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Resonant and antiresonant transport through a fluctuating cage

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We consider an idealized model of diffusion in a cage. The boundary of the cage can be occupied by various correlated obstacles which fluctuate in time according to a dynamic of a Glauber-type. A particle enters the cage and travels through it according to a given stochastic process. Its exit may be blocked by the presence of the obstacles at the surface of the cage. We show that the probability of transmission through the cage can have a maximum and a minimum as a function of the frequency of fluctuation of the obstacles, provided a certain simple condition on the dynamics inside the cage is satisfied. © *1999 American Institute of Physics.* [S0021-9606(99)51027-1]

I. INTRODUCTION

It is now well known that the transport properties of a particle in a complex medium cannot always be described by diffusion type processes which do not take into account strong short range forces, fluctuating in space and time, such as for example a strong barrier potential. The subject is of considerable importance in chemical kinetics[1,2] or in diffusion inside proteins.[3–6]

Given the fact that the fluctuating strong and short range forces can be extremely complicated in their details, we have recently introduced very idealized models of such forces, which are simply represented by barriers which can appear or disappear at random times,[7,8] in order to capture new qualitative phenomena, in particular enhanced transport in presence of barriers.

If the barriers are uncorrelated, we found in previous papers[8,9] that the transmission probability of the medium may present a resonance in term of the probability of presence of the barriers; by choosing conveniently this parameter, it is possible to optimize the transmission of the medium. However, there is no such resonance in term of the fluctuation frequency.[9] On the contrary, if the barriers are sufficiently strongly correlated, there can be a resonance in term of the frequency of fluctuation of the barriers,[10] as in more standard fluctuating potentials.[11–13]

Until now, our models were only one dimensional. In this work, we consider a d-dimensional model where $d>1$. Initially, a particle enters a sphere and moves inside that sphere according to a certain stochastic dynamics, until it hits again the sphere and finds there a barrier closed, in which case it is reflected back, or opened, in which case it leaves the sphere. If the barriers on the surface of the sphere are weakly correlated, we find that the transmission probability is an increasing function of the overall frequency of fluctuation of the barriers. For a sufficiently strong correlation between the barriers, the transmission probability, as a function of the fluctuations of the barriers, presents both a maximum *and* a minimum for certain frequencies; this is a new feature, which was absent in the one-dimensional model treated in Ref. 10. Thus, this behavior seems to be due to the more complex topological structure of the present model.

As we have said, our motivations concern the problem of chemical reactivity in the presence of the cage effect, and the diffusion of particles in spatial structures like complex channels in proteins or in biological membranes. Another example is the diffusion of a proton in water, which is well known to be influenced by the cage formed by the first layer of three water molecules, itself influenced by the second layer.[14] Our model could permit to take into account the cage explicitly, although in a very crude way (see Ref. 15 for a model which does not take into account the explicit cage effect).

In the next section, we describe the model and in particular the stochastic dynamics of the cage, using Glauber dynamics.[16] The third section describes the equations for the transmission probabilities and gives a formal solution. The fourth section gives the asymptotic properties of the solution and proves that for strong coupling between the obstacles forming the cage, the transmission probability, as a function of the frequency of fluctuation of the cage, has a maximum and a minimum, which we call resonance and antiresonance, respectively. We also present numerical simulations. The case of the ballistic motion is studied in Sec. V. Appendices of a rather technical nature give detailed calculations.

II. TRANSMISSION THROUGH A CAGE WITH FLUCTUATING BOUNDARY

A. Evolution of a particle in a cage

We consider the motion of a particle through a certain domain whose surface Σ is divided in three adjacent regions

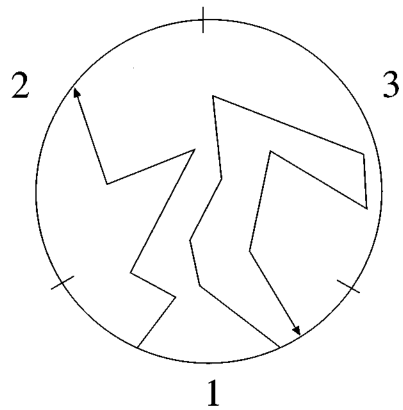

FIG. 1. Symbolic representation of the cage. The cage is symbolized by a circle divided in three regions 1, 2, 3. Two typical particle trajectories inside the cage are represented.

called $i=1,2,3$. The particle enters the domain through a region, say i, and has a certain stochastic motion inside the domain until it leaves the domain through the region j. We call

$$S_{ji}(t)dt \tag{1}$$

the probability that the particle leaves the domain through region j of Σ between times t and $t+dt$, when it entered the domain at time 0, through region i (Fig. 1). We do not make any assumption on this stochastic motion, which can only be given by a detailed analysis of the particle evolution inside the domain. It can be Markovian or not. We will use only the data (1). Imagine now that the domain is part of a complex medium, like a solvent, and that an obstacle can appear and disappear on the regions i. The state of the surface Σ is determined by the configurations $\{\sigma_i\}$, where

(a) $\sigma_i=+1$ if the obstacle is present in the region i of Σ,
(b) $\sigma_i=-1$ if the obstacle is absent.

Because of the possible presence of the obstacles, the motion of the particle through the domains is strongly perturbed in the following manner. Suppose again that the particle enters region i at time 0 (so that the obstacle is absent at that time from region i, which allows the particle to enter the domain). Then, the particle follows its stochastic motion in the domain and hits the surface Σ between t and $t+dt$ in some region j. Now, if $\sigma_j=-1$ (no obstacle in j) at time t, the particle leaves the domain. If $\sigma_j=+1$ (an obstacle is present on j), the particle is reflected and starts a new stochastic motion from j, and then hits Σ at region k between t' and $t'+dt'$ with probability $S_{kj}(t'-t)dt'$. Again depending on σ_k at t', the particle leaves the domain or is reflected back and starts a new motion in the domain, etc. The quantity of interest is the probability $P(j|i;\sigma)$ that the particle leaves the domain through region j (at any time), knowing that it enters the domain through region i, the configuration of the obstacles being $\{\sigma\}$ (when it enters the domain, with $\sigma_i=-1$ necessarily).

