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Macroscopic equation of motion in inhomogeneous media: A microscopic treatment

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Abstract. The dynamical evolution of a Brownian particle in an inhomogeneous medium with spatially varying friction and temperature field is important to understand conceptually. It requires to address the basic problem of relative stability of states in nonequilibrium systems which has been a subject of debate for over several decades. The theoretical treatments adopted so far are mostly phenomenological in nature. In this work we give a microscopic treatment of this problem. We derive the Langevin equation of motion and the associated Fokker–Planck equation. The correct reduced description of the Kramers equation in the overdamped limit (Smoluchowski equation) is obtained. Our microscopic treatment may be helpful in understanding the working of thermal ratchets, a problem of much current interest.

Keywords. Brownian particle; diffusion; inhomogeneous systems; relative stability of states; Fokker–Planck equation.

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1. Introduction

Thermodynamic equilibrium states are ideal limiting cases and are convenient and often theoretically amenable to study with relative ease. However, one commonly encounters systems that are away from equilibrium. All nonequilibrium systems relax naturally toward their respective equilibrium or stationary states. In nature, evolution is an ongoing and dominant process. Naturally, the process of relaxation of the nonequilibrium systems is of great interest in all branches of natural science, be it physics, chemistry or biology. Moreover, one comes across nonuniform systems more often than uniform systems. Uniform systems are characterized by a constant (space independent) diffusion coefficient throughout the system and having the same temperature in all parts of the system. There are well established theoretical formalisms for uniform systems to describe their evolution towards equilibrium or steady states [1]. However, the same is not true for nonuniform systems. There exist phenomenological descriptions but often without microscopic foundations. The ad hoc nature of these descriptions have led to some controversies, too, in the past. For instance, should the diffusion equation of a Brownian particle in the absence of external potential have the form [2–8]

$$\frac{\partial P}{\partial t} = \frac{\partial^2}{\partial q^2} D(q) P$$

or

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial q} D(q) \frac{\partial P}{\partial q} ?.$$

However, considerable progress has been made to make the theories of relaxation of nonuniform systems self-consistent [2, 4, 8, 10].

In this work, we seek to clarify some of the issues pertaining to this important case of nonuniform systems in a systematic manner. We derive, from microscopic theory, the Kramers equation for the joint probability distribution of position and velocity of a Brownian particle in an inhomogeneous, nonisothermal medium. We then proceed to find the correct Smoluchowski limit to the Kramers equation. This, however, is not a mathematical problem alone; the underlying conceptual development is quite appealing and, as mentioned earlier, is subject to ongoing controversies for over several decades [2–8].

The evolution of a Brownian particle in condensed media is the most familiar example of a nonequilibrium process. The process is accompanied by frictional dissipation but aided by associated fluctuations. Nonequilibrium behaviour of macroscopic uniform systems is described well by linear-response theory when the initial state of the system is close to equilibrium. The fluctuation-dissipation theorem relating the power absorbed by the system to the intrinsic fluctuations in the system in equilibrium has foundations in the linear response theory. But, when the system is far from equilibrium the linear response theory cannot be relied upon. In most of the physical systems, whether close to or far from equilibrium, the approach to equilibrium can, however, be likened to one kind or other of a diffusion process; it may be translational diffusion of particles, rotational diffusion of macromolecules, spin diffusion of spin systems, heat or thermal diffusion in solids, energy diffusion in excitonic motion in semiconductors, and so on. The diffusion process in inhomogeneous systems, therefore, calls for added attention.

In the case of uniform systems the diffusion constant $D = \eta^{-1} k_B T$, where η is the friction coefficient and T the temperature. However, for nonuniform systems the space, q, dependence of the diffusion comes separately through $\eta(q)$ and $T(q)$. The origin of $\eta(q)$ and $T(q)$ and the manner in which they influence the relaxation of the nonequilibrium system are entirely different. The variation of $\eta(q)$ (in the absence of spatial variation of temperature) influences the dynamics of particle in a potential field and helps the system to approach towards its equilibrium or steady states. The relative stability of the competing states is generally governed by the usual Boltzmann factor in the local neighbourhood of the corresponding (representative) potential wells. A change in the potential barrier between two potential well minima changes the relaxation rate but leaves the relative stability of the two well states unchanged. This simple fact, however, may not apply for more general systems when the temperature is nonuniform along the potential surface (or spatial coordinate).

