Incoherent neutron scattering functions for diffusion inside two concentric spheres

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We consider the diffusion of a particle inside two concentric spheres as a model for diffusing motions inside and between two semipermeable subregions or sublayers of a confining region. Analytic expressions for the elastic incoherent structure factor (EISF) and the incoherent scattering correlation function, $C(\mathbf{Q},t)$, are derived for this model. It is found that, as a result of interferences between regions, the EISF is a weighted coherent summation over amplitudes corresponding to subregions and the relaxation rate of $C(\mathbf{Q},t)$ has a turnover behavior with a minimum at $\mathbf{Q}_m$. In addition to the single exponential behavior for $\mathbf{Q}<\mathbf{Q}_m$, $C(\mathbf{Q},t)$ also shows a biexponential decay as a function of time for intermediate values of $\mathbf{Q}\geqslant\mathbf{Q}_m$. The rate of decay at short times is related to diffusion over length scales under consideration while at long times it is given by the relaxation to equilibrium in fluctuations of population between subregions.

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I. INTRODUCTION

Incoherent neutron scattering from single-particle hydrogen atoms provides a means for investigating motions of atoms, molecules, chemical species, or macromolecules in liquids, crystals, or powders [1]. In this technique, the spatial and temporal information on the particle motions are obtained from the incoherent scattering function $S(\mathbf{Q},\omega)$, which describes the distributions of the scattering wave vector $\mathbf{Q}$ and energy transfer $\hbar\omega$. In the Born approximation the function $S(\mathbf{Q},\omega)$ is related by the double Fourier transformation in space and time to the Van Hove self-correlation function [2], $G(\mathbf{r},t|\mathbf{r}_0)$, which describes the correlations between positions of one and the same particle at different times, i.e., the probability density of finding the particle at the position $\mathbf{r}$ at time t conditional that it was initially at $\mathbf{r}_0$ (in general, $\mathbf{r}$ and $\mathbf{r}_0$ describe many degrees of freedom, such as translation, rotation, ..., but for simplicity we will be concerned only with the translation). For a particle diffusing in a potential $V(\mathbf{r})$ due to interactions with its environment, $G(\mathbf{r},t|\mathbf{r}_0)$ is the Green's function of the diffusion equation describing the particle dynamics. From a theoretical standpoint, this is, however, a rather difficult task of determining the Green's function and hence computing the incoherent scattering function for diffusion in an arbitrary potential.

However, for many physical situations of interests like molecules at surfaces, in micellar systems, or in vesicles and structural cages, the interacting system can be modeled by a geometrically confining potential $V(\mathbf{r})$ and the problem reduces to diffusion of a particle in a bounded space. For these situations, there is, for instance, the model of diffusion inside a sphere with an impermeable surface for which the analytical expressions of $S(\mathbf{Q},\omega)$ have been previously calculated by Volino and Dianoux [3] for the continuous diffusion. The main features of the model are that the elastic incoherent structure factor (EISF) provides the single confining length (i.e., the sphere radius) and the almost Lorentzian $S(\mathbf{Q},\omega)$ [or equivalently, the exponential incoherent scattering correlation function $C(\mathbf{Q},t)$] is characterized by the time scale for the particle to diffuse over the entire sphere. Similar results were derived by Hall and Ross [4] for the jump-diffusion motions in a segment and a cube. All these results have been subsequently used, for example, to study the dynamics of water molecules on the surface of proteins as done by Bellissent-Funel *et al.* [5] with an extension to account for the presence of immobile particles.

In this paper we consider the situation where particles diffuse within a large closed region or cage containing another semipermeable cage that divides the system into two subregions. For simplicity, we consider spherical symmetric cages that fit together and model the problem by the diffusion of a particle inside two concentric spheres with the inner sphere (of smaller size) having a semipermeable surface and the outer one (of larger size) an impermeable surface, i.e., confining. Our goal is to derive for this model the analytical expressions and approximations for the EISF and the incoherent scattering correlation function $C(\mathbf{Q},t)$ which carries the same information as the inelastic part of $S(\mathbf{Q},\omega)$.