B. Evolution of the obstacles on the cage

We specify now the evolution of the obstacles. We shall essentially assume a Glauber dynamics[16] (see Appendix A). More precisely, we assume that a configuration $\{\sigma\}$ of the obstacles has an energy $H(\sigma)$. The equilibrium distribution is then, if β denotes the inverse temperature,

$$p_0(\sigma)\propto\exp(-\beta H(\sigma)), \tag{2}$$

and we call $\mathbf{R}_{\sigma'\sigma}$ the transition probabilities per unit time from the configuration $\{\sigma\}$ to the configuration $\{\sigma'\}$, assuming that only one of the σ_j changes into $-\sigma_j$ in each transition. The Glauber dynamics is essentially a detailed balance dynamics, so that

$$\mathbf{R}_{\sigma'\sigma}p_0(\sigma)=\mathbf{R}_{\sigma\sigma'}p_0(\sigma'). \tag{3}$$

We call

$$\phi(\sigma',t|\sigma) \tag{4}$$

the probability to find the configuration $\{\sigma'\}$ at time t, knowing that the configuration was $\{\sigma\}$ at time 0. So that

$$\begin{cases} \dfrac{\partial\phi(\sigma',t|\sigma)}{\partial t}=\displaystyle\sum_{\sigma''}\mathbf{R}_{\sigma'\sigma''}\phi(\sigma'',t|\sigma) \\ \phi(\sigma',0|\sigma)=\delta_{\sigma\sigma'}. \end{cases} \tag{5}$$

Following Ref. 16 we now describe the matrix R more precisely. Let us assume that in any allowed transition $\{\sigma\}\to\{\sigma'\}$, only a single σ_j changes into $-\sigma_j$. We take a ‘‘ferromagnetic’’ interaction

$$H(\sigma)=-J\sum_k \sigma_k\sigma_{k+1}, \tag{6}$$

with $\sigma_4=\sigma_1$ and J being a positive constant. Thus, in the transition $\{\sigma\}\to\{\sigma'\}$ where σ_j is changed into $-\sigma_j$, and all other σ_k are unchanged,

$$H(\sigma')-H(\sigma)=2J\sigma_j(\sigma_{j-1}+\sigma_{j+1}). \tag{7}$$

Then,

$$\begin{aligned}\frac{p_0(\sigma')}{p_0(\sigma)}&=\frac{\exp(-\beta H(\sigma'))}{\exp(-\beta H(\sigma))}\\ &=\frac{\exp(-\beta J\sigma_j(\sigma_{j-1}+\sigma_{j+1}))}{\exp(-\beta J\sigma_j(\sigma_{j-1}+\sigma_{j+1}))}.\end{aligned} \tag{8}$$

From this expression, it is easy to see that one can take for $R_{\sigma'\sigma}$ (where only σ_j changes its sign)

$$\mathbf{R}_{\sigma'\sigma}=\tfrac{1}{2}\alpha(1-\tfrac{1}{2}\gamma\sigma_j(\sigma_{j-1}+\sigma_{j+1}))\equiv w(\sigma), \tag{9}$$

with

$$\gamma=\tanh(2J\beta), \tag{10}$$

and α is the overall time scale of the fluctuation of the state of the surface [recall that Eqs. (2) and (3) do not specify the time scale, but only assure that p_0 is the equilibrium state of the dynamics]. Obviously, Eq. (9) is not the only possible choice for $\mathbf{R}$ that satisfies Eq. (3). However, it has the advantage that the eigenvalues and eigenvectors of $\mathbf{R}$ can be computed exactly, and $\mathbf{R}_{\sigma\sigma'}$ tends to a constant when γ tends to 0, which is reasonable (see Glauber[16]).

The matrix $\mathbf{R}$ is an 8×8 matrix (described in Appendix A) whose elements are indexed by configuration $\{\sigma\}$. We call λ_ν, $\nu=1,...,8$ its eigenvalues ordered by decreasing order,

$$0=\lambda_1\geqslant\lambda_2\geqslant\cdots\geqslant\lambda_8 \tag{11}$$

and $|\nu\rangle$ the right eigenvector of eigenvalue λ_ν, in Dirac notations,

$$\mathbf{R}|\nu\rangle=\lambda_\nu|\nu\rangle. \tag{12}$$

The components of $|\nu\rangle$ are indexed by configuration $\{\sigma\}$ and we denote $\langle\sigma/\nu\rangle$ the component of $|\nu\rangle$ with index $\{\sigma\}$.

The left eigenvectors are denoted by $\langle\nu|$,

$$\langle\nu|\mathbf{R}=\lambda_\nu\langle\nu|. \tag{13}$$

Similarly, $\langle\nu/\sigma\rangle$ is the component of $\langle\nu|$ with index $\{\sigma\}$. It is easy to obtain the left eigenvectors in term of the right eigenvectors because R satisfies the detailed balance conditions Eq. (3),

$$\langle\nu|\sigma\rangle=k\frac{\langle\sigma|\nu\rangle}{p_0(\sigma)}, \tag{14}$$

where k is a constant independent of σ. Notice that, with this numbering of the eigenvalues, $|1\rangle$ is the stationary state,

$$\langle\sigma|1\rangle=p_0(\sigma) \tag{15}$$

and $\langle 1|$ is the constant eigenvector,

$$\langle 1|\sigma\rangle=1 \tag{16}$$

for all $\{\sigma\}$. We can assume that the vectors $|\nu\rangle$ and $\langle\nu|$ are chosen so that

$$\langle\nu|\nu'\rangle\equiv\sum_{\{\sigma\}}\langle\nu|\sigma\rangle\langle\sigma|\nu'\rangle=\delta_{\nu\nu'}. \tag{17}$$

With these notations, we see that

$$\phi(\sigma',t|\sigma)=\langle\sigma'|\exp(t\mathbf{R})|\sigma\rangle, \tag{18}$$

$$\exp(t\mathbf{R})=\sum_{\nu=1}^{8}\exp(t\lambda_\nu)|\nu\rangle\langle\nu|. \tag{19}$$

Detailed expressions of the eigenvalues and eigenvectors are necessary for obtaining our results. Unfortunately, heavy but exact calculations are needed; they are given in Appendix A.

