FROM A CLANNISH RANDOM WALK TO GENERALIZED SMOLUCHOWSKI EQUATION

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A diffusion equation with a functional drift (generalized Smoluchowski equation) has been derived from the clannish random walk (nonlinear discrete master equation) for both probability density and velocity fields, in case of 1D. A relation between Burgers and generalized Smoluchowski equations as well as between concentration and velocity fields, has been discussed.

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1. Introduction

Diffusion as a random molecular motion has been successfully described for the first time by Einstein and Smoluchowski while considering the Brownian particles suspended in a fluid. In their approach the concentration W of suspended particles was given by:

$$\frac{\partial W}{\partial t} = D\,\mathbf{div}\,\mathbf{grad}\,W\,, \tag{1}$$

where $D = \kappa T/\beta$ is a diffusion coefficient with $\beta = 6\pi a\eta m = \xi m$, "$a$" is a radius of the particle of mass m, η and ξ are viscosity and friction coefficients, respectively.

This simple diffusion equation is valid only when there is no external force present. When the force "κ" acts on a system then equation (1) must be replaced by the following Smoluchowski equation:

$$\frac{\partial W}{\partial t} = \mathbf{div}[D\mathbf{grad}W - cW]\,, \tag{2}$$

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where $c = \kappa/\beta$ is velocity of a Brownian particle under the force κ in a viscous solution (drift constant).

In $1D$ case, and D, c constant, we can rewrite equation (2) as:

$$\frac{\partial W}{\partial t} = -c\frac{\partial W}{\partial x} + D\frac{\partial^2 W}{\partial x^2}\,. \tag{3}$$

Equation (3) will stand for the reference point in our further considerations. It is worthy to observe that concentration $W(x,t)$, when properly normalized, can be treated as probability density [1].

A very natural extension of equation (1), especially for experimentalists, is to consider it when diffusion coefficient depend upon concentration (probability density) [2,3]

$$\frac{\partial W}{\partial t} = \mathbf{div}[D(W)\mathbf{grad}W]\,, \tag{4}$$

where $D(W) = D_0[1 + f(W)]$ or $D(W) = D_0\mathrm{e}^{aW}$.

In this paper we will consider the process in which diffusion coefficient is constant but the drift coefficient depends on concentration *i.e.*

$$\frac{\partial W}{\partial t} = -cf(W)\frac{\partial W}{\partial x} + D\frac{\partial^2 W}{\partial x^2} \tag{5}$$

and we will call it the generalized Smoluchowski equation. The function $f(W)$ takes some special forms resulting from the clannish random walk consideration.

2. The generalized Smoluchowski equation as continuum limit of clannish random walk process

This is a well known fact that one of the fundamental problems of nonequilibrium statistical physics *i.e.* how does the microscopic dynamics of atoms and molecules lead to equations, such as Burgers, Navier–Stokes, *etc.* can be, at least partially, answered by the suitably constructed random walks problems. The answers have been provided in case of a simple Smoluchowski equation (3) [6,8], its extension based on the generalized master equation to time dependent coefficients [9], and also to diffusion equation (1) with diffusion coefficient depending upon concentration [10]. A very elegant, alternative approach to the transport dynamics has been presented by means of fractional calculus [11]. In this paper we will show, however, how to derive the nonlinear Smoluchowski type equation with nonlinear drift term from the generalized master equation *i.e.* we will follow the traditional way of introducing the interactions between particles which give rise to local equilibrium states characterized by the conserved quantities which then satisfy hydrodynamic-type equations. Following Montroll and West [10] we develop our consideration of diffusion with functional drift by analysis of a phenomenological random walk known as a "clannish random walk". Considering a single species of random walk in a manner in which each step reflects the concentration of walkers to the left and right of the one being examined, we can write a sort of discrete master equation for the particle's probability density

$$W(x,t+\tau) = \hat{p}W(x-\delta,t) + \hat{q}W(x+\delta,t)\,, \tag{6}$$

where

$$\hat{p} = p\Big\{1+\mu[W(x,t)-W(x-2\delta,t)]\Big\}, \tag{7}$$

$$\hat{q} = q\Big\{1+\mu[W(x,t)-W(x+2\delta,t)]\Big\}, \tag{8}$$

are the probabilities of going to the right or left respectively, p, q are constants, and $\mu = \mu(W)$ is a coupling function reflecting the nature of interactions (long range) between random walkers.