The outline of the paper is as follows. Section II and the Appendix introduce notations, describe the general formalism, and define the relevant quantities to be calculated. In Sec. III the formalism described in Sec. II is applied to the case of diffusion inside two concentric spheres in order to derive explicit expressions for the EISF and $C(\mathbf{Q},t)$. The single and biexponential approximations for $C(\mathbf{Q},t)$ are considered subsequently. In Sec. IV we complete this detailed analysis with illustrative examples. Finally, Sec. V contains a brief summary of the paper.

II. INCOHERENT SCATTERING FUNCTION AND RELAXATION RATE

Consider a particle undergoing a diffusive motion in a potential $V(\mathbf{r})$ and assume that the potential is such that there exists a normalized equilibrium distribution:

$$P_{\mathrm{eq}}(\mathbf{r})=\frac{e^{-\beta V(\mathbf{r})}}{\int e^{-\beta V(\mathbf{r})}d\mathbf{r}},\quad \mathbf{r}=(r,\Omega), \tag{2.1}$$

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where r is the particle position, Ω stands for polar and azimuthal coordinates, and $\beta^{-1}=k_BT$ is the thermal energy. When the potential is of spherical symmetry, i.e., $V(\mathbf{r})=V(r)$, the equilibrium distribution can be factorized as, $P_{\rm eq}(\mathbf{r})=Y_{\rm eq}(\Omega)p_{\rm eq}(r)$, where $Y_{\rm eq}(\Omega)=1/(4\pi)$ is the uniform distribution for angular coordinates and

$$p_{\rm eq}(r)=\frac{e^{-\beta V(r)}}{\int e^{-\beta V(r)}r^2dr}. \tag{2.2}$$

The dynamics of the particle diffusing in the potential is described by the Green's function, $G(\mathbf{r},t|\mathbf{r}_0)$, which is the probability density of finding the particle at the position $\mathbf{r}$ at time t given that it was initially at $\mathbf{r}_0$. When both the potential and the diffusion are isotropic, the Green's function is given by (see the Appendix)

$$G(\mathbf{r},t|\mathbf{r}_0)=\sum_{l=0}^{\infty} g_l(r,t|r_0)\sum_{m=-l}^{m=+l} Y_l^m(\Omega)Y_l^{*m}(\Omega_0), \tag{2.3}$$

where $Y_l^m(\cdots)$ are spherical harmonic functions,

$$g_l(r,t|r_0)=\frac{e^{-\beta[V(r)-V(r_0)]/2}}{rr_0}\sum_{n=0}^{\infty}\psi_n^l(r)\psi_n^{*l}(r_0)\exp\{-\Gamma_n^l t\}, \tag{2.4}$$

and

$$\Gamma_n^l=\begin{cases}(q_n^l)^2D, & \text{continuous diffusion}\\ \gamma[1-e^{-(q_n^l b)^2/2}], & \text{jump diffusion,}\end{cases} \tag{2.5}$$

in which D is the diffusion coefficient, b the jump length, and γ the jump frequency. $-(q_n^l)^2$ and $\psi_n^l(r)$ are the eigenvalues and eigenfunctions of the self-adjoint operator $\mathrm{H}_l(r)$ defined as [see Eq. (A4)]

$$H_l(r)=\frac{e^{\beta V(r)/2}}{r}\frac{d}{dr}r^2e^{-\beta V(r)}\frac{d}{dr}\frac{e^{\beta V(r)/2}}{r}-\frac{l(l+1)}{r^2}. \tag{2.6}$$

