qquad (108)$$

Appendix B lists kernels corresponding to various choices of the waiting time distribution $\phi(t)$ (Table II).

As a simple example, consider the case of a shifted Dirac delta waiting time distribution,

$$\phi(t) = \delta\big(t - \nu_{\mathrm{detrap}}^{-1}\big), \qquad (109)$$

corresponding to traps of fixed duration $\nu_{\mathrm{detrap}}^{-1}$. In this case, the subordination transformation, (107), simply becomes the summation

$$n(t,\mathbf{r}) = \sum_{k \geqslant 0} n^{(k)}\big(t - k\nu_{\mathrm{detrap}}^{-1}, \mathbf{r}\big), \qquad (110)$$

the terms of which can be physically interpreted as those free particles which have been trapped k times in the past,

$$n^{(k)}(\tau, \mathbf{r}) \equiv H(\tau) \frac{\left(e^{-\frac{\nu_{\mathrm{loss}}^{(\mathrm{trap})}}{\nu_{\mathrm{detrap}}}} \nu_{\mathrm{trap}}\tau \right)^k}{k!} e^{-(\nu_{\mathrm{loss}}^{(\mathrm{free})} + \nu_{\mathrm{trap}})\tau} u(\tau, \mathbf{r}), \qquad (111)$$

where $H(\tau)$ is the Heaviside step function. Figure 5 plots this solution on a one-dimensional unbounded domain $z \in (-\infty, \infty)$ for the impulse initial condition $n(0,z) \equiv N(0)\delta(z)$ and shows its construction in terms of the corresponding Gaussian solution of the standard diffusion equation, (105):

$$u(t,z) = \frac{N(0)}{2\sqrt{\pi D t}} \exp\left[-\left(\frac{z - Wt}{2\sqrt{D t}} \right)^2 \right]. \qquad (112)$$

Note that as the subordination transformation acts on time alone, the same mapping operator $\mathcal{A}$ can be used to map between spatial moments of the normal and generalized diffusion equations,

$$\langle \mathbf{r} \rangle^{(\mathrm{GDE})}(t) = \mathcal{A}\langle \mathbf{r} \rangle^{(\mathrm{SDE})}(t), \qquad (113)$$

$$\langle \mathbf{rr} \rangle^{(\mathrm{GDE})}(t) = \mathcal{A}\langle \mathbf{rr} \rangle^{(\mathrm{SDE})}(t), \qquad (114)$$

where the superscript "(GDE)" denotes the generalized diffusion equation, (88), and "(SDE)" denotes the standard diffusion equation, (105). Additionally, the commutation relationship,

$$\left[\mathcal{A}, \frac{\mathrm{d}}{\mathrm{d}t} \right] \equiv \big[\nu_{\mathrm{loss}}^{(\mathrm{free})} + \nu_{\mathrm{trap}}(1 - \Phi(t)*) \big] \mathcal{A}, \qquad (115)$$

also allows the CM transport coefficients for each diffusion equation to be related through the subordination transformation $\mathcal{A}$,

$$\mathbf{W}_{\mathrm{CM}}^{(\mathrm{GDE})}(t) = \mathcal{A}\mathbf{W}_{\mathrm{CM}}^{(\mathrm{SDE})}(t) - \big[\nu_{\mathrm{loss}}^{(\mathrm{free})} + \nu_{\mathrm{trap}}(1 - \Phi(t)*) \big]$$

$$\times \mathcal{A}\langle \mathbf{r} \rangle^{(\mathrm{SDE})}(t), \qquad (116)$$
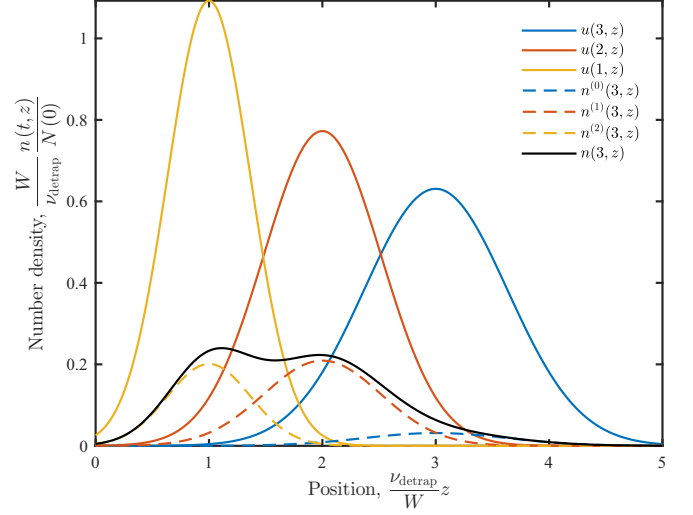