III. THE EQUATIONS FOR THE EXIT PROBABILITIES

A. Equations in detailed form

We define the quantity

$$S_{ji}(\sigma'|\sigma)=\int_0^\infty S_{ji}(t)\,\phi(\sigma',t|\sigma)\,dt. \tag{20}$$

$S_{ji}(\sigma'|\sigma)$ is the probability that the particle, entering the domain in region i, the configuration of the surface being $\{\sigma\}$, reaches the region j before the two other regions the configuration of the surface being $\{\sigma'\}$ (and the time of exit is not specified). With these notations, we have the following equations:

$$\begin{aligned}P(2|1;\sigma)=&\sum_{s_1,s_2}S_{21}(s_1,-1,s_2|\sigma)\\&+\sum_{s_1,s_2}P(2|1;\{1,s_1,s_2\})S_{11}(1,s_1,s_2|\sigma)\\&+\sum_{s_1,s_2}P(2|2;\{s_1,1,s_2\})S_{21}(s_1,1,s_2|\sigma)\\&+\sum_{s_1,s_2}P(2|3;\{s_1,s_2,1\})S_{31}(s_1,s_2,1|\sigma).\end{aligned} \tag{21}$$

We comment briefly on Eq. (21). The particle starts from region 1 of the surface Σ, the configuration of obstacles being $\{\sigma\}$. We want to compute the probability that it leaves Σ through region 2 to Σ. The first term of the second member of Eq. (21) is the probability that, in its stochastic motion in the domain, the particle starts at 1 and arrives at 2 and finds no obstacle, so the configuration is $\{s_1,-1,s_2\}$ on regions 1, 2, 3, respectively, so that it leaves the domain. This is $S_{21}(s_1,-1,s_2|\sigma)$ and we sum over $s_1,s_2=\pm 1$. The second term is the probability $S_{11}(1,s_1,s_2|\sigma)$ that the particle, in its stochastic motion, starts from 1, comes back at 1 and finds an obstacle in the region 1 (configurations of the type $\{1,s_1,s_2\}$ on regions 1, 2, 3). Then, the particle starts again a motion in the domain, from region 1, with the configuration $\{1,s_1,s_2\}$ and finally leaves the domain through region 2, which gives $P(2|1;\{1,s_1,s_2\})$. This explains the term $P(2|1;\{1,s_1,s_2\})S_{11}(1,s_1,s_2|\sigma)$. The other terms are explained in an analogous way.

B. Transformation of the equations

We shall assume a certain symmetry, namely all regions are equivalent and

$$S_{j+1,j}(t),S_{jj}(t)\ \text{are independent of } j. \tag{22}$$

Then in Eq. (21) we have

$$P(2|2;\{s_1,1,s_2\})=P(1|1;\{1,s_1,s_2\}), \tag{23}$$

$$P(2|3;\{s_1,s_2,1\})=P(2|1;\{1,s_2,s_1\}), \tag{24}$$

$$\begin{aligned}P(1|1;\{1,s_1,s_2\})=1-[&P(2|1;\{1,s_1,s_2\})\\&+P(3|1;\{1,s_1,s_2\})]\end{aligned} \tag{25}$$

(this last equation due to the conservation of probability),

$$S_{31}(s_1,s_2,1|\sigma_1,\sigma_2,\sigma_3)=S_{21}(s_1,1,s_2|\sigma_1,\sigma_3,\sigma_2). \tag{26}$$

From these identities, Eq. (21) can be transformed as

$$P(2|1;\{\sigma\})=\sum_{s_1,s_2} S_{2,1}(s_1,-1,s_2|\sigma)+\sum_{s_1,s_2} P(2|1;\{1,s_1,s_2\})S_{11}(1,s_1,s_2|\sigma)+\sum_{s_1,s_2}[1-P(2|1;\{1,s_1,s_2\}) -P(2|1;\{1,s_2,s_1\})]S_{21}(s_1,1,s_2|\sigma)+\sum_{s_1,s_2} P(2|1;\{1,s_2,s_1\})S_{21}(s_1,1,s_2|\sigma_1,\sigma_3,\sigma_2). \tag{27}$$

In Eq. (27), we notice that

$$\sum_{s_1,s_2}[S_{21}(s_1,-1,s_2|\sigma)+S_{21}(s_1,1,s_2|\sigma)] =\sum_{\sigma'} S_{21}(\sigma'|\sigma)=S_{21}, \tag{28}$$

where we denote

$$S_{21}=\int_0^\infty S_{21}(t)dt. \tag{29}$$

Taking into account Eq. (28), we can rewrite Eq. (27), by renaming the variables of summation as

$$P(2|1,\sigma)=S_{21}+\sum_{s_1,s_2} P(2|1;\{1,s_1,s_2\})[S_{11}(1,s_1,s_2|\sigma) -S_{21}(s_1,1,s_2|\sigma)-S_{21}(s_2,1,s_1|\sigma) +S_{21}(s_2,1,s_1|\sigma_1,\sigma_3,\sigma_2)]. \tag{30}$$

This system is still a system of 8 equations for 8 unknowns. We can rewrite it, using matrix notations. Call $\langle P|$ the left vector with components,

$$\langle P|\sigma\rangle=P(2|1;\sigma). \tag{31}$$

We number the configuration σ according to the numbering of Appendix A, that is the lexicographic order, $((-1,-1,-1),(-1,-1,1),(-1,1,-1),(-1,1,1),\ldots,(1,1,1))$. We define

$$(\Phi_{11})_{\sigma\sigma'}\equiv S_{11}(\sigma|\sigma'), \tag{32}$$

$$(\Phi_{21})_{\sigma\sigma'}\equiv S_{21}(\sigma|\sigma'). \tag{33}$$

Using the definition Eq. (20) as well as Eq. (18) and Eq. (19), and introducing the projectors $|\nu\rangle\langle\nu|$, we see that,

$$\Phi_{ji}=\sum_{\nu=1}^{8} \hat{s}_{ji}(\lambda_\nu)|\nu\rangle\langle\nu|, \tag{34}$$