The Green's function is subjected to the initial condition, $G(\mathbf{r},t=0|\mathbf{r}_0)=\delta(\mathbf{r}-\mathbf{r}_0)$ and has the following properties:

$$\int G(\mathbf{r},t|\mathbf{r}_0)d\mathbf{r}=1\Rightarrow\int g_l(r,t|r_0)r^2dr=\delta_{l0}, \tag{2.7a}$$

$$\lim_{t\to\infty}G(\mathbf{r},t|\mathbf{r}_0)=P_{\rm eq}(\mathbf{r}_0)\Rightarrow\lim_{t\to\infty}g_l(r,t|r_0)=\delta_{l0}p_{\rm eq}(r_0), \tag{2.7b}$$

$$\begin{aligned}\int G(\mathbf{r},t|\mathbf{r}_0)P_{\rm eq}(\mathbf{r}_0)d\mathbf{r}_0 &=P_{\rm eq}(\mathbf{r})\Rightarrow\int g_l(r,t|r_0)p_{\rm eq}(r_0)r_0^2dr_0\\ &=\delta_{l0}p_{\rm eq}(r).\end{aligned} \tag{2.7c}$$

Equation (2.7a) means that the probability is conserved, (2.7b) reflects the relaxation to the equilibrium distribution, and (2.7c) means that the equilibrium distribution is stationary.

The quantity measured in incoherent neutron scattering experiments is the incoherent dynamic structure factor,

$$S_{\rm inc}(\mathbf{Q},\omega)=\frac{1}{\pi}\int_0^{\infty}I(\mathbf{Q},t)\cos(\omega t)dt, \tag{2.8}$$

where $\hbar\omega$ is the energy transfer from the neutron beam to the system. The incoherent intermediate scattering function, $I(\mathbf{Q},t)$, which contains the same information as $S_{\rm inc}(\mathbf{Q},\omega)$, is defined as

$$\begin{aligned}I(\mathbf{Q},t)&=\langle e^{i\mathbf{Q}\cdot\mathbf{r}(t)}e^{-i\mathbf{Q}\cdot\mathbf{r}(0)}\rangle\\ &=\int d\mathbf{r}_0\int d\mathbf{r}e^{i\mathbf{Q}\cdot\mathbf{r}}G(\mathbf{r},t|\mathbf{r}_0)e^{-i\mathbf{Q}\cdot\mathbf{r}_0}P_{\rm eq}(\mathbf{r}_0),\end{aligned} \tag{2.9}$$

in which $\mathbf{Q}$ is the scattering wave vector of the neutron. For an isotropic problem (i.e., both the potential and the diffusion are isotropic), the angular coordinates can be eliminated from the expression of $I(\mathbf{Q},t)$ as follows. One first expands $e^{i\mathbf{Q}\cdot\mathbf{r}}$ as

$$e^{i\mathbf{Q}\cdot\mathbf{r}}=\sum_{k=0}^{\infty}[4\pi(2k+1)e^{ik\pi}]^{1/2}j_k(Qr)Y_k^0(\Omega), \tag{2.10}$$

where $j_k(\cdots)$ is the spherical Bessel function of the first kind of order k. These expansions for $e^{i\mathbf{Q}\cdot\mathbf{r}}$ and Eq. (2.3) are then plugged back into Eq. (2.9), and using the orthogonality property of $Y_l^m(\cdots)$ when performing the operation, $\int d\Omega_0\int d\Omega(\cdots)$, yield the result

$$\begin{aligned}I(Q,t)&=\sum_{l=0}^{\infty}(2l+1)\int r_0^2dr_0\int r^2drj_l(Qr)\\ &\quad\times g_l(r,t|r_0)j_l(Qr_0)p_{\rm eq}(r_0)\\ &=\sum_{n,l=0}^{\infty}A_n^l(Q)\exp\{-\Gamma_n^l t\},\end{aligned} \tag{2.11}$$

in which we have used the expression for $g_l(r,t|r_0)$ in Eq. (2.4). The amplitude $A_n^l(Q)$ are given by

$$A_n^l(Q)=(2l+1)\left|\int[r^2p_{\rm eq}(r)]^{1/2}j_l(Qr)\psi_n^l(r)dr\right|^2. \tag{2.12}$$

