Approach to equilibrium of particles diffusing on curved surfaces

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Abstract

We present a simple numerical analysis of the diffusion on a curved surface given by the equation $\phi(r) = 0$ in a finite domain $D \subset R^3$. The first non-vanishing eigenvalue of the Beltrami–Laplace operator with the reflecting boundary conditions is determined in our simulations for the P, D, G, S, S1 and I-WP, nodal periodic surfaces, where $D$ is their respective cubic unit cell. We observe that the first eigenvalue for the surfaces of simple topology (P, D, G, I-WP) is smaller than for the surfaces of complex topology (S, S1).

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1. Introduction

There is a growing interest in diffusion on curved surfaces. This interest stems partially from experiments, where diffusions on curved membranes are studied by optical techniques with small gold particles [1–5], fluorescent lipoproteins LDL [6], a photobleaching technique [7], or a photothermal self-diffracting technique [8].

The formal representation of the diffusion equation on any two dimensional surface [9–11], or on a distorted lattice [12,13] is known and different mathematical methods have been developed to study isotropic transport processes on the Riemannian manifolds [14–18]. We have recently implemented numerically a simple algorithm [18,19] for
describing the diffusion on a curved surface. Here we apply it to study the diffusion on nodal, periodic surfaces with reflecting boundary conditions at the border of their cubic unit cells. From the mean-square displacement of diffusing particles in the long time limit we determine numerically the first non-zero eigenvalue of the Beltrami–Laplace operator. This eigenvalue divided by the diffusion coefficient is the inverse of the mean time needed to reach equilibrium in the system. This problem is important in mathematics [20–22] and its physical realization is found in the flow of heat [8,23,24]. In the case of heat flow this eigenvalue gives the inverse of the mean time needed to achieve a uniform distribution of temperature on a surface heated by a point heater attached to it (for example by a laser beam [8]).

The paper is organized as follows. In Section 2 we present the simulation technique and discuss behavior of the mean-square displacement at long times. In Section 3 we apply the algorithm to the diffusion on a variety of nodal surfaces and analyze the mean-square displacement at long times. From this analysis the first eigenvalue of the Beltrami–Laplace operator follows. A summary is contained in Section 4.

2. Simulation method and the analysis of the mean-square displacement

In this paper we study the diffusion on surfaces given by the general equation:

$$\phi(r) = 0.$$  \hspace{1cm} (1)

In the finite, cubic domain $D \subset \mathbb{R}^3$ is defined as follows:

$$\frac{L}{2} \leq \{x, y, z\} \leq \frac{L}{2}.$$  \hspace{1cm} (2)

We set reflecting (Neumann) boundary conditions on the border of the domain $D$ (vanishing currents for $x = \pm L/2$, or $y = \pm L/2$, or $z = \pm L/2$). At each point of the surface described by Eq. (1) we define the plane tangent to the surface. At point $r_0 = (x_0, y_0, z_0)$ the plane is described by the following equation:

$$\mathbf{n}(r_0)(r - r_0) = 0,$$  \hspace{1cm} (3)

where $\mathbf{n}(r_0)$ is the vector normal to the surface. Our numerical method [19] consists of a sequence of elementary steps. A particle at point $r_0$ jumps along randomly chosen direction in the plane tangent to the surface. The length of the jump $J$ is drawn from the distribution:

$$T(J) = \frac{J}{2D_0\tau_0} \exp\left(-\frac{J^2}{4D_0\tau_0}\right),$$  \hspace{1cm} (4)

where $D_0$ is the planar diffusion coefficient, $\tau_0$ is the duration of the elementary time step. After the jump the particle is at point $r_1$ on the tangent plane $(\mathbf{n}(r_0)(r_1 - r_0) = 0)$. Then we project the point $r_1$ back to the curved surface along the direction given by $\nabla \phi(r_1)$ (approximately normal to the surface). The final location is given by the
formula: 

\[ r_2 = r_1 - \frac{\phi(r_1) \nabla \phi(r_1)}{|\nabla \phi(r_1)|^2}. \]  

(5)

The elementary step is next repeated from the point \( r_2 \). The algorithm satisfies the detailed balance condition and is stable [19], provided that steps are much smaller than the typical radius of curvature averaged over the surface.

In the numerical simulations we determine the mean-square displacement

\[ X_2^2 = \langle |r(t) - r_0|^2 \rangle, \]  

(6)

of the particle during time \( t \). The average, \( \langle \cdots \rangle \) is taken with the probability density \( P(r, r_0, t) \) of finding a particle at point \( r(t) \) at time \( t \), and over all initial positions \( r_0 : P(r, t = 0) = \delta(r - r_0) \) i.e.,

\[ X_2^2 = \frac{1}{A} \int_{r \in S} \int_{r_0 \in S} |r - r_0|^2 P(r, r_0, t), \]  

(7)

where the integrations are over the two dimensional domain \( S \) of area \( A \), defined by Eq. (1) and the boundary conditions. It follows that:

\[ X_2^2 = a_0 + a_1 e^{-\lambda_1 t} + a_2 e^{-\lambda_2 t} + \cdots, \]  