where

$$\hat{s}_{ji}(\lambda)=\int_0^\infty \exp(\lambda t)S_{ji}(t)dt. \tag{35}$$

With $\mathbf{I}_n$ denoting the $n\times n$ identity matrix, we introduce the following matrices:

$$\mathbf{Q}=(0|\mathbf{I}_4),\quad \mathbf{T}_1=\begin{pmatrix}\mathbf{I}_2&0&0&0\\0&0&\mathbf{I}_2&0\\0&\mathbf{I}_2&0&0\\0&0&0&\mathbf{I}_2\end{pmatrix},$$

$$\mathbf{T}_2=\begin{pmatrix}1&0&0&0&0&0&0&0\\0&0&1&0&0&0&0&0\\0&1&0&0&0&0&0&0\\0&0&0&1&0&0&0&0\\0&0&0&0&1&0&0&0\\0&0&0&0&0&0&1&0\\0&0&0&0&0&1&0&0\\0&0&0&0&0&0&0&1\end{pmatrix}, \tag{36}$$

and

$$\mathbf{T}_3=\mathbf{T}_2\mathbf{T}_1. \tag{37}$$

$\mathbf{T}_1,\mathbf{T}_2,\mathbf{T}_3$ are matrices of permutations corresponding to various permutations of the σ_j appearing in Eq. (30). The matrix $\mathbf{Q}$ is a matrix which projects on the components of $\langle P|$ with $\sigma=1$. Then, Eq. (30) can be written as

$$\langle P|=S_{21}\langle 1|+\langle P|\mathbf{Q}^T\mathbf{Q}(\Phi_{11}-\mathbf{T}_1\Phi_{21}) +\langle P|\mathbf{Q}^T\mathbf{Q}\mathbf{T}_3\Phi_{21}(\mathbf{T}_2-\mathbf{I}_8), \tag{38}$$

$\mathbf{Q}^T$ being the transposed $\mathbf{Q}$ matrix. Equation (38) can be reduced to a 4×4 system by introducing

$$\langle\overline{P}|=\langle P|\mathbf{Q}^T,\ \langle\overline{\nu}|=\langle\nu|\mathbf{Q}^T,\ |\overline{\nu}\rangle=\mathbf{Q}|\nu\rangle. \tag{39}$$

It is shown in Appendix B that

$$\langle\overline{P}|=S_{21}\langle\overline{1}|+\sum_{\nu=1}^{8} a_\nu\langle\overline{P}|\overline{\nu}\rangle\langle\overline{\nu}|+\hat{s}_{21}(\lambda_3)\langle\overline{P}|\overline{4}\rangle \times(\langle\overline{4}|+3\langle\overline{3}|)+\hat{s}_{21}(\lambda_6)\langle\overline{P}|\overline{6}\rangle(\langle\overline{6}|+3\langle\overline{7}|), \tag{40}$$

with

$$a_\nu=\hat{s}_{11}(\lambda_\nu)-\epsilon_\nu\hat{s}_{21}(\lambda_\nu),$$
$$\epsilon_\nu=+1\ \text{ for }\ \nu\neq 4,6,\ \ \epsilon_\nu=-1\ \text{ for }\ \nu=4,6. \tag{41}$$

Once $\langle\overline{P}|$ is found from Eqs. (40) and (41), the full vector $\langle P|$ is obtained using Eq. (38).

IV. ASYMPTOTIC SOLUTIONS AND RESONANCE

A. The transmission probability across the cage

We are interested in the calculation of the transmission probability across the cage, this is, by definition, the probability that the particle entering the cage through region 1, leaves the cage through region 2, at any time, conditioned on the fact that region 1 contains no obstacles at the initial time and the other regions are at thermal equilibrium for the Hamiltonian H. The probability that region 1 does not contain any obstacle is $1-\langle\overline{1}|\overline{1}\rangle=\frac{1}{2}$ (recall that the bar operation is the projection on the configuration σ such that $\sigma_1 = +1$). So the transmission probability across the cage is

$$D \equiv \frac{\langle P|1\rangle - \langle \overline{P}|\overline{1}\rangle}{1-\langle \overline{1}|\overline{1}\rangle} = 2[\langle P|1\rangle - \langle \overline{P}|\overline{1}\rangle]. \tag{42}$$

We use Eq. (B6) and the fact that $\langle \nu|1\rangle = \delta_{\nu 1}$,

$$\langle P|1\rangle = S_{21} + (S_{11}-S_{21})\langle \overline{P}|\overline{1}\rangle, \tag{43}$$

so that, using $S_{11} = 1-2S_{21}$, we obtain

$$D = 2S_{21}[1-3\langle \overline{P}|\overline{1}\rangle]. \tag{44}$$

In particular, Eq. (44) implies that $\langle \overline{P}|\overline{1}\rangle$ is always less than $\frac{1}{3}$.

B. Asymptotic values

1. Asymptotic value for large frequencies $\alpha \to \infty$

For $\alpha \to \infty$, all the $\lambda_\nu, \nu \neq 1$, tend to ∞ and the $\hat{s}_{ij}(\lambda_\nu)$ tend to 0. The important point is that the eigenvectors $|\nu\rangle$ and $\langle \nu|$ do not depend on α. Then Eq. (40) reduces to

$$\langle \overline{P}| = S_{21}\langle \overline{1}| + (S_{11}-S_{21})\langle \overline{P}|\overline{1}\rangle\langle \overline{1}| \tag{45}$$

or

$$\langle \overline{P}| = S_{21}\langle \overline{1}|(\overline{\mathbf{I}} - (S_{11}-S_{21})|\overline{1}\rangle\langle \overline{1}|)^{-1}$$

$$= S_{21}\langle \overline{1}|\left(\overline{\mathbf{I}} + \frac{(S_{11}-S_{21})|\overline{1}\rangle\langle \overline{1}|}{1-(S_{11}-S_{21})\langle \overline{1}|\overline{1}\rangle}\right), \tag{46}$$

and thus

$$\langle \overline{P}| = \frac{2S_{21}}{1+3S_{21}}\langle \overline{1}| \tag{47}$$