It is clear from Eq. (2.9) that $I(Q,t=0)=1$ but

$$\lim_{t\to\infty}I(Q,t)=A_0^0(Q)=\left|\int r^2p_{\rm eq}(r)j_0(Qr)dr\right|^2, \tag{2.13}$$

where $A_0^0(Q)$, the elastic incoherent structure factor, describes to the spatial structure of the potential. It thus follows from this that $I(Q,t)$ can be split into two parts as

$$I(Q,t)=A_0^0(Q)+[1-A_0^0(Q)]C(Q,t), \tag{2.14}$$

where $C(Q,t)$ is the incoherent scattering correlation function containing all information about the relaxation dynamics in the potential, i.e., the quasielastic part of neutron scattering. This correlation function is defined as

$$\begin{aligned} C(Q,t) &= \frac{\langle e^{i\mathbf{Q}\cdot\mathbf{r}(t)}e^{-i\mathbf{Q}\cdot\mathbf{r}(0)}\rangle-|\langle e^{i\mathbf{Q}\cdot\mathbf{r}}\rangle|^2}{1-|\langle e^{i\mathbf{Q}\cdot\mathbf{r}}\rangle|^2} \\ &= \sum_{\{n,l\}\neq\{0,0\}}^{\infty}\left[\frac{A_n^l(Q)}{1-A_0^0(Q)}\right]\exp\{-\Gamma_n^l t\}. \end{aligned} \tag{2.15}$$

It is clear from this that $C(Q,0)=1$ and $C(Q,t)\to 0$ as $t\to\infty$. When $Q\to 0$, the scattering correlation function reduces to the position correlation function defined as

$$C(0,t)=\frac{\langle \mathbf{r}(t)\mathbf{r}(0)\rangle-\langle\mathbf{r}\rangle^2}{\langle\mathbf{r}^2\rangle-\langle\mathbf{r}\rangle^2}=\frac{\langle r(t)r(0)\rangle_1}{\langle r^2\rangle}, \tag{2.16}$$

with $\langle r(t)r(0)\rangle_1=\int r_0^2dr_0\int r^2drrg_1(r,t|r_0)r_0p_{\mathrm{eq}}(r_0)$ [we note that $g_l(r,t|r_0)=\delta(r-r_0)/r^2$ and $g_l(r,t\to\infty|r_0)=0$ for $l\neq 0$.] In the opposite limit of $Q\to\infty$ (i.e., for very short length scales) the boundaries of the system become insignificant and the particle motion can be described by a boundary-free diffusion. In this case, $C(Q,t)$ is a single exponential given by

$$\lim_{Q\to\infty} C(Q,t)=e^{-\Gamma t},$$

$$\Gamma=\begin{cases} Q^2D, & \text{continuous diffusion} \\ \gamma[1-e^{-(Qb)^2/2}], & \text{jump diffusion.}\end{cases} \tag{2.17}$$

In general, $C(Q,t)$ is a nonexponential function of time and its relaxation time $1/k(Q)$ is defined through

$$\frac{1}{k(Q)}=\int_0^\infty C(Q,t)dt=\sum_{\{n,l\}\neq\{0,0\}}^{\infty}\left[\frac{A_n^l(Q)}{1-A_0^0(Q)}\right]\frac{1}{\Gamma_n^l}. \tag{2.18}$$