Landauer, in a series of papers [2–5], argues that for systems with nonuniform temperature the relative stability of two states will be affected by the detailed kinetics all along the pathways (on the potential surface) between the two states under comparison. It is the effect of thermal fluctuations that plays a crucial role and the resulting effective potential surface may have completely different nature from that of uniform temperature. With the help of his blowtorch theorem Landauer [3] shows that a change of temperature away from uniformity even at very unlikely positions of the system on the potential surface may cause probability currents to set in moving the system towards a new steady state situation changing thereby the relative stability of the otherwise locally stable states. This known important fact, however, has received much less attention in the literature

than it deserves. This effect can have important consequences on the particle motion in nonuniform systems, for instance, the kinetics of growth of crystalline nuclei in the melt around its critical size. The latent heat generation being, in this example, responsible for the creation of nonuniform temperature field across the surface of the nucleus. Nonuniform temperature field can also be generated by shining light on semiconductors. One can have nonuniform temperature field also because of nonuniform distribution of electrons and of phonons (or of quasiparticles in general) with different characteristic temperatures in a solid. It has been suggested that the nonuniform temperature field can produce current in a closed ring [3, 6, 9]. There has been a lot of theoretical work reported in recent times on thermal ratchets [10]. These works are inspired by the observed predominantly unidirectional protein (macromolecule) motion in biological systems even in the absence of obvious external forces and thermal gradients. The idea of relative stability of states in nonuniform temperature systems can help to understand the working of the thermal ratchets better [11, 12]. These are but few examples where nonuniform temperature field can have important bearing on the dynamical evolution. A systematic formalism to deal with such a situation is, therefore, essential.

In the following sections we proceed systematically to set up a formalism from microscopic theory. We derive the Kramers equation for space dependent friction coefficient and nonuniform temperature field. We then go over to obtain the correct Smoluchowski limit of the Fokker–Planck equation. Before concluding we also give the correct Langevin equation in the overdamped limit that is approximated properly to order $\eta(q)^{-1}$.

2. Microscopic derivation of Langevin equation in a space dependent friction field

To obtain Langevin equation in a space dependent friction field we consider the motion of a subsystem (Brownian particle) described by its coordinate Q and momentum P and subjected to an external potential field $V(Q)$ of the system. We assume the subsystem to be in contact with a thermal (phonon) bath. The bath oscillators are described by coordinates q_α and momentum p_α with characteristic frequencies ω_α. For our calculation we consider the total Hamiltonian

$$\mathscr{H} = \frac{P^2}{2M} + V(Q) + \sum_\alpha \left[\frac{p_\alpha^2}{2m_\alpha} + \frac{m_\alpha \omega_\alpha^2}{2} \left(q_\alpha - \lambda_\alpha \frac{A(Q)}{m_\alpha \omega_\alpha^2} \right)^2 \right], \tag{1}$$

where M is the Brownian particle mass and m_α are the masses of the bath oscillators. The interaction of the subsystem with the thermal bath [13] is through the linear coordinate–coordinate coupling term $\lambda_\alpha q_\alpha A(Q)$. From (1) one obtains the following equations of motion

$$\dot{Q} = \frac{P}{M}, \tag{2a}$$

$$\dot{P} = -V'(Q) + \sum_\alpha \lambda_\alpha A'(Q) \left[q_\alpha - \lambda_\alpha \frac{A(Q)}{m_\alpha \omega_\alpha^2} \right], \tag{2b}$$

$$\dot{q}_\alpha = \frac{p_\alpha}{m_\alpha}, \tag{2c}$$

and

$$\dot{p}_\alpha = -m_\alpha \omega_\alpha^2 q_\alpha + \lambda_\alpha A(Q), \tag{2d}$$

where $A'(Q)$ is the derivative of $A(Q)$ with respect to Q. After solving (2c) and (2d) for q_α using the method of Laplace transform and substituting its value in (2b), we obtain the Langevin equation of motion for Q and P.