so using Eqs. (44) and (47), the transmission probability becomes

$$D(\alpha = +\infty) = \frac{2S_{21}}{1+3S_{21}}. \tag{48}$$

2. Asymptotic values for small frequencies $\alpha \to 0$

In this case, all the $\lambda_\nu \to 0$, $\hat{s}_{ij}(0) = S_{ij}$ and again the eigenvectors $|\nu\rangle$, $\langle \nu|$ do not depend on α. The calculations are in Appendix C, Eq. (B14) and give the result

$$D(\alpha = 0) = 2S_{21}[e + \tfrac{3}{2}f]. \tag{49}$$

C. Resonant and antiresonant behavior of the transmission probability

We want to calculate the first derivative of D,

$$\frac{dD}{d\alpha} = -6S_{21}\frac{d\langle \overline{P}|}{d\alpha}|\overline{1}\rangle \tag{50}$$

at $\alpha = 0$ and as α is going to ∞. It is proved in Appendix C, that $(dD/d\alpha)(\alpha = 0)$ is always positive. From this last fact, it is clear that a sufficient condition for $D(\alpha)$ to have a maximum at a certain value of $\alpha > 0$ is that

$$D(\alpha = 0) > D(\alpha = \infty). \tag{51}$$

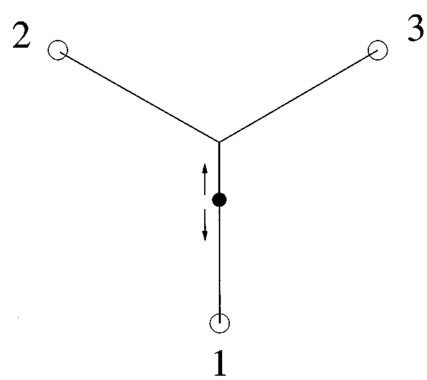

FIG. 2. Description of the simulated model. One particle (black circle) with three fluctuating obstacles (white circles).

Using Eqs. (48) and (49), Eq. (51) means that using the values of e,f in Eqs. (A4),

$$\frac{\exp(3\hat{J}) + \frac{3}{2}\exp(-\hat{J})}{\exp(3\hat{J}) + 3\exp(-\hat{J})} > \frac{2}{1+3S_{21}}. \tag{52}$$

In particular, if $S_{21} > \frac{1}{3}$, there exists a value of the coupling constant $\hat{J}_0$ so that Eq. (52) is valid for all $\hat{J} > \hat{J}_0$, so that for this domain of $\hat{J}$, $D(\alpha)$ has a maximum at a positive value of the frequency α, and we have resonance for the diffusion probability across the cage.

Moreover, it is shown in Appendix D that $(dD/d\alpha)(\alpha = \infty)$ is always negative [provided that $s_{21}(0) = 0$, which is a very reasonable assumption, and that $s_{11}(0) > 0$], so that as soon as $D(\alpha)$ presents a maximum with respect to α, it has a minimum too (we call this behavior ''antiresonance'').

In conclusion, for sufficiently strong transmission probability, $S_{21} > \frac{1}{3}$, and for a strong coupling between the obstacles in the surface of the cage, *we proved that the overall diffusion probability across the cage has a resonant and an antiresonant behavior as a function of the overall time scale of the dynamics of the obstacles on the surface of the cage*.

D. Numerical simulations

In order to check our analytical predictions, we have performed numerical simulations using a random telegraph process; the particle has a constant velocity, but the sign of the velocity can be positive or negative. The support of this random walk is a kind of discretized star with three branches (Fig. 2). At each node the particle has a probability p to keep the sign of its velocity, and a probability $(1-p)$ to change this sign. Moreover, at the central node (center of the star), and in the case when the particle decides not to reverse the sign of its velocity, it has a probability of one-half to go on the left branch of the star, and a probability of one-half to go on the right branch of the star. A barrier's dynamics is simulated by using the Gillespie method.[17] This method is a Monte Carlo simulation procedure that allows us to examine numerically the predictions of the master equation. The simulations parameters take the following values: probability

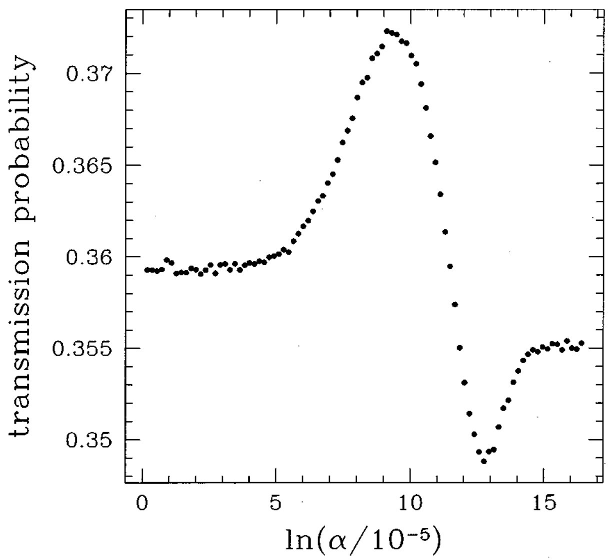

FIG. 3. Graph of transmission probability as a function of the frequency fluctuation α, obtained from numerical simulations, $p=0.95$ and $\hat{J}=0.8$. The extrema of the transmission probability corresponds to the resonant and antiresonant situations.

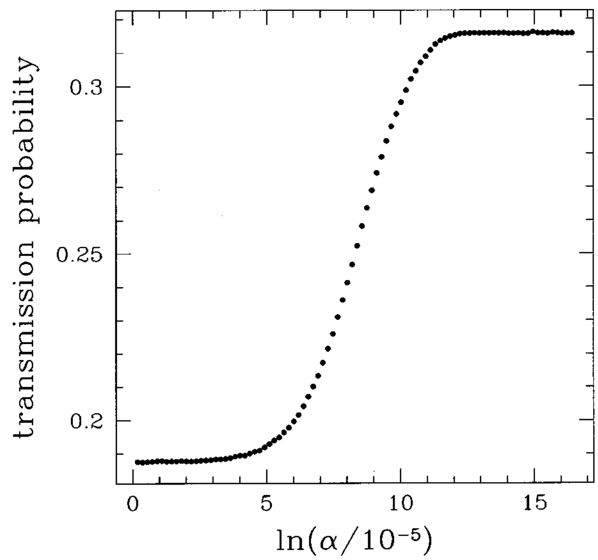

FIG. 4. Graph of transmission probability as a function of the frequency fluctuation α, obtained from numerical simulations, $p=0.95$ and $\hat{J}=0$. Transmission probability increases with α.