III. DIFFUSION INSIDE TWO CONCENTRIC SPHERES

We consider now the situation where the particle diffuses within two concentric spheres corresponding to the potential

$$V(r)=\begin{cases}-\varepsilon, & 0\leqslant r\leqslant a \\ 0, & a<r\leqslant R,\end{cases} \tag{3.1}$$

where a and R are the radii of inner and outer spheres, respectively. The inner sphere is semipermeable since it is energetically more stable than the region comprised between the inner and the outer spheres by $\varepsilon\geqslant 0$. In other words, $\beta\varepsilon$ controls the permeability of the inner spherical cage. The normalized thermal equilibrium distribution $p_{\mathrm{eq}}(r)$ of any position r is

$$p_{\mathrm{eq}}(r)=\frac{e^{-\beta V(r)}}{Z_0^0}=\frac{1}{R^3+a^3(e^{\beta\varepsilon}-1)}\times\begin{cases}e^{\beta\varepsilon}, & 0\leqslant r\leqslant a \\ 1, & a<r\leqslant R.\end{cases} \tag{3.2}$$

A. Elastic incoherent structure factor (EISF)

Using the above expression for $p_{\mathrm{eq}}(r)$ in Eq. (2.13), we find that the EISF for the incoherent scattering law is obtained as a weighted coherent summation over amplitudes corresponding to subregions as

$$A_0^0(Q)=\left|\phi\left[\frac{3j_1(QR)}{QR}\right]+(1-\phi)\left[\frac{3j_1(Qa)}{Qa}\right]\right|^2, \tag{3.3}$$

where ϕ, the degree of permeability describing the fraction of equivalent particles considered as mobile within the entire sphere of radius R, is defined as

$$\phi=\frac{R^3}{a^3(e^{\beta\varepsilon}-1)+R^3}. \tag{3.4}$$

When $\phi=0$ (i.e., $\beta\varepsilon=\infty$) or $\phi=1$ (i.e., $\beta\varepsilon=0$), Eq. (3.3) reduces to the EISF for a particle diffusing inside a sphere [3] of radius a or R, respectively. On the other hand, when $\varepsilon<0$ the situation is otherwise, and in the $\beta\varepsilon\to-\infty$ limit the problem reduces to diffusion *between* two concentric spheres [1,6].

B. General expression of the amplitudes, $A_n^l(Q)$

The computation of the scattering correlation function $C(Q,t)$ and of the relaxation rate constant $k(Q)$ requires the calculation of all the amplitudes $A_n^l(Q)$ and hence to determine the eigenvalues q_n^l and eigenfunctions $\psi_n^l(r)$ of the operator $\mathrm{H}_l(r)$. To this end, and using the expression for $V(r)$ in Eq. (3.1), we end up solving the Riccati-Bessel differential equation [7],

$$r^2\frac{d^2\psi^l}{dr^2}+[(q^lr)^2-l(l+1)]\psi^l(r)=0, \quad r\neq a \tag{3.5}$$

and subject to the reflecting boundary conditions at edges

$$\left.\frac{d}{dr}\left[\frac{\psi^l(r)}{r}\right]\right|_{r=0,R}=0. \tag{3.6}$$

Since the potential $V(r)$, as defined in Eq. (3.1), is discontinuous at $r=a$, Eq. (3.5) has to be solved separately in the region $r\leqslant a_-$ (inner space) and in the region $r\geqslant a_+$ (outer space). These solutions are next matched using the conditions

$$\mathrm{e}^{-\beta\varepsilon/2}\psi^l(r)|_{r=a_-}=\psi^l(r)|_{r=a_+}, \tag{3.7a}$$

$$\mathrm{e}^{\beta\varepsilon/2}\frac{d}{dr}\left[\frac{\psi^l(r)}{r}\right]\bigg|_{r=a_-}=\frac{d}{dr}\left[\frac{\psi^l(r)}{r}\right]\bigg|_{r=a_+}. \tag{3.7b}$$