Consequently

$$\hat{p} + \hat{q} = 1\,. \tag{9}$$

Expanding subsequent terms in equation (6) in a Taylor series with remainder, and taking into account that:

$$\lim_{\delta\to 0}(\hat{p}-\hat{q}) = -W(x,t)(p-q) \tag{10}$$

for suitably chosen function $\mu(W)$, we have

$$W_t = -(p-q)\frac{\delta}{\tau}WW_x + \frac{1}{2}\frac{\delta^2}{\tau}W_{xx} \tag{11}$$

which can be rewritten as

$$W_t = -cWW_x + DW_{xx}\,, \tag{12}$$

where

$$c = (p-q)\frac{\delta}{\tau} \qquad \text{and} \qquad D = \frac{1}{2}\frac{\delta^2}{\tau}\,. \tag{13}$$

Equation (12), known as Burgers equation [17], can be rewritten as the generalized Smoluchowski equation

$$W_t = -\hat{c}W_x + DW_{xx}\,, \tag{14}$$

where $\hat{c}(W) = cW$ is a functional drift coefficient.

Following essentially the same procedure we can arrive at the more general equation

$$W_t = -cf(W)W_x + DW_{xx} \tag{15}$$

which has the following divergence form

$$W_t = \frac{\partial}{\partial x}\left(-c\int f(W)dW + DW_x\right) \tag{16}$$

for some functions of C^0 class.

3. The probability density versus velocity fields

To derive an equation of the transport type on the phenomenological level two things are required:

(i) an equation of flux (current) $-j$,

(ii) continuity equation $\frac{\partial W}{\partial t} + \nabla j = 0$.

Taking into account that the flux can also be expressed in terms of the local particle velocity $V(x,t)$ through

$$j(x,t) = V(x,t)W(x,t) \tag{17}$$

we can derive a set of PDEs for the particle probability density (normalized concentration) and corresponding local particle velocity fields.

If we restrict ourselves to the case of a constant diffusion coefficient then for a simple, Fickian diffusion

$$\frac{\partial W}{\partial t} = D\frac{\partial^2 W}{\partial x^2} \tag{18}$$

we obtain a Burgers type equation for the corresponding velocity field [10] *i.e.*

$$V_t = \frac{\partial}{\partial x}\left(-V^2 + D\frac{\partial V}{\partial x}\right). \tag{19}$$

It is interesting to see how it looks like in case of more complicated equations of concentration fields.

3.1. Smoluchowski equation with constant drift

This is the case represented by Eq. (3) for which flux is given by

$$j = -D\frac{\partial W}{\partial x} + cW \tag{20}$$

and, at the same time

$$j = V(x,t)W(x,t) \tag{21}$$

from Eqs. (20) and (21) we get

$$V(x,t) = -D\frac{\partial \ln W}{\partial x} + c\,. \tag{22}$$

After differentiating equation (22) with respect to time, and changing the order of differentiation, we get

$$\frac{\partial V}{\partial t} = -D\frac{\partial}{\partial x}\left(\frac{1}{W}\frac{\partial W}{\partial t}\right) = -D\frac{\partial}{\partial x}\left(\frac{\partial \ln W}{\partial t}\right). \tag{23}$$

Taking into account the continuity equation

$$\frac{\partial V}{\partial t} = -\frac{\partial j}{\partial x} = -\frac{\partial (VW)}{\partial x} \tag{24}$$

we can write

$$\frac{\partial V}{\partial t} = D\frac{\partial}{\partial x}\left(\frac{\partial V}{\partial x} + V\left(\frac{\partial \ln W}{\partial x}\right)\right) \tag{25}$$

and further, through equation (22),

$$\frac{\partial V}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial V}{\partial x} - V(V-c)\right) \tag{26}$$

or

$$\frac{\partial V}{\partial t} = D\frac{\partial^2 V}{\partial x^2} - (2V-c)\frac{\partial V}{\partial x} \tag{27}$$

i.e. type of Burgers equation or Smoluchowski equation with drift coefficient $\hat{c}(V) = 2V - c$.

3.2. Smoluchowski equation with a "functional" drift — Burgers equation

The case is represented by equation (12) for which the flux is given by

$$j = -D\frac{\partial W}{\partial x} + \frac{1}{2}cW^2\,, \tag{28}$$

where the drift coefficient $\hat{c}(W) = \frac{1}{2}cW$.