$$\dot{Q} = \frac{P}{M}, \tag{3a}$$

$$\dot{P} = -V'(Q) - \eta[A'(Q)]^2 \frac{P}{M} + A'(Q) f(t). \tag{3b}$$

Thus, the effect of interaction of the Brownian particle with the thermal bath is to introduce a friction term and a fluctuating term $f(t)$ in the equation of its motion. The fluctuating term is given by

$$f(t) = \sum_\alpha \lambda_\alpha \left[q_\alpha(0)\cos(\omega_\alpha t) + \frac{\dot{q}_\alpha(0)}{\omega_\alpha} \sin(\omega_\alpha t) \right], \tag{4a}$$

where $q_\alpha(0)$ and $\dot{q}_\alpha(0)$ are the initial positions and velocities of the bath variables. The force $f(t)$ is fluctuating in character because of the associated uncertainties in these initial conditions of the bath variables. However, as the thermal bath is characterized by its temperature T, the equilibrium distribution of bath variables is given by the Boltzmannian form, so that $f(t)$ follows the following statistics

$$\langle f(t) \rangle = 0 \tag{4b}$$

and

$$\begin{aligned} \langle f(t) f(t') \rangle &= \sum_\alpha \frac{\lambda_\alpha^2 k_B T}{m_\alpha \omega_\alpha^2} \cos(\omega_\alpha (t - t')) \\ &= 2 k_B T \eta \delta(t - t'). \end{aligned} \tag{4c}$$

To arrive at equations (3b) and the last term of (4c) we have assumed [13, 14, 15] ohmic spectral density for the bath oscillators, i.e.,

$$\rho(\omega) = \frac{\pi}{2} \sum_\alpha \frac{\lambda_\alpha^2}{m_\alpha \omega_\alpha} \delta(\omega - \omega_c) = \eta \omega \exp(-\omega/\omega_c).$$

The upper cut-off frequency ω_c is assumed to be much larger than the characteristic frequencies of the system. Equations (3b) and (4c) correspond to the well known Markovian limit and are valid for time scales $t > 1/\omega_c$, which can be made arbitrarily small by appropriately choosing ω_c. For details we refer to [14, 15]. It should be noted that the transient terms have been neglected at time scales $t > \omega_c^{-1}$ to arrive at (3b), and is perfectly valid under Markovian approximation [15]. It is noted that $A'(Q) =$ constant corresponds to a uniform friction coefficient. Redefining, $\eta[A'(Q)]^2 = \eta(Q)$ and $f(t)/\sqrt{T\eta} \to f(t)$, and putting $M = 1$, we get,

$$\dot{Q} = P, \tag{5a}$$

$$\dot{P} = -V'(Q) - \eta(Q) P + \sqrt{\eta(Q) T} f(t), \tag{5b}$$

with

$$\langle f(t)f(t')\rangle = 2k_B\delta(t-t'). \tag{5c}$$

It is instructive to note that one could take $\eta(Q)$ to be constant piecewise along Q; in each piece of these Q segments (5b) would correspond to a constant friction coefficient but with the same statistical character of $f(t)$ as in any other Q intervals.

3. Microscopic Markovian Langevin equation with space dependent friction and temperature

We have so far derived the Langevin equation of motion (from a microscopic Hamiltonian) of a Brownian particle with space dependent friction keeping the temperature constant. We, now, consider a system for which the temperature too is space dependent $T(Q)$. At this point it is pertinent to note the following important fact, however. It is quite well known that when a charged Brownian particle is subjected to an electric field charge current results. Similarly, when it is subjected to a thermal gradient thermal current flows in the system. However, in the former case the effect of the electric field can be incorporated in the particle Hamiltonian as a potential term whereas temperature gradient cannot be incorporated as the potential term in the Hamiltonian formalism. Therefore, in order to incorporate the effect of the temperature inhomogeneity we reason as follows. The Brownian particle comes in contact with a continuous sequence of independent temperature baths as its coordinate Q changes in time. Equivalently, each space point of the system is in equilibrium with a thermal bath of characteristic temperature $T(Q)$. In what follows we accept this idea and incorporate temperature inhomogeneity into the equations of motion (5). Henceforth, for notational simplicity, the coordinate Q and momentum P are replaced by the corresponding lower case letters q and p, respectively, reserving P for probability distribution.

