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Phase-space diffusion in a system with a partially permeable wall

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Abstract. A new boundary condition for a diffusive system with a partially permeable wall described by the Klein–Kramers equation is proposed. The Green functions for such a system are given and a generalization to the system with a series of walls is briefly discussed. It is shown that the well known boundary condition for the case of a partially absorbing wall (which gives the so-called radiation boundary condition for the diffusion equation) cannot be used for the system under consideration.

1. Introduction

The Brownian motion in a system with a partially permeable wall (PPW) is of potential interest in many fields of physics, technology and biophysics. The wall can represent a membrane, potential barrier or thin slab [1–3]. A partially permeable wall is understood here as a 'barrier' which can be passed with given probability by particles moving towards the wall. Although the diffusion problem in such a system is usually considered on the basis of Smoluchowski equation, it is convenient to discuss it in phase space, where the diffusion process is described by the Klein–Kramers equation. The main reason is that the boundary conditions at the wall can be expressed through the fluxes of Brownian particles J_+, J_- flowing towards the wall and in the opposite direction, respectively. Thus, to obtain the boundary conditions for the diffusion equation, we first perform the following considerations in phase space.

Previously, diffusion in systems with fully reflecting, fully absorbing or partially absorbing (which is sometimes called 'partially reflecting') walls have been considered [4–12]. The Brownian motion is then investigated only in the half-space bounded by the wall. To the best of our knowledge, phase-space diffusion in a system with partially permeable wall has not been studied. We note that Brownian motion in a system with partially absorbing wall is qualitatively different from that in a system with PPW, because in the former the absorbed particle has no chance to return to the system. The main problem is to fix the boundary conditions at the wall. For a system with fully reflecting or fully absorbing walls the boundary conditions are well known. The Brownian motion in a system with partially absorbing wall has been considered in many papers in the last two decades [4–12]. The following boundary condition for the system of one spatial dimension has been taken:

$$f(x_{\rm w}, v, t) = \kappa f(x_{\rm w}, -v, t) \qquad 0 < \kappa < 1 \tag{1}$$

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where $f(x, v, t)$ is the density of particles with velocity v in a position x, and x_{w} is the location of the wall. The coefficient κ, which characterizes the absorbing property of the wall, is assumed to be constant in time and $v > 0$.

We are going to show that the boundary condition (1) must be replaced by another boundary condition when the Brownian motion is studied in a system with PPW. We present the phase-space Green function of the considered system, which is obtained by means of the modified method of images. Then, we deduce the boundary conditions from this function.

2. The model

The Brownian motion in phase space is determined by the one-dimensional Klein–Kramers equation:

$$\frac{\partial f}{\partial t} + v\frac{\partial f}{\partial x} = \varepsilon^{-1}\frac{\partial}{\partial v}\left(vf + \frac{\partial f}{\partial v}\right) \tag{2}$$

where ε^{-1} is the friction constant; the variables t, v and x are in appropriate units [13]. The Green function $G(x, v, t; x', v', t')$, which fulfils equation (2) with appropriate boundary conditions and the initial condition

$$G(x, v, t; x', v', t')|_{t=t'} = \delta(x - x')\delta(v - v')$$

is interpreted as a probability density for finding a particle in the state (x, v) at time t after departure from the initial state (x', v') at an earlier time t' (for simplicity we put $t' = 0$). When additional sources of particles do not occur at any time $t > 0$, one obtains the distribution function $f(x, v, t)$ of Brownian particles through the integral formula

$$f(x, v, t) = \int \mathrm{d}x' \int \mathrm{d}v'\, G(x, v, t; x', v', 0) f(x', v', 0) \tag{3}$$

where the integrations with respect to x' and v' are taken over the whole range of these variables.

The Green function for a system without a membrane is [4, 5]

$$G_0(x, v, t; x', v', 0) = \frac{1}{2\pi\sqrt{\Delta}} \exp[-aV_d^2 + bV_d(X + \varepsilon V) - c(X + \varepsilon V)^2] \tag{4}$$

where

$$V = v - v' \qquad X = x - x' \qquad e_1 = 1 - \exp\left(-\frac{t}{\varepsilon}\right)$$

$$e_2 = 1 - \exp\left(-\frac{2t}{\varepsilon}\right) \qquad V_d = v - v' \exp\left(-\frac{t}{\varepsilon}\right)$$

$$\Delta = 2t\varepsilon e_2 - 4(\varepsilon e_1)^2 \qquad a = \frac{\varepsilon t}{\Delta} \qquad b = \frac{2\varepsilon e_1}{\Delta} \qquad c = \frac{e_2}{2\Delta}.$$