FIG. 5. The solution $n(t,z)$ of the generalized diffusion equation, (88), is written by sampling from the Gaussian solution $u(t,z)$ of the standard diffusion equation, (105), at multiple points in time. This is done using the subordination transformation, (107). Here, traps are of a fixed duration, $\nu_{\mathrm{detrap}}t = 1$, as described by the waiting time distribution $\phi(t)/\nu_{\mathrm{detrap}} = \delta(\nu_{\mathrm{detrap}}t - 1)$. In this case, the subordination transformation becomes the summation, (110), whose individual terms $n^{(k)}(t,z)$ correspond to those free particles which have been trapped k times in the past. Here, there is no recombination, $\nu_{\mathrm{loss}}^{(\mathrm{free})} = \nu_{\mathrm{loss}}^{(\mathrm{trap})} = 0$, the trapping rate is set to $\nu_{\mathrm{trap}}/\nu_{\mathrm{detrap}} = 1$, and the diffusion coefficient is made small so as to emphasize each individual Gaussian's contribution to the solution, $D\nu_{\mathrm{detrap}}/W^2 = 1/15$.

$$\mathbf{D}_{\mathrm{CM}}^{(\mathrm{GDE})}(t) = \mathcal{A}\mathbf{D}_{\mathrm{CM}}^{(\mathrm{SDE})}(t) - \tfrac{1}{2}\big[\nu_{\mathrm{loss}}^{(\mathrm{free})} + \nu_{\mathrm{trap}}(1 - \Phi(t)*) \big]$$

$$\times \mathcal{A}[\langle \mathbf{rr} \rangle^{(\mathrm{SDE})}(t) - \langle \mathbf{r} \rangle^{(\mathrm{SDE})}(t)\langle \mathbf{r} \rangle^{(\mathrm{SDE})}(t)], \qquad (117)$$

where the CM transport coefficients are defined in terms of spatial moments according to Eqs. (39) and (40).

VII. CONCLUSION

We have considered a general phase-space kinetic equation, (1), which considers transport of charged particles via both delocalized and localized states, including collisional trapping, detrapping, and recombination processes. The solution of this model was found analytically in Fourier-Laplace space, which in turn provided analytical expressions for phase-space averaged spatial and velocity moments. These moments provided determination of both CM and flux transport coefficients. As a consequence of the processes of trapping and detrapping, the free particle CM transport coefficients were found to be transiently negative for high trapping rates. We have also shown that, in the hydrodynamic regime, a number of diffusion equations accurately describe the generalized Boltzmann equation, (1). These include the standard diffusion equation, (82), the generalized diffusion equation, (88), and, when transport is dispersive, the Caputo fractional diffusion equation, (101). Finally, we have written the solution of the generalized diffusion equation, (88), as a subordination transformation, (107), from the corresponding solution of a standard diffusion equation, (105).

The model of focus in this work, Eqs. (1)–(8), was considered only for constant process rates, independent of the particle energy. Extension to higher order balance equations (e.g., momentum and energy) including energy-dependent rates represents the next step in development of this model. This will facilitate the generalization of well-known empirical relationships (e.g., generalized Einstein relations, Wannier energy relation, mobility expressions) to include combined localized/delocalized transport systems. Additionally, for our model to be applied to transport in dense fluids, it is necessary to have reasonable inputs ν_{trap} and $\phi(t)$. Although there are many investigations of trapping, for example, light-particle solvation, in the literature [26–28], including free energy changes and solvation time scales, none of these directly produces an energy-dependent trapping frequency or waiting time distribution. The *ab initio* calculation of such capture collision frequencies and waiting time distributions in liquids and dense gases remains the focus of our current attention.

APPENDIX A: LIST OF LIMITING RATIOS OF DETRAPPING AND TRAPPING RATES R

TABLE I. Specific cases of the dimensionless quantity R that is defined in Eq. (62) as the limiting ratio of particle detrapping and trapping rates. From its alternate definition, (63), it can be seen that R is a function of the difference in recombination loss rates $\Delta\nu_{\text{loss}} \equiv \nu_{\text{loss}}^{(\text{free})} - \nu_{\text{loss}}^{(\text{trap})}$.