For the sake of argument we consider, for the time being, the system to be subdivided in space q into several small segments and represent the segments Δq around q by indices i. Each segment is connected to an independent thermal bath at temperature T_i with corresponding random forces $f_i(t)$. The last term on the right hand side of (5b), is therefore replaced by $\sqrt{\eta(q)\ T_i}f_i(t)$ for the segment i. As the two different segments are each coupled to an independent temperature bath we have $\langle f_i(t)f_j(t')\rangle = 2k_B\delta_{ij}\delta(t-t')$. Because $f(t)$ is δ-correlated in time, as the particle evolves dynamically the fluctuation force $f_i(t)$ experienced by the Brownian particle while in the space segment i at time t will have no memory about the fluctuating force experienced by it at some previous time t' while in the space segment $j \neq i$. Hence the space-dependent index i in $f_i(t)$ can be ignored. Now, taking a continuum limit, the stochastic equations of motion of the Brownian particle, in an inhomogeneous medium with space dependent friction and nonuniform temperature, are given by,

$$\dot{q} = p, \tag{6a}$$

and

$$\dot{p} = -V'(q) - \eta(q)p + \sqrt{\eta(q)\ T(q)}f(t), \tag{6b}$$

with

$$\langle f(t)f(t')\rangle = 2k_B\delta(t-t'). \tag{6c}$$

It is also important to note and repeat that as long as the random force is delta correlated

in time, the final results remain unaffected provided we incorporate space dependence in $f(t) \to f(q,t)$ such that $\langle f(q,t) f(q',t) \rangle = 2g(q-q')\delta(t-t')$ with $g(0) = 1$.

4. Derivation of Kramers and Smoluchowski equations

It is, now, a straightforward exercise to derive the corresponding Fokker–Planck equation. We put $M = 1$ so that $p = v$, the velocity of the Brownian particle. The stochastic differential equations (6a) and (6b) can be converted into an equation for probability density $P(q,v,t)$ using the well-known van Kampen lemma [16]. To this end, we consider a cloud of initial phase points of density $\rho(q,v,t)$ in (q,v) phase space each point (q,v) of which is evolving in time according to (6a) and (6b). The phase fluid evolves according to the stochastic Liouville equation (continuity equation)

$$\frac{\partial \rho}{\partial t} = -\nabla_q(\dot{q}\rho) - \nabla_v(\dot{v}\rho). \tag{7}$$

In order to obtain the equation for the evolution of $P(q,v,t)$ we ensemble average ($\langle \cdots \rangle$) eq. (7) over all realizations of the random force of given statistics and use the well-known result (van Kampen lemma) [16]

$$\langle \rho \rangle = P(q,v,t). \tag{8}$$

The averaging procedure is carried out after substituting for $\dot{q}$ and $\dot{v}$ in (7) from (6). A term like $\langle \rho f(t) \rangle$ appears which is evaluated using the Novikov theorem [17]. For details see refs [18, 19]. From this we obtain the desired Fokker–Planck equation

$$\frac{\partial P(q,v,t)}{\partial t} = -v\frac{\partial P(q,v,t)}{\partial q} - V'(q)\frac{\partial P(q,v,t)}{\partial v} + \eta(q)\frac{\partial}{\partial v}\left\{vP(q,v,t) + k_B T(q)\frac{\partial}{\partial v}P(q,v,t)\right\}. \tag{9}$$

This is the Kramers equation for space dependent friction coefficient $\eta(q)$ and nonuniform temperature $T(q)$, derived from microscopic theory. It should be noted that van Kampen had assumed (9) as the model Kramers equation to start with to study the diffusion of a Brownian particle in a ring due to the combined effect of space dependent friction coefficient and the temperature inhomogeneity [6]. Equations (6) and (9) are valid for all friction coefficients, low as well as high. It is, however, hard to slove (9) in general cases. Moreover, in many of the practical situations one does not need the detailed motion of the Brownian particle at time scales much smaller than the characteristic time scales of order η^{-1}. Therefore, sometimes it is unnecessary to retain the fast variables v.