3. The necessity of a new boundary condition

At first we note that the boundary condition for the partially absorbing wall (1) is equivalent to the following boundary condition:

$$J_+(x_{\mathrm{w}}, t) = \kappa J_-(x_{\mathrm{w}}, t) \qquad 0 \leqslant \kappa \leqslant 1 \tag{5}$$

where the fluxes J_+ and J_- are defined as

$$J_+(x, t) = \int_0^{\infty} \mathrm{d}v\, v f(x, v, t) \qquad J_-(x, t) = -\int_{-\infty}^{0} \mathrm{d}v\, v f(x, v, t). \tag{6}$$

Let us now consider the possibility of applying the boundary condition (5) for a system with PPW. Then, the permeability properties of the wall are described by the parameter κ, which is again assumed to be independent of time. This assumption can be replaced by the assumption that the passing of any particles through the wall does not depend on the locations and motion of other particles. Moreover, we assume that the total flux J is continuous at the PPW, i.e.

$$J(x_w^+, t) = J(x_w^-, t) \tag{7}$$

where $x_w^-(x_w^+)$ denotes the left (right) limit $x \to x_w$ and

$$J(x, t) = J_+(x, t) - J_-(x, t). \tag{8}$$

Let us consider N particles with the same initial velocities v_0 which depart from the location x_0 at the initial moment $t' = 0$. Then,

$$f(x', v', 0) = N\delta(x' - x_0)\delta(v' - v_0). \tag{9}$$

The system without a wall can be treated formally as the system with a fully permeable wall. For this case the Green function is given by (4). Using (4), (8) and (9) we obtain, after elementary calculations, the relation

$$J_{0+}(x_w, t) = \alpha(t) J_{0-}(x_w, t) \tag{10}$$

where

$$\alpha(t) = \frac{2 + \sqrt{\pi} B(t)}{2 - \sqrt{\pi} B(t)}$$

with

$$B(t) = [(2a - \varepsilon b)\exp(-t/\varepsilon) - b\varepsilon + 2c\varepsilon^2]v_0 + (b - 2c\varepsilon)(x_w - x_0).$$

The index 0 in equation (10) denotes the fluxes generated (through equations (3) and (6)) by the function G_0 (4), i.e. the fluxes in the system without a wall. We note that in the limit of large friction ($\varepsilon \to 0$) relation (10) takes the form

$$J_{0+}(x_w, t) = \frac{(8 + \sqrt{\pi} v_0)t + x_w - x_0}{(8 - \sqrt{\pi} v_0)t + x_w - x_0} J_{0-}(x_w, t). \tag{11}$$

From (10) and (11) one sees that the coefficient κ from equation (5) *depends on time* for the limiting case of a fully permeable wall. We expect that the Green function is continuous with respect to the permeability coefficient. So, the time dependence of κ also occurs in the case of 'almost fully' permeable walls, which is in contradiction with our initial assumption. Thus, the boundary condition (5) (and the equivalent one (1)) is not suitable for a system with PPW.

4. The Green functions for the system with PPW

We formulate the boundary condition (BC) in the following manner:

If at a unit of time N particles try to pass through the wall, $(1 - \delta)N$ of them will go through, whereas δN will be reflected by the wall.

We are now going to find the Green functions which satisfy this condition.

At first we construct the Green function for the case when the points x and x' are located in the same half-space bounded by the wall. In this case we find the Green functions which fulfil the above condition using the method of images. The method consists of replacing the wall by additional particle sources in such a way that the boundary condition is fulfilled [14]. Then, using the function we deduce the boundary condition which is employed to construct the Green functions for the case when the points x and x' lie in different half-spaces.

The situation which is described in the above BC occurs when the wall is simulated by the additional function δG_0 with the initial state $(2x_{\rm w} - x', -v')$, which is the 'mirror reflection' of the state (x', v') with respect to $x_{\rm w}$. Indeed, using the mirror symmetry of the initial states, it is easy to see that if N particles which depart from the state (x', v') go through the point $x_{\rm w}$, δN particles which depart from the initial state $(2x_{\rm w} - x', -v')$ go through this point moving in the opposite direction. Thus, the Green function for the system with partially permeable wall reads

$$G_{++}(\cdot) = G_{--}(\cdot) = G_0(\cdot) + \delta G_0(x, v, t; 2x_{\rm w} - x', -v', 0) \tag{12}$$

where $(\cdot) \equiv (x, v, t; x', v', 0)$, and the indices of the Green functions refer to the signs of $(x - x_{\rm w})$ and $(x' - x_{\rm w})$, respectively. The factor δ controls the permeability properties of the wall: for $\delta = 1$ the flux J flowing through the PPW is equal to zero and for $\delta = 0$ the flux is equal to the flux J_0 flowing in the system without the wall. The above equation means that the Green functions G_{++} and G_{--} are only expressed by the same equation; however, their domains with respect to the space variable are different.