$p=0.995$; size of each branch of the star, $L=5$; average performed over 10^7 realizations. The results of these simulations confirm the possibility of a resonance of the transmission probability if the coupling between the barriers is strong enough (Fig. 3). On the contrary, the phenomena does not occur if the coupling is too weak (Fig. 4). Indeed, it seems that the transmission probability is an increasing function of the frequency α when the coupling $\hat{J}$ between the barriers is equal to 0. This assertion is supported on the one hand by previous results (we proved it was true in the case of a model with two barriers[9]), and on the other hand by all the numerical simulations we performed. Further on, as we shall see in next section, this property is true in the special case when the free motion is a ballistic motion. However, we were not able to prove this result in the general case.

Moreover, numerical simulations yield another kind of interesting result. For certain values of parameters of the problem, it is possible to obtain a range of frequency α for which the transmission probability is constant (Fig. 5).

V. STUDY OF THE BALLISTIC MOTION

In the special case of the ballistic motion, we have

$$S_{21}=\tfrac{1}{2}, \tag{53}$$

$$s_{11}(t)=0, \tag{54}$$

$$s_{21}(t)=\tfrac{1}{2}\delta(t-T), \tag{55}$$

where δ is the Dirac distribution, and T is a deterministic time corresponding to a direct transmission.

Now, we find an explicit expression of D in the case when there is no coupling between the barriers. Using Eqs. (44), (B7), (53), (54), and (55), we obtain after straightforward but lengthy calculations,

$$D=1-3/4\,\frac{-64-20e^{-3\alpha T}+12e^{-4\alpha T}+e^{-7\alpha T}+e^{-6\alpha T}+4e^{-2\alpha T}}{-80-23e^{-3\alpha T}+13e^{-2\alpha T}+14e^{-4\alpha T}+e^{-7\alpha T}+2e^{-5\alpha T}+e^{-6\alpha T}}. \tag{56}$$

Then, it is easy to see that $dD/d\alpha$ is positive. This shows that when there is no coupling between the barriers, and in the special case of the ballistic motion, the transmission probability is an increasing function of the frequency of fluctuation of the barriers. As already explained, it appears that this result is not limited to the special case of the ballistic motion. Besides, knowing that $S_{21}>\frac{1}{3}$, we deduce from Sec. IV C that for sufficiently strong coupling between the obstacles, the transmission probability has a resonant behavior as a function of the frequency of the barriers.

VI. CONCLUSION

We have proved that a stochastic motion inside a cage and a fluctuation of the state of the cage may conspire to produce an enhanced transmission probability through the cage, provided the motion of the degrees of freedom of the cage are sufficiently correlated. In fact, we have shown the existence of a resonance and an antiresonance of the transmission probability in term of the overall frequency of fluctuation of the cage. It should be again noticed that our model is completely general with respect to the dynamics of the particle inside the cage. In the special case of a ballistic motion, we were able to give a completely explicit expression for the transmission coefficient. In further articles, we will address the effect of fluctuating obstacles on chemical reactivity (rather than transmission), assuming that the cage contains one reactive center. This work is in progress.

APPENDIX A: EIGENSTATES OF THE OBSTACLES DYNAMICS

First, we number the configurations σ by increasing lexicographic order starting from $(-1,\ -1,\ -1)$,

$$\begin{aligned} &1=(-1,-1,-1) \qquad 2=(-1,-1,+1)\\ &3=(-1,+1,-1) \qquad 4=(-1,+1,+1),\\ &5=(+1,-1,-1) \qquad 6=(+1,-1,+1)\\ &7=(+1,+1,-1) \qquad 8=(+1,+1,+1). \end{aligned} \tag{A1}$$

The $\mathbf{R}$ matrix can be written as

$$\mathbf{R}=\frac{\alpha}{2}\begin{pmatrix} a & 1+\gamma & 1+\gamma & 0 & 1+\gamma & 0 & 0 & 0\\ 1-\gamma & b & 0 & 1 & 0 & 1 & 0 & 0\\ 1-\gamma & 0 & b & 1 & 0 & 0 & 1 & 0\\ 0 & 1 & 1 & b & 0 & 0 & 0 & 1-\gamma\\ 1-\gamma & 0 & 0 & 0 & b & 1 & 1 & 0\\ 0 & 1 & 0 & 0 & 1 & b & 0 & 1-\gamma\\ 0 & 0 & 1 & 0 & 1 & 0 & b & 1-\gamma\\ 0 & 0 & 0 & 1+\gamma & 0 & 1+\gamma & 1+\gamma & a \end{pmatrix}, \tag{A2}$$

where γ has been defined by Eq. (10) and

$$a=-3(1-\gamma),\ \ b=-3-\gamma. \tag{A3}$$

We define

$$\begin{aligned} &e=\frac{1}{Z}\exp(3\hat{J}),\ \ f=\frac{1}{Z}\exp(-\hat{J}),\\ &Z=2(\exp(3\hat{J})+3\exp(-\hat{J})),\ \ \hat{J}=\beta J. \end{aligned} \tag{A4}$$

Using the symmetries of $\mathbf{R}$ and noting that $\mathbf{R}$ commutes with $\mathbf{T}_1$ and $\mathbf{T}_2$, it is possible to compute the eigenvalues and eigenvectors of $\mathbf{R}$ exactly. They are given by

(1) $\lambda_1=0$

$$|1\rangle\equiv p_0\equiv(e,f,f,f,f,f,f,e)^T \quad \langle 1|\equiv(1,1,1,1,1,1,1,1).$$