(8)

where

\[ a_0 = \frac{1}{A^2} \int_{r \in S} \int_{r_0 \in S} |r - r_0|^2 \]  

and

\[ a_n = \frac{1}{A} \int_{r \in S} \int_{r_0 \in S} |r - r_0|^2 p_n(r) p_n(r_0), \]  

(10)

where \( p_n \) are the eigenfunctions and \( \lambda_n \) the corresponding eigenvalues of the Beltrami–Laplace operator on \( S \) with Neumann boundary conditions. The smallest eigenvalue which determines the long time behavior of \( X_2^2 \) is \( \lambda_1 \) unless \( a_1 = 0 \) due to some special symmetries of the system. For a sphere of radius \( R \) we find that \( X_2^2 \) is given exactly by the first two terms in the expansion since \( a_n(n \geq 2) \) vanish due to the symmetry. We find

\[ X_2^2 = a_0 + a_1 e^{-\lambda_1 t} \]  

(11)

with \( a_0 = -a_1 \). Here \( a_0 \) is given by the Eq. (9), but can also be determined independently from the simulations since

\[ a_0 = \lim_{t \to \infty} \langle X_2^2 \rangle = 2R^2. \]  

(12)
The determination of $a_0$ is an additional test of the simulations. For a sphere the first eigenvalue is given by

$$\lambda_1 = \frac{\alpha}{a_0},$$

where $\alpha = 4D_0$.

In the simulations, we use one random walker, and take averages over all its trajectories on the surface. Because of the ergodicity of the random walk the precise location of the starting point is unimportant. A typical simulation consists of $K = 3 \times 10^3$ trajectories (we take last point of each trajectory as a starting point $r_0$ for the next one), each of $M = 10^6$ steps. A typical size of the elementary jump is equal to $J_0 = \sqrt{4D_0 \pi_0}$ and the typical linear size of the cubic cell $L \approx 100J_0$ is expressed in the units of $J_0$.

The averaged value of $X_t^2$ at time $t = N\pi_0$ is taken over $m = (M - N)K$ steps, and given by the formula:

$$X_t^2 = \frac{K}{(M-N)} \sum_{j=1}^{K} \sum_{i=1}^{M-N} \frac{|r_j(t_i + t) - r_j(t_i)|^2}{K(M-N)}.$$

The trajectories are indexed by $j$ and the steps by $i$.

In the short time limit, the mean-square displacement is equal to the typical jump length, $J_0$. In the long time limit, it tends towards a constant $a_0$. The characteristic time for approaching this limit is proportional to the surface area and inversely proportional to the diffusion coefficient. So in order to compare the time evolution of $X_t^2$ for different surfaces we rescale the size $L$ of the domain $D$ in order to have the same surface area for all studied surfaces.

### 3. Mean-square displacement on nodal surfaces

In this section we determine the first non-zero eigenvalue of the Beltrami–Laplace operator for a variety of nodal structures. We have found that for these surfaces $X_t^2$ in the long time limit is given by

$$X_t^2 \approx a_0(1 - e^{-\alpha/\pi_0})$$

with $\alpha \sim 3D_0$ and $a_0$ defined by Eqs. (9) and (12).

All structures presented here are defined in a cubic box (domain $D$) with edges of length $L$. For each surface we rescale the size $L$ of the domain $D$ to ensure the same surface area for all studied surfaces. Below we give the definitions of the studied structures.

The P nodal surface [25] is given by Eq. (1) and

$$\phi(r) = \cos X + \cos Y + \cos Z,$$
Fig. 1. The $P$ (top), $D$ (bottom picture) nodal surfaces given by Eqs. (16) and (17) in a unit cell (domain $D$).

Fig. 2. The $G$ (top, Eq. (18)), $S$ (bottom picture, Eq. (19)) nodal surfaces in a unit cell (domain $D$).

where $X = 2\pi x/L$, $Y = 2\pi y/L$, $Z = 2\pi z/L$, and the size of the cubic cell $L = 100\sqrt{4D_0^{0.9}}$. It is shown in Fig. 1 together with the $D$ nodal surface [19,25]. The latter is defined by Eq. (1) and

$$\phi(r) = \cos X \cos Y \cos Z - \sin X \sin Y \sin Z .$$

(17)

The $G$ nodal surface [19,25] is shown in Fig. 2 and defined by Eq. (1) and

$$\phi(r) = \sin X \cos Z + \sin Y \cos X + \sin Z \cos Y .$$

(18)
Fig. 3. The I-WP (top), S1 (for $A_2 = 0.1$—bottom picture) surfaces described by Eqs. (20) and (21) in a unit cell (domain D).

