Physica A 515 (2019) 665–670

Contents lists available at ScienceDirect

Physica A

journal homepage: www.elsevier.com/locate/physa

Equilibrium of a Brownian particle with coordinate dependent diffusivity and damping: Generalized Boltzmann distribution

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HIGHLIGHTS

- Derivation of Fick's law for coordinate dependent diffusivity is given.
- Modified Fick's law indicates the validity of the Fokker–Planck equation as derived from Kramers–Moyal expansion.
- The outcome is a modified Boltzmann distribution involving coordinate dependent diffusivity and damping.
- This modified Boltzmann distribution indicates that a Langevin dynamics with additive noise can be used for such systems.

ARTICLE INFO

Article history:
Received 6 February 2018
Received in revised form 26 September 2018
Available online xxxx

Keywords:
Diffusion
Brownian motion
Coordinate dependent damping
Equilibrium
Fick's law

ABSTRACT

Fick's law for coordinate dependent diffusivity is derived. Corresponding diffusion current in the presence of coordinate dependent diffusivity is consistent with the form as given by Kramers–Moyal expansion. We have obtained the equilibrium solution of the corresponding Smoluchowski equation. The equilibrium distribution is a generalization of the Boltzmann distribution. This generalized Boltzmann distribution involves an effective potential which is a function of coordinate dependent diffusivity. We discuss various implications of the existence of this generalized Boltzmann distribution for equilibrium of systems with coordinate dependent diffusivity and damping.

1. Introduction

Coordinate dependence of diffusivity and damping [1] of Brownian particles in a confined liquid has been observed in many experiments [2–4]. In the context of protein folding, position dependent diffusion is supposed to play a major role [5,6]. Position dependent diffusion is being taken into consideration even for hydrodynamics of optical systems [7,8]. In the context of equilibrium, coordinate dependent damping and diffusion are sources of long standing controversy [9–15]. Brownian motion with coordinate dependent diffusion and damping, in general, is discussed in this paper. In such systems, homogeneity of space broken by space dependent damping and diffusion (boundary effects in small systems [2]) cannot be captured by a conservative force. We show that the equilibrium probability distribution in such systems is a generalization of the Boltzmann distribution. The generalization is in the appearance of an effective potential which is a function of the coordinate dependent diffusivity.

This generalized distribution is normally overlooked as the equilibrium distribution of such systems in the conventional literature [9–15]. To arrive at the Boltzmann distribution for such systems, in the standard literature [9–15], one effectively considers the diffusion current to be Fickian. Whereas, in the Smoluchowski dynamics the diffusion current comes out

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https://doi.org/10.1016/j.physa.2018.10.017
0378-4371/

to be non-Fickian. In this paper, we try to resolve this controversy by giving an alternative derivation of the non-Fickian form of the diffusion current based on the definition of local diffusivity. This derivation assumes importance in view of the controversy over the form of diffusion current [9,16] or effective consideration of the Fickian current to arrive at Boltzmann distribution [10–15].

The paper is organized in the following way. We first present a short discussion of standard Brownian motion in the presence of constant diffusion and damping. Then we discuss the Kramers–Moyal expansion and coefficients to outline the standard derivation of the drift and diffusion coefficients in the Itô/Stratonovich [17,18] convention. After that, we show the derivation of non-Fickian diffusion current starting from the definition of the local diffusivity and obtain the generalized Boltzmann distribution as the equilibrium solution of the standard Smoluchowski equation. We conclude the paper with a discussion on the implications of existence of this generalized Boltzmann distribution.

2. Brownian motion with constant diffusion and damping

The Langevin dynamics of a Brownian particle (of centre of mass x) with a damping constant Γ, diffusivity D, in equilibrium at the minimum of a potential $\mathrm{U}(x)$ at temperature T is

$$\frac{\partial x}{\partial t} = -\frac{1}{\Gamma}\frac{\partial \mathrm{U}(x)}{\partial x} + \frac{\sqrt{2\mathrm{kT}\Gamma}}{\Gamma}\eta(t). \tag{1}$$

In this dynamics, k is the Boltzmann constant and $\eta(t)$ is a Gaussian white noise of zero mean. The part of the stochastic term under square root is present to ensure eventual convergence at large times to equilibrium characterized by the Boltzmann distribution. Considering diffusion alone in the absence of the confining potential $\mathrm{U}(x)$, diffusivity of the system can be identified easily to follow the Stokes–Einstein relation $\mathrm{D} = \frac{\mathrm{kT}}{\Gamma}$ [19]. This identification practically fixes the strength of the stochastic term which is also extensively looked at from the perspective of fluctuation–dissipation theorem [20].

