Physica A 494 (2018) 218–224

Contents lists available at ScienceDirect

Physica A

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

Equilibrium stochastic dynamics of a Brownian particle in inhomogeneous space: Derivation of an alternative model

A. Bhattacharyay

Indian Institute of Science Education and Research, Pune, India

HIGHLIGHTS

- Derivation of Brownian dynamics from a microscopic Hamiltonian is given.
- Derivation is based on state dependent coupling with the bath.
- The model has a modified Boltzmann distribution in equilibrium.

ARTICLE INFO

Article history:
Received 21 December 2016
Received in revised form 3 October 2017
Available online 9 December 2017

Keywords:
Fluctuation–dissipation
Diffusion
Brownian motion

ABSTRACT

An alternative equilibrium stochastic dynamics for a Brownian particle in inhomogeneous space is derived. Such a dynamics can model the motion of a complex molecule in its conformation space when in equilibrium with a uniform heat bath. The derivation is done by a simple generalization of the formulation due to Zwanzig for a Brownian particle in homogeneous heat bath. We show that, if the system couples to different number of bath degrees of freedom at different conformations then the alternative model gets derived. We discuss results of an experiment by Faucheux and Libchaber which probably has indicated possible limitation of the Boltzmann distribution as equilibrium distribution of a Brownian particle in inhomogeneous space and propose experimental verification of the present theory using similar methods.

Complex molecules like proteins, colloids etc., in contact with a homogeneous heat bath form a unique class of statistical systems. The most important characteristic feature of such systems is that such systems can be modelled by a Brownian particle (BP) with coordinate dependent damping [1–3]. In different conformations (structural configuration of a complex molecule e.g. a protein), the accessible surface area of such a molecule to bath degrees of freedom can be different. Coupling of the molecule to the uniform heat bath can then be conformation dependent [4–6]. The motion of the complex molecule in its conformation space under equilibrium fluctuations is then similar to the motion of a BP in a multidimensional space with coordinate dependent damping. The source of inhomogeneity being damping, even in the absence of any homogeneity breaking potential (conservative force), the conformation space remains inhomogeneous. This is a situation for equilibrium statistics where there exists an inhomogeneous space in contact with a homogeneous heat bath and no extra energetics is involved in maintaining the inhomogeneity of space. This is different from an inhomogeneous heat bath where to maintain the inhomogeneity of the heat bath some external agent (presence of at least a third system) must be involved and one cannot talk of equilibrium without taking into account the presence of that external agent and the entropy produced by that involvement.

E-mail address: a.bhattacharyay@iiserpune.ac.in.

https://doi.org/10.1016/j.physa.2017.12.029

Relevant questions that one can ask, given such a system, are—a. If the equilibrium probability distribution is the Boltzmann distribution when the damping is constant over space, what is the general probability distribution when damping is a function of space? This is an important question because the damping term cannot be accommodated in a Hamiltonian. b. When damping is inhomogeneous, what is the diffusivity? This is a relevant point because, damping being local can be inhomogeneous, but, diffusivity is a non-local quantity and should, therefore, be some average over space and time [7]. c. How should one generalize the expression of stochastic force to decouple the local damping from the non-local diffusivity in equilibrium? As the present paper will elaborate, in the answer of this third question lie the answers of the previous two questions.

In the conventional approach, coordinate dependent damping makes the equilibrium stochastic problem involve multiplicative noise. In so far existing literature on such theories, the condition for equilibrium is considered to be the appearance of the Boltzmann distribution. This is questionable because the distribution does not involve damping which also breaks the homogeneity of space. Moreover, these standard procedures give rise to a host of other issues involving the dilemma of Itô vs Stratonovich conventions [8–11] etc.