Now, we derive the mathematical form of the boundary condition at the wall. Using the relations (4), (5) and (8), and observing that

$$G_0(x, v, t; x', v', 0) = G_0(-x, -v, t; -x', -v', 0)$$

one can show that the function (12) fulfils the following boundary conditions,

$$J_+(x_{\rm w}^-, t; x', v', 0) = (1 - \delta)J_{0+}(x_{\rm W}, t; x', v', 0) \qquad \text{if } x' < x_{\rm w} \tag{13a}$$

$$J_-(x_{\rm w}^+, t; x', v', 0) = (1 - \delta)J_{0-}(x_{\rm W}, t; x', v', 0) \qquad \text{if } x' > x_{\rm w} \tag{13b}$$

where

$$J_+(x, t; x', v', 0) = N \int_0^\infty {\rm d}v\, vG(x, v, t; x', v', 0)$$

$$J_-(x, t; x', v', 0) = -N \int_{-\infty}^0 {\rm d}v\, vG(x, v, t; x', v', 0)$$

denotes the value of the flux at point x and time t, which is generated by the point source of N particles placed at the initial moment in the state (x', v'). Equations (13a) and (13b) appear as the mathematical formulation of the BC, but they are not useful when obtaining the Green function for the case when points x and x' lie at the opposite half-spaces bounded by the wall. Now we are going to find the general boundary condition at the wall.

The Green function (12) also fulfils the following boundary condition:

$$J(x_{\rm w}, t; x', v', 0) = (1 - \delta)J_0(x_{\rm w}, t; x', v', 0). \tag{14}$$

Since the flux J is assumed to be continuous with respect to the space variable (equation (7)), we do not specify the left or right limit of this variable in the above equation. We note that equation (14) links the values of the fluxes flowing in opposite regions bounded by the walls. So, this equation is suitable to determine the Green functions G_{+-} and G_{-+}. It is easy to see that the function

$$G_{+-}(\cdot) = G_{-+}(\cdot) = (1 - \delta)G_0(\cdot) \tag{15}$$

(where as previously $(\cdot) \equiv (x, v, t; x', v', 0)$) generates the fluxes which satisfy condition (14).

From equations (3), (6) and (8) we find that the whole flux flowing in the system $J(x,t)$ is a superposition of the 'partial fluxes' $J(x, t; x', v', 0)$, i.e.

$$J(x,t) = \int \mathrm{d}x' \int \mathrm{d}v' \, J(x, t; x', v', 0). \tag{16}$$

Taking into account (14) and (16) we obtain the boundary condition at the wall, which is fulfilled for any initial distribution:

$$J(x_{\mathrm{w}}, t) = (1-\delta) J_0(x_{\mathrm{w}}, t). \tag{17}$$

We note that the boundary conditions (7) and (17) do not depend on the particle initial velocity; therefore, they can be used for the Smoluchowski diffusion equation. In fact, we have deduced the boundary condition (17) in the configuration space [15, 16]. At that time, however, the applicability of this boundary condition in phase space was unclear.

5. Final remarks

The Green functions (12) and (15) greatly simplify the calculations of the distribution function of the system with a thin membrane, potential barrier etc. The only problem is to determine the coefficient δ. We assume that this coefficient is independent of the fluxes flowing through the PPW, so thus we can perform the calculations of the coefficient δ, based on equation (17), in a stationary state. A phenomenological model (as Kedem–Katchalsky formalism [17] for the membrane transport), which provides the fluxes from equation (2), can be applied here. When the wall represents the thin potential barrier, the fluxes present in relation (17) are known in the stationary state [18, 19]:

$$J = \frac{kT\lambda}{h} \exp\left[-\frac{\Delta U}{RT}\right] \Delta C \qquad J_0 = \frac{D}{\lambda} \Delta C$$

where ΔC is the difference in the particle concentration between the opposite sides of the barrier, h, k, D are the Planck, Boltzmann and diffusion constants, respectively, T is the temperature, λ is the thickness of the barrier (which is small with respect to the size of the system) and finally ΔU is the height of the potential barrier. Then, the coefficient δ reads

$$\delta = 1 - \frac{kT\lambda^2}{hD} \exp\left[-\frac{\Delta U}{kT}\right].$$

The boundary condition (14) is useful to determine the Green function for a system with a series of PPWs. In this case the following procedure can be invoked: let us assume that for a system with $(n-1)$ PPWs the Green functions are known. We now add to the system a new nth wall. In such a system the boundary condition (14) can be used, but δ refers to the new wall and J_0 is generated by the Green functions for $(n-1)$ walls.

If the permeability coefficient δ depends on the concentration (as, for example, happens in some types of membrane transport), the procedure of the concentration calculations should be modified. One can divide the time domain into intervals which are small enough so that the assumption of the concentration independence of δ is approximately valid for a given interval. Then, the Green functions (12) and (15) can be used for every interval.

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