In most of the problems of physical interest (overdamped case) the marginal distribution $P(q,t)$ suffices to describe the motion of a Brownian particle. In the case of uniform systems, that is, when η = constant and T = constant, the reduction of $P(q,v,t)$ to $P(q,t)$ is well known and goes by the name of adiabatic elimination. One simply sets $\dot{p} = 0$ in (6b) to obtain the overdamped Langevin equation. From these one obtains the Fokker–Planck equation for $P(q,t)$. The overdamped Langevin equation so obtained is correct to order η^{-1}. For inhomogeneous systems, however, the integration of (7) to

obtain the equation for $P(q,t)$ is not easy. Moreover, simply ignoring the p term in (6b) is not correct. For instance, the resulting marginal distribution function so obtained does not conform to the correct equilibrium distribution. However, Sancho *et al* [20] have given a systematic procedure to go over to the overdamped Langevin equation for a system with space dependent friction coefficient but at uniform temperature. The overdamped Langevin equation obtained by Sancho *et al* is correct to order $[\eta(q)]^{-1}$ and leads to physically valid equilibrium distribution function.

Following the prescription of Sancho *et al* [20], we obtain the overdamped Langevin equation for an inhomogeneous system with nonuniform temperature field $T(q)$ and is given as

$$\dot{q} = -\frac{V'(q)}{\eta(q)} - \frac{1}{2[\eta(q)]^2}\{T(q)\eta'(q) + \eta(q)\,T'(q)\} + \left(\frac{T(q)}{\eta(q)}\right)^{1/2} f(t), \tag{10}$$

with

$$\langle f(t)f(t')\rangle = 2k_B\delta(t-t').$$

The corresponding Fokker–Planck equation for the overdamped case (the Smoluchowski equation), with k_B set equal to 1, is

$$\frac{\partial P(q,t)}{\partial t} = \frac{\partial}{\partial q}\frac{1}{\eta(q)}\left[\frac{\partial}{\partial q}T(q)P(q,t) + V'(q)P(q,t)\right]. \tag{11}$$

As pointed out earlier by van Kampen, the diffusion equation (11) in the absence of external potential has neither the form $\partial P/\partial t = (\partial^2/\partial q^2)D(q)P(q)$, nor $\partial P/\partial t = (\partial/\partial q)$ $D(q)(\partial/\partial q)P(q)$. It is clear that $T(q)$ and $\eta(q)$ influence the motion of the Brownian particle in different ways and their combined effect cannot be plugged together as the effect of an effective diffusion coefficient $D(q)$. We note that our equation (11) agrees with one of the forms obtained by van Kampen [6–8].

As already mentioned earlier the friction coefficient $\eta(q)$ only affects the relaxation process and not the equilibrium distribution function in a constant temperature field. Given enough time the system finds its equilibrium state. In contrast, the case of nonuniform temperature field changes the concept of steady states. It can be readily verified that if the external potential is unbounded at infinity, i.e., $V(q) \to \infty$ as $q \to \pm\infty$, then the system evolves to a steady state $P_s(q)$ obtained by setting the probability current equal to zero

$$P_s(q,t) = \frac{C}{T(q)}\exp\left(-\int^q (V'(q)/T(q'))dq'\right) \tag{12}$$

where C is a normalization constant. The solution in no way resembles the distribution decided by the usual Boltzmann factor alone. P_s is not a local function of $V(q)$. The non-local dependence of $P_s(q)$ on $T(q)$ and $V(q)$ forces the relative stability of the system in two different local minima to depend sensitively on the temperature profile along the entire pathway connecting the two minima [2–5]. Moreover for particular choices of $T(q)$ it may so happen that $P_s(q)$ may show extrema at positions completely unrelated to the minima of the external potential $V(q)$. Such a system with nonuniform temperature field is inherently nonequilibrium and $P_s(q)$ describes distribution of nonequilibrium steady states.

5. Conclusion

We have given a systematic microscopic derivation of Kramers equation of motion of a Brownian particle in a medium where friction coefficient is space dependent and having nonuniform temperature. We further obtain the Smoluchowski limit of the Kramers equation following the procedure given by Sancho *et al* [20]. We thus arrive at the correct overdamped Langevin equation for such a system. The microscopic treatment followed in this work helps resolve the controversy regarding the correct form of the diffusion equation followed by a Brownian particle in an inhomogeneous medium. We argue that the microscopic derivation of the equations makes their application to systems such as the thermal ratchets self-consistent [10–12]. Moreover, in many cases the numerical solution of the Langevin equation is much more transparent to appreciate physically, and the derived overdamped Langevin equation could thus be of some practical use.

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