Let us first introduce the alternative approach here that has been introduced and elaborated in Refs. [12,13]. Consider the Brownian dynamics over a homogeneous space characterized by a damping constant Γ

$$\frac{dx}{dt} = \frac{F(x)}{\Gamma} + \frac{g}{\Gamma}\eta(t).$$

In the above expression $F(x) = -\frac{\partial V(x)}{\partial x}$ is the conservative force and $g = \sqrt{2\Gamma k_B T}$ is the stochastic noise strength where T is the temperature and k_B is the Boltzmann constant. The Gaussian white noise $\eta(t)$ of unit strength has correlations $\langle \eta_i(t) \rangle = 0$ and $\langle \eta_i(t_i)\eta_j(t_j) \rangle = \delta_{ij}\delta(t_i - t_j)$ as usual. The equilibrium probability distribution for the position of the BP given as $P(x) = Ne^{-V(x)/k_B T}$ where N is a normalization constant. Taking an average on the above equation one gets $\langle \frac{dx}{dt} \rangle = 0$ where the noise term vanishes on average and the conservative force induced current identically vanishes on average using the Boltzmann distribution.

Now consider a generalization of the above model where $\Gamma(x)$ and $g(x)$ are space dependent functions as

$$\frac{dx}{dt} = \frac{F(x)}{\Gamma(x)} + \frac{g(x)}{\Gamma(x)}\eta(t).$$

Choosing $g(x) = \sqrt{2\Gamma(x) k_B T}$ and $\eta(t)$ being the same zero average white noise one conventionally obtains the same Boltzmann distribution for the so called equilibrium of the particle. Take an average of the above equation again and $\langle F(x)/\Gamma(x) \rangle \neq 0$ is the case now. The average over the noise term is then supposed to cancel out this non-zero current contribution in equilibrium.

The noise term is locally Gaussian with a locally fixed width and zero average. A system to equilibrate over an inhomogeneous space like the given one the space must be of finite extent. Given a long enough trajectory which revisits a particular coordinate many times, the noise term in principle can locally everywhere sample enough realizations to become increasingly small on average as the length of the trajectory increases. This simple fact means that given a locally Gaussian noise everywhere the noise term can tend towards zero on average everywhere over increasingly larger sampling i.e. over large time scales. If the noise is locally Gaussian, this should be true independent of whatever technicality is involved in the multiplicative noise integration. Therefore, there would remain a residual current in the form of $\langle F(x)/\Gamma(x) \rangle \neq 0$ as a result of having Boltzmann distribution and some *ad hoc* cancellation of this current in this so called equilibrium will be required.

In two previous papers [12,13] we have discussed these issues and it has been shown on the basis of the sole consideration of the non-existence of any average current over inhomogeneous space in equilibrium that the stochastic force strength for equilibrium dynamics should be generalized to $g(x) = \Gamma(x)\sqrt{2k_B T/\langle \Gamma(x) \rangle}$. This choice also explicitly decouples the local damping $\Gamma(x)$ from the global diffusivity $D = k_B T/\langle \Gamma(x) \rangle$ in the dynamics.

With the above mentioned modified stochastic force strength which is a linear function of $\Gamma(x)$ the over-damped dynamics (Langevin dynamics) becomes a stochastic problem with additive noise and the distribution one gets readily as

$$P(x) = N \exp\left(\frac{\langle \Gamma(x) \rangle}{k_B T} \int dx \frac{F(x)}{\Gamma(x)} \right), \tag{1}$$

where N is normalization constant. It is important to note that, according to this present model, the local diffusivity (when defined as $k_B T/\Gamma(x)$) does not characterize equilibrium. It is the global diffusivity of the system defined over the whole finite inhomogeneous space of the system that features in the equilibrium dynamics. Now, using this distribution it is straight forward to see that there is no average current in equilibrium and the distribution becomes the standard Boltzmann distribution when $\Gamma(x)$ is a constant. There are previous attempts to generalize Boltzmann distribution based on the entropy proposed by Tsallis and in this regard the Refs. [14,15] are interesting works involving nonlinear Fokker–Planck equation.

In this paper we are going to show a full derivation of the generalized Langevin dynamics including the inertial term and the above mentioned modified noise strength starting from a Hamiltonian that includes bath degrees of freedom as well as the system. We will follow here a formalism due to Zwanzig [16]. It will be shown that if there exists a local conformation dependent coupling of the system to the harmonic bath the mesoscopic dynamics of the system will have the stochastic noise of the modified form as has been mentioned above. In the following we first summarize the results of the generalized