1. The S nodal surface [26] is shown together with the G nodal surface. It is given by Eq. (1) and the following function:

$$\phi(r) = \cos Y \cos 2Z \sin X + \cos 2X \cos Z \sin Y$$
$$+ \cos X \cos 2Y \sin Z.$$  \hfill (19)

2. The I-WP nodal surface is shown in Fig. 3 and is defined by Eq. (1) with [26]:

$$\phi(r) = 2(\cos X \cos Y + \cos Y \cos Z + \cos Z \cos X)$$
$$- (\cos 2X + \cos 2Y + \cos 2Z).$$  \hfill (20)

The S1 nodal surface is defined by [27]

$$\phi(r) = \cos X \sin Y \sin 2Z + \cos Y \sin Z \sin 2X$$
$$+ \cos Z \sin X \sin 2Y + 2A_2(\cos 2X \cos 2Y$$
$$+ \cos 2Y \cos 2Z + \cos 2Z \cos 2X),$$  \hfill (21)

where $X = 2\pi/L$, $Y = 2\pi y/L$, $Z = 2\pi z/L$, and $A_2$ is a parameter ($A_2 = 0.1$).

The following sizes of the unit cell, $L$, have been chosen: $L_P = 100J_0$, $L_G = 87J_0$, $L_D = 78J_0$, $L_S = 65J_0$, $L_{I-\text{WP}} = 80J_0$, and $L_{S1, A_2 = 0.1} = 60J_0$, in the units of the typical jump length $J_0 = \sqrt{4D_0\tau_0}$. For these values of $L$ all surfaces have the same area in the unit cell $A = 2.34 \times 10^4J_0^2$.

Our results are summarized in Table 1. In Table 1 we present the coefficient $a_0$ given by Eq. (9) or (12), $x$ and $\lambda_1$. We also show in the table the genus [28] for each surface per unit cell. It is a measure of topological complexity. For a closed surface it is equal to the number of holes in the surface e.g. a sphere has genus 0 and a tori
Table 1
The $x$ coefficient (in the units of $D_0$) and the value of $\sqrt{a_0}$ (in units of the average jump length $J_0$), together with the inverse of the first eigenvalue of the Beltrami–Laplace operator $(1/\lambda_1)$ in the units of $J_0^2/D_0$ and the genus of a surface$^a$

<table>
<thead>
<tr>
<th>Structure</th>
<th>$x$</th>
<th>$\sqrt{a_0}$</th>
<th>$1/\lambda_1 = a_0/x$</th>
<th>Genus</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>3.0</td>
<td>68.5</td>
<td>1564.1</td>
<td>3</td>
</tr>
<tr>
<td>G</td>
<td>2.84</td>
<td>61.4</td>
<td>1327.5</td>
<td>5</td>
</tr>
<tr>
<td>I-WP</td>
<td>2.92</td>
<td>56.1</td>
<td>1077.8</td>
<td>7</td>
</tr>
<tr>
<td>D</td>
<td>2.28</td>
<td>52.5</td>
<td>1208.9</td>
<td>9</td>
</tr>
<tr>
<td>S1($A_2 = 0.1$)</td>
<td>2.72</td>
<td>45.9</td>
<td>774.5</td>
<td>25</td>
</tr>
<tr>
<td>S</td>
<td>3.08</td>
<td>45.8</td>
<td>681.1</td>
<td>21</td>
</tr>
</tbody>
</table>

$^a$ For a sphere we have $x_{\text{sphere}}/D_0 = 4$, and $\sqrt{a_0} = 60.8 J_0$, and $1/\lambda_1 \approx 924.2$. All the nodal surfaces and the sphere have the same surface area. The P, D surfaces are shown in Fig. 1 and defined by Eqs. (16) and (17), G, S surfaces are shown in Fig. 2 and defined by Eqs. (18) and (19), and I-WP, S1 surfaces are shown in Fig. 3 and defined by Eqs. (20) and (21). The typical error for the $x$ coefficient and $\sqrt{a_0}$ is equal to 1%.

Fig. 4. The plot of $F(t) = \ln[a_0 - \langle X^2 \rangle]$ as a function of time for the P nodal surface. According to Eq. (15) it is a linear function of time with the slope equal to the first eigenvalue of the Beltrami–Laplace operator. The squares are the results of the simulations, and the dashed line is the linear fit. For this surface we find $\lambda_1 \approx 3D_0/a_0$. 

1 has genus 1. It follows from the table that the first eigenvalue depends strongly on the topology. The nodal surfaces have small mean curvature almost everywhere and they resemble minimal surfaces. Therefore, the increase of the first eigenvalue with the genus is significant, although it is not a rule as observed by comparing $\lambda_1$ for I-WP and D surfaces or S and S1 surfaces.

The typical fit to Eq. (15) is presented in Fig. 4 for the P nodal surface. The estimated error of the $x$ coefficient is about 1%.
4. Summary

We have studied the diffusion with the reflecting boundary conditions on the nodal surfaces in the unit cell and from the analysis of the long time behavior of the mean-square displacement we have determined the first eigenvalue of the Beltrami–Laplace operator. This eigenvalue is equal to the inverse of the time needed to uniformly distribute particles over the surface, i.e., to reach equilibrium in the system. We find a correlation between this time and the topology of the surface. The time is much longer for the surfaces of simple topology (small genus) than for the surfaces of complex topology (high genus). One of the possible interpretations is that the surfaces of a complex topology have more inside connections which speeds up the process of equilibration.

Uncited Reference

[29–32]

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References