(2) $\lambda_2=-\alpha(1-\gamma)$

$$|2\rangle\equiv(-3e,-f,-f,f,-f,f,f,3e)^T$$

$$\langle 2|\equiv\frac{1}{6(3e+f)}(-3,-1,-1,1,-1,1,1,3).$$

(3) $\lambda_3=\lambda_4=-\alpha(1+\gamma/2)$

$$|3\rangle\equiv(0,2,-1,1,-1,1,-2,0)^T \quad \langle 3|\equiv\tfrac{1}{12}|3\rangle^T$$

$$|4\rangle\equiv(0,0,-1,-1,1,1,0,0)^T \quad \langle 4|\equiv\tfrac{1}{4}|4\rangle^T.$$

(4) $\lambda_5=-\alpha(2-\gamma)$

$$|5\rangle\equiv(3,-1,\ldots,-1,3)^T$$

$$\langle 5|\equiv\frac{1}{18/e+6/f}\left(\frac{3}{e},-\frac{1}{f},\ldots,-\frac{1}{f},\frac{3}{e}\right).$$

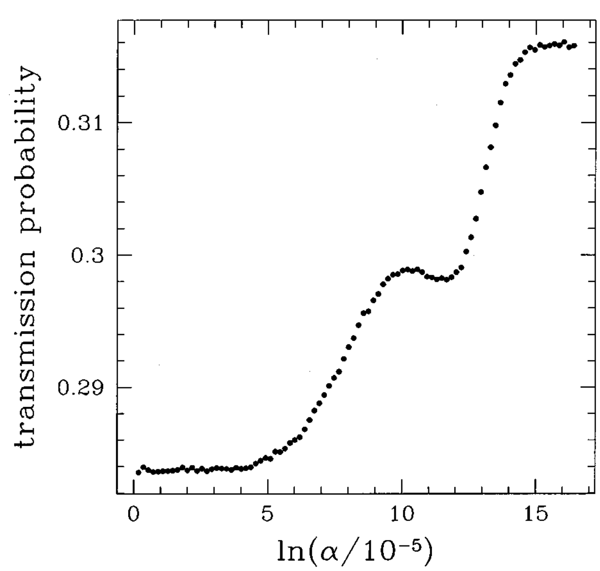

FIG. 5. Graph of transmission probability as a function of the frequency fluctuation α, obtained from numerical simulations, $p=0.9$ and $\hat{J}=0.8$. The figure displays a ''plateau'' behavior.

(5) $\lambda_6=\lambda_7=-\alpha(2+\gamma/2)$

$$|6\rangle\equiv(0,0,1,-1,-1,1,0,0)^T \quad \langle 6|\equiv\tfrac{1}{4}|6\rangle^T$$
$$|7\rangle\equiv(0,-2,1,1,1,1,-2,0)^T \quad \langle 7|\equiv\tfrac{1}{12}|7\rangle^T.$$

(6) $\lambda_8=-3\alpha$

$$|8\rangle\equiv(-1,1,1,-1,1,-1,-1,1)^T$$
$$\langle 8|\equiv\frac{1}{2/e+6/f}\left(-\frac{1}{e},\frac{1}{f},\frac{1}{f},-\frac{1}{f},\frac{1}{f},-\frac{1}{f},-\frac{1}{f},\frac{1}{e}\right).$$

Remark: The expressions of the eigenvalues eigenvectors given by Glauber[16] only apply for the simple eigenvalues. The multiple eigenvalues expressions are not correct even for this example of 3 spins.

APPENDIX B: RESOLUTION OF EQUATION (38)

We start from Eq. (38) and examine its different terms. First we have

$$\langle P|\mathbf{Q}^T\mathbf{Q}\Phi_{11}=\sum_{\nu=1}^{8}\hat{s}_{11}(\lambda_\nu)\langle\overline{P}|\overline{\nu}\rangle\langle\nu|. \tag{B1}$$

Now,

$$\mathbf{T}_1|\nu\rangle=\epsilon_\nu|\nu\rangle, \tag{B2}$$

where $\epsilon_\nu=-1$, for $\nu=4,6$, $\epsilon_\nu=1$, for $\nu\neq 4,6$, according to the table of eigenvectors $|\nu\rangle$, and

$$\langle P|\mathbf{Q}^T\mathbf{Q}\mathbf{T}_1\Phi_{21}=\sum_{\nu=1}^{8}\epsilon_\nu\hat{s}_{21}(\lambda_\nu)\langle\overline{P}|\overline{\nu}\rangle\langle\nu|, \tag{B3}$$

$$\langle P|\mathbf{Q}^T\mathbf{Q}(\Phi_{11}-\mathbf{T}_1\Phi_{21})=\sum_{\nu=1}^{8}a_\nu\langle\overline{P}|\overline{\nu}\rangle\langle\nu|, \tag{B4}$$

where a_ν is given as in Eq. (41)

$$a_\nu=\hat{s}_{11}(\lambda_\nu)-\epsilon_\nu\hat{s}_{21}(\lambda_\nu). \tag{B5}$$

One checks that $\langle\nu'|(\mathbf{T}_2-\mathbf{I}_8)=0$ for $\nu'=1,2,5,8$. Furthermore, it is easy to compute the action of $\mathbf{T}_2$ and $\mathbf{T}_3$ on the eigenvectors of $\mathbf{R}$, so that Eq. (38) can be written,

$$\langle P|=S_{21}\langle 1|+\sum_{\nu=1}^{8}a_\nu\langle\overline{P}|\overline{\nu}\rangle\langle\nu|+\langle\overline{P}|\overline{4}\rangle s_{21}(\lambda_3)(3\langle 3| +\langle 4|)+\langle\overline{P}|\overline{6}\rangle s_{21}(\lambda_6)(\langle 6|+3\langle 7|). \tag{B6}$$

If we multiply by $\mathbf{Q}^T$ on the right, we obtain exactly Eq. (40) for $\langle\overline{P}|$.