The Fokker–Planck equation (also called the Smoluchowski equation in the context of over-damped dynamics) for the dynamics of the probability density $\rho(x,t)$ of the Brownian particle is given by

$$\frac{\partial \rho(x,t)}{\partial t} = \frac{\partial}{\partial x}\left[\frac{\rho(x,t)}{\Gamma}\frac{\partial \mathrm{U}(x)}{\partial x} + \mathrm{D}\frac{\partial \rho(x,t)}{\partial x}\right] = -\frac{\partial}{\partial x}j(x,t). \tag{2}$$

This is the equation of continuity for the conserved probability where $j(x,t)$ is probability current density. For a non-equilibrium stationary state the divergence of the probability current density has to vanish, whereas, for equilibrium $j(x,t)$ should be zero everywhere in space to maintain detailed balance. Since the space is inhomogeneous in the presence of a conservative force, presence of any probability current will produce entropy which cannot be there in equilibrium. This is where the local cancellation of the drift produced by conservative force $\mathrm{F}(x) = -\frac{\partial \mathrm{U}(x)}{\partial x}$ and diffusion component of the probability current is required in equilibrium. Equilibrium distribution as obtained by balancing the drift and diffusion currents is the Boltzmann distribution $\rho(x) = \mathrm{N}e^{-\frac{\mathrm{U}(x)}{\Gamma \mathrm{D}}} = \mathrm{N}e^{-\frac{\mathrm{U}(x)}{\mathrm{kT}}}$ where N is a suitable normalization constant.

Keeping in mind the fundamental requirement of the local vanishing of the probability current in equilibrium, the next most important thing is the Fick's law that provides the structure of the diffusion current. Having the Fick's law in place, the equilibrium distribution is completely determined by detailed balance to be $\rho(x) = \mathrm{N}e^{-\frac{\mathrm{U}(x)}{\Gamma \mathrm{D}}}$. The Stokes–Einstein relation provides additional structure and brings in the Boltzmann distribution through the introduction of the temperature. However, neither the Stokes–Einstein relation nor the resulting Boltzmann distribution is an essential requirement for equilibrium because detailed balance never explicitly needs these conditions.

Existence of coordinate dependent damping and diffusion brings in additional parameters on top of conservative force that break the homogeneity of space even in the absence of a conservative force. But, the Boltzmann distribution does not at all reflect this reality. It completely disregards the presence of these additional symmetry breaking agents and hence cannot, in general, represent equilibrium distribution for systems with coordinate dependent damping and diffusivity.

3. Kramers–Moyalexpansion and the Smoluchowski equation

The Smoluchowski (over-damped Fokker–Planck) equation is the one obtained by truncating the Kramers–Moyal expansion at the term containing the second Kramers–Moyal coefficient and that is a very standard result. The dynamics of the probability density as obtained from the Kramers–Moyal expansion can be written as

$$\frac{\partial P(x,t)}{\partial t} = \sum_{n=1}^{\infty}\left(-\frac{\partial}{\partial x}\right)^{n} D^{(n)}(x,t)P(x,t), \tag{3}$$

where the Kramers–Moyal expansion coefficients are given by

$$D^{(n)}(x,t) = \frac{1}{n!}\lim_{\tau\to 0}\frac{1}{\tau}\langle[\xi(t+\tau)-x]^{n}\rangle \tag{4}$$

with $\xi(t) = x$ and the angular brackets represent average over noise [21]. By Pawula's theorem, the transition probability remaining positive, the number of terms Eq. (3) can have on the right hand side are either for $n = 1, 2$ or infinitely many. The