Trap type	Waiting time distribution $\phi(t)$	Limiting ratio of detrapping and trapping rates R
Instantaneous	$\delta(t)$	1
Fixed delay	$\delta(t - \nu_{\text{detrap}}^{-1})$	$\frac{\nu_{\text{detrap}}}{\nu_{\text{trap}}} W_{\text{Lambert}}\left[\frac{\nu_{\text{trap}}}{\nu_{\text{detrap}}} \exp\left(\frac{\Delta\nu_{\text{loss}} + \nu_{\text{trap}}}{\nu_{\text{detrap}}}\right)\right]$ [a]
Poisson process	$\nu_{\text{detrap}} e^{-\nu_{\text{detrap}} t}$	$\frac{\Delta\nu_{\text{loss}} + \nu_{\text{trap}} - \nu_{\text{detrap}} + \sqrt{(\Delta\nu_{\text{loss}} + \nu_{\text{trap}} + \nu_{\text{detrap}})^2 - 4\nu_{\text{detrap}}\Delta\nu_{\text{loss}}}}{2\nu_{\text{trap}}}$
Multiple trapping model	$\alpha\nu_0(\nu_0 t)^{-\alpha-1}\gamma(\alpha+1, \nu_0 t)$	[b]

[a]The Lambert W function is defined as satisfying

$$W_{\text{Lambert}}(z) e^{W_{\text{Lambert}}(z)} \equiv z. \tag{A1}$$

[b]R is the positive solution of the transcendental equation,

$$R = -\frac{\alpha\pi}{\sin\alpha\pi}\left(-\frac{\Delta\nu_{\text{loss}} + \nu_{\text{trap}}(1-R)}{\nu_0}\right)^\alpha - \alpha\Phi_{\text{Lerch}}\left(\frac{\Delta\nu_{\text{loss}} + \nu_{\text{trap}}(1-R)}{\nu_0}, 1, -\alpha\right), \tag{A2}$$

where the Lerch transcendent is defined as

$$\Phi_{\text{Lerch}}(z, s, a) \equiv \sum_{n \geq 0} \frac{z^n}{(n+a)^s}. \tag{A3}$$

APPENDIX B: LIST OF SUBORDINATION TRANSFORMATION KERNELS $A(\tau, t)$

TABLE II. Specific cases of the integral kernel, (108), $A(\tau, t)$, used in the subordination transformation, (107), that maps from the solution of the standard diffusion equation, (105), to that of the generalized diffusion equation, (88).

Trap type	Waiting time distribution $\phi(t)$	Scaled subordination kernel $e^{(\nu_{\text{loss}}^{(\text{free})} + \nu_{\text{trap}})\tau} A(\tau, t)$
Instantaneous	$\delta(t)$	$e^{\nu_{\text{trap}}\tau} e^{-\nu_{\text{loss}}^{(\text{trap})} t}\delta(t)$
Fixed delay	$\delta(t - \nu_{\text{detrap}}^{-1})$	$e^{-\nu_{\text{loss}}^{(\text{trap})} t}\frac{(\nu_{\text{trap}}\tau)^{\nu_{\text{detrap}} t}}{\Gamma(1 + \nu_{\text{detrap}} t)} \text{Ш}_{\nu_{\text{detrap}}^{-1}}(t)$ [a]
Poisson process	$\nu_{\text{detrap}} e^{-\nu_{\text{detrap}} t}$	$\delta(t) + \frac{1}{t} e^{-\nu_{\text{detrap}} t}\sqrt{\nu_{\text{trap}}\tau\nu_{\text{detrap}} t} I_1(2\sqrt{\nu_{\text{trap}}\tau\nu_{\text{detrap}} t})$ [b]
Multiple trapping model	$\alpha\nu_0(\nu_0 t)^{-\alpha-1}\gamma(\alpha+1, \nu_0 t)$	$e^{-\nu_{\text{loss}}^{(\text{trap})} t}\left[\frac{1}{t_\alpha} l_\alpha\left(\frac{t}{t_\alpha}\right) * g(t)\right]$ [c]

[a]The Dirac comb of period T is defined as

$$\text{Ш}_T(t) \equiv \sum_{n \in \mathbb{Z}} \delta(t - nT). \tag{B1}$$

[b]The modified Bessel function of the first kind of order ν is defined as

$$I_\nu(z) \equiv \sum_{n \geq 0} \frac{(\frac{z}{2})^{2n+\nu}}{n!\Gamma(1 + n + \nu)}. \tag{B2}$$

^{c}The characteristic time t_α is defined as

$$v_0 t_\alpha \equiv \sqrt[\alpha]{\frac{\alpha\pi}{\sin\alpha\pi}\, v_{\text{trap}}\tau}\,; \tag{B3}$$

we define in Laplace space the one-sided Lévy density,

$$l_\alpha(p) \equiv e^{-p^\alpha}, \tag{B4}$$

and in Laplace space

$$g(p) \equiv \exp\left[-\alpha\Phi_{\text{Lerch}}\left(-\frac{p}{v_0}, 1, -\alpha\right)\right], \tag{B5}$$

where the Lerch transcendent $\Phi_{\text{Lerch}}(z,s,a)$ is given by Eq. (A3).

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