Following similar steps as in Section 3.1 we finally get

$$\frac{\partial V}{\partial t} = D\frac{\partial^2 V}{\partial x^2} - 2V\frac{\partial V}{\partial x} \tag{29}$$

i.e. equation identical to equation (19) derived for a simple, Fickian diffusion.

4. Results and discussion

To begin with we would like to comment on the nature of drift and convective terms that appear in Smoluchowski (3) or/and Burgers (12) equations. Drift is a consequence of a potential field under which the Brownian particle undergoes the deterministic displacement. Convection is a process in which the whole phase with the Brownian particle immerse in it, flows due to the external force. So, in spite of formal, mathematical similarities these two processes are entirely different. In the present work we consider the process of diffusion with drift contrary to "diffusion process in a flow" considered elsewhere [4]. In this situation we also would like to comment on the differences between the Burgers and generalized Smoluchowski equations. Namely, Burgers equation, when addressed to velocity field [17], shows nonlinear behaviour controlled by velocity itself — which is a bifurcation parameter. In this context velocity is unbounded quantity fulfilling however the energy conservation. In our work the Burgers equation is used for description of normalized concentration (probability density) field which is bounded [0,1], and essentially shows a linear behaviour as well as fulfils the mass conservation law. Since we deal with high viscosity limit, at which the Fokker–Planck equation simplifies to Smoluchowski equation, respective velocity field is regular and bounded (it is pretty natural to expect a small velocity of Brownian particle in a high viscosity medium). In this situation, we call the Burgers equation the generalized Smoluchowski equation with drift coefficient linearly dependent upon the concentration or velocity.

We can easily find that on a molecular level, at which the drift coefficient is proportional to the difference between probabilities of a molecules jump to the left or right, these probabilities should depend on probability density (concentration). This is equivalent, in a sense, to the long correlation between molecules with a short correlation not present (constant diffusion coefficient). It is interesting to notice that the vector field whose components are W and $DW_x - \frac{1}{2}cW^2$ in $x - t$ plane is irrotational, so that a potential field must exist $Q(x,t)$ such that [19]

$$W = Q_x\,, \qquad DW_x - \frac{1}{2}cW^2 = Q_t\,. \tag{30}$$

Replacing W by Q_x we obtain

$$Q_t = DQ_{xx} - \frac{1}{2}cQ_x^2 \,. \tag{31}$$

Although this equation is still nonlinear, the nonlinearity is quadratic and an exponential transformation is sometimes effective. Namely,

$$\Psi(x,t) = \exp\left(-\frac{c}{2D}Q(x,t)\right) \tag{32}$$

leads to

$$\Psi_t = D\,\Psi_{xx} \tag{33}$$

i.e. the familiar simple diffusion equation.

To obtain $W(x,t)$ *i.e.* a solution of generalized Smoluchowski equation from any solution of (33) we use

$$W(x,t) = -\frac{2D}{c}\frac{\Psi_x(x,t)}{\Psi(x,t)} \,. \tag{34}$$

As can be seen from the above the generalized Smoluchowski equation is a high viscosity limit of the Fokker–Planck equation, and, on the other hand of the Burgers equation as well, since the high viscosity implies small average velocity of a Brownian particle, and consequently no singularities in a velocity field.

5. Concluding remarks

The clannish random walk approach, concluded in a form of nonlinear discrete master equation is an effective tool for generating a wide class of transport equations. In this paper we have considered a functional drift due to the concentration dependence of jumping probability of a Brownian particle. The high viscosity limit (polymer solutions) gave us the possibility to distinguish between two, mathematically identical equations

$$W_t = -cWW_x + DW_{xx} \tag{35}$$

i.e. the Burgers equations known as being a simplified version of the Navier–Stokes equation, and showing an essential nonlinear behaviour [18] and

$$W_t = -\hat{c}(W)W_x + DW_{xx} \,, \tag{36}$$

where $\hat{c}(W) = cW$ is a functional drift coefficient. Equation (36) gives regular solutions with a functional drift coefficient $\hat{c}(W)$ that accounts for the mutual interactions between transported molecules. Last but not least we would like to mention that in spite of a clear procedure of solving a Burgers type equations, provided by Eqs. (30)–(34), a particular problem might be difficult to handle.

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