APPENDIX C: ASYMPTOTIC BEHAVIORS OF *D*

Equation (40) can be written,

$$\langle\overline{P}|=S_{21}\langle\overline{1}|(\overline{\mathbf{I}}-\overline{\mathbf{X}})^{-1}, \tag{B7}$$

where

$$\overline{\mathbf{X}}=\sum_{\nu=1}^{8}a_\nu|\overline{\nu}\rangle\langle\overline{\nu}|+[\hat{s}_{21}(\lambda_3)|\overline{4}\rangle+\hat{s}_{21}(\lambda_6)|\overline{6}\rangle] \times[\langle\overline{4}|+3\langle\overline{3}|]. \tag{B8}$$

1. The fluctuating frequency α tends to 0

Expanding $\langle\overline{P}|$ and $\overline{X}$ in powers of α,

$$\langle\overline{P}|=\langle\overline{P}|^{(0)}+\alpha\langle\overline{P}|^{(1)}+O(\alpha^2), \tag{B9}$$

$$\overline{\mathbf{I}}-\overline{\mathbf{X}}=(\overline{\mathbf{I}}-\overline{\mathbf{X}}^{(0)})-\alpha\overline{\mathbf{X}}^{(1)}+O(\alpha^2), \tag{B10}$$

we get

$$\langle\overline{P}|^{(0)}=S_{21}\langle\overline{1}|(\overline{\mathbf{I}}-\overline{\mathbf{X}}^{(0)})^{-1}, \tag{B11}$$

and

$$\langle\overline{P}|^{(1)}=\langle\overline{P}|^{(0)}\overline{\mathbf{X}}^{(1)}(\overline{\mathbf{I}}-\overline{\mathbf{X}}^{(0)})^{-1}. \tag{B12}$$

It is straightforward to find that

$$\overline{\mathbf{I}}-\overline{\mathbf{X}}^{(0)}=S_{21}\begin{pmatrix}2&0&0&0\\0&1&1&0\\0&0&3&0\\0&0&0&3\end{pmatrix}, \tag{B13}$$

then

$$\langle\overline{P}|^{(0)}\overline{1}\rangle=\tfrac{1}{3}e+\tfrac{3}{2}f. \tag{B14}$$

$\overline{\mathbf{X}}^{(1)}$ is obtained by taking the first derivative with respect to α of $\overline{\mathbf{X}}$ at $\alpha=0$. Now, the eigenvalues are proportional to α (see Appendix A) and the eigenvectors are independent of α. We notice that

$$\frac{d\hat{s}_{ij}}{d\alpha}(\lambda_\nu)|_{\alpha=0}=\frac{d\lambda_\nu}{d\alpha}\tau_{ij}, \tag{B15}$$

where

$$\tau_{ij}=\int_0^\infty ts_{ij}(t)dt \tag{B16}$$

is the average time to leave the cage through region *j* when we know that the particle has entered through region *i*. To obtain $\overline{\mathbf{X}}^{(1)}$, it is enough to take the derivative of the $a_\nu,\hat{s}_{21}$. The $d\lambda_\nu/d\alpha$ in Eq. (B15) are given in Appendix A. Moreover,

$$\langle\overline{P}|^{(0)}=(\tfrac{1}{2},1,0,\tfrac{1}{3})^T. \tag{B17}$$

A tedious calculation gives

$$\langle\overline{P}|^{(1)}\overline{1}\rangle=-\frac{1}{24}\frac{e^{-4\hat{J}}}{S_{21}}\frac{12\tau_{11}+12\tau_{21}+4\tau_{21}e^{-4\hat{J}}+5\tau_{11}e^{-4\hat{J}}}{(1+e^{-4\hat{J}})(1+3e^{-4\hat{J}})} \tag{B18}$$

which is always negative (here $\hat{J}=\beta J$). Thus, $(dD/d\alpha)$ $(\alpha=0)$ is always positive.

2. The fluctuating frequency α tends to ∞

We write,

$$\langle\overline{P}|=\langle\overline{P}|^{(a)}+\frac{1}{\alpha}\langle\overline{P}|^{(b)}+O\left(\frac{1}{\alpha^2}\right), \tag{B19}$$

$$\overline{\mathbf{X}}=\overline{\mathbf{X}}^{(a)}+\frac{1}{\alpha}\overline{\mathbf{X}}^{(b)}+O\left(\frac{1}{\alpha^2}\right), \tag{B20}$$

where the matrix $\overline{X}$ was defined by Eq. (B8). From Eqs. (B7), (B19), and (B20), we have

$$\langle\overline{P^{(b)}}| = \langle\overline{P^{(a)}}|\overline{\mathbf{X}}^{(b)}(\overline{\mathbf{I}} - \overline{\mathbf{X}}^{(a)})^{-1}. \tag{B21}$$

We know from Eq. (47) that

$$\langle\overline{P}|^{(a)} = \frac{2S_{21}}{1+3S_{21}}\langle\overline{1}|, \tag{B22}$$

and from Eq. (46) that

$$(\overline{\mathbf{I}} - \overline{\mathbf{X}}^{(a)})^{-1} = \overline{\mathbf{I}} + \frac{(S_{11}-S_{21})|\overline{1}\rangle\langle\overline{1}|}{1-(S_{11}-S_{21})\langle\overline{1}|\overline{1}\rangle}. \tag{B23}$$

Moreover, as soon as $s_{21}(0)=0$, what is physically reasonable assumption, we have

$$\overline{\mathbf{X}}^{(b)} = -s_{11}(0)\sum_{\nu=2}^{8}\frac{\alpha}{\lambda_\nu}|\overline{\nu}\rangle\langle\overline{\nu}|. \tag{B24}$$

Using Eqs. (B21), (B22), (B23), and (B24), we find after some calculations that

$$\langle\overline{P^{(b)}}|\overline{1}\rangle = \frac{S_{21}s_{11}(0)e^{4\hat{J}}}{2} \times \frac{11e^{-12\hat{J}}+13e^{-8\hat{J}}+5e^{-4\hat{J}}+3}{(3-S_{21})(1+3S_{21})(1+3e^{-4\hat{J}})(3+e^{-4\hat{J}})} \tag{B25}$$

which is always positive. Thus $(dD/d\alpha)(\infty)$ is always negative [as soon as $s_{21}(0)=0$ and $s_{11}(0)>0$].

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