In this way we find that the eigenvalues q_n^l are solutions of

$$\frac{(\alpha_1 - e^{\beta\varepsilon}) j_{-l-1}(x)}{(1-\alpha_1) j_l(x)} = \frac{(l+1) j_{-l-1}(x) + x j_{-l}(x)}{l j_l(x) - x j_{l+1}(x)}, \tag{3.8}$$

where

$$\alpha_1 = \frac{[(l+1) j_{-l-1}(y) + y j_{-l}(y)] j_l(x)}{[(l+1) j_{-l-1}(y) + y j_{-l}(y)] j_l(x) + [l j_l(y) - y j_{l+1}(y)] j_{-l-1}(x)}, \tag{3.9a}$$

$$\alpha_2 = \frac{(1-\alpha_1) j_l(x)}{j_{-l-1}(x)}, \quad x = q_n^l a \quad \text{and} \quad y = q_n^l R, \quad n = 0,1,2,\ldots. \tag{3.9b}$$

The corresponding eigenfunctions $\psi_n^l(r)$ are given by

$$\psi_n^l(r) = \frac{r}{[Z_n^l]^{1/2}} \times \begin{cases} e^{\beta\varepsilon/2} j_l(q_n^l r), & 0 \leqslant r \leqslant a, \\ \alpha_1 j_l(q_n^l r) + \alpha_2 j_{-l-1}(q_n^l r), & a < r \leqslant R, \end{cases} \tag{3.10}$$

where normalization constants Z_n^l are obtained from the condition, $\int_0^1 \psi_m^l(r) \psi_n^l(r) dr = \delta_{mn}$. Note that $q_0^0 = 0$, and $|\psi_0^0(r)|^2 = r^2 p_{\mathrm{eq}}(r)$, where $p_{\mathrm{eq}}(r)$ is the equilibrium distribution given in Eq. (3.2).

Now using in Eq. (2.12) the expression of $\psi_n^l(r)$ given in Eq. (3.10) and after having evaluated the integrals [7], we obtain the following expression for the amplitudes:

$$A_n^l(Q) = (2l+1) |F_n^l(Q)|^2, \tag{3.11a}$$

$$\begin{aligned} F_n^l(Q) = \frac{1}{[Z_0^0 Z_n^l]^{1/2}} \times \Bigg\{ & (e^{\beta\varepsilon} - \alpha_1) a^3 \left[\frac{Qa j_{l+1}(Qa) j_l(q_n^l a) - q_n^l a j_{l+1}(q_n^l a) j_l(Qa)}{(Qa)^2 - (q_n^l a)^2} \right] \\ & + \alpha_1 R^3 \left[\frac{QR j_{l+1}(QR) j_l(q_n^l R) - q_n^l R j_{l+1}(q_n^l R) j_l(QR)}{(QR)^2 - (q_n^l R)^2} \right] \\ & + \alpha_2 R^3 \left[\frac{QR j_{l+1}(QR) j_{-l-1}(q_n^l R) - q_n^l R j_{-l}(q_n^l R) j_l(QR) - (2l+1) j_l(QR) j_{-l-1}(q_n^l R)}{(QR)^2 - (q_n^l R)^2} \right] \\ & - \alpha_2 a^3 \left[\frac{Qa j_{l+1}(Qa) j_{-l-1}(q_n^l a) - q_n^l a j_{-l}(q_n^l a) j_l(Qa) - (2l+1) j_l(Qa) j_{-l-1}(q_n^l a)}{(Qa)^2 - (q_n^l a)^2} \right] \Bigg\}. \end{aligned} \tag{3.11b}$$

These expressions for q_n^l (i.e., for Γ_n^l) and $A_n^l(Q)$ can next be used in Eqs. (2.15) and (2.18) for determination of the scattering correlation function $C(Q,t)$ and its relaxation rate constant $k(Q)$. However, it may be useful for practical uses to derive approximations of $C(Q,t)$.

C. Single exponential approximation

Let us consider the expression of $C(Q,t)$ when $Q \to 0$, i.e., the position correlation function [see Eq. (2.16)]. In this limit we have $1 - A_0^0(Q) \sim Q^2$ and the other amplitudes $A_n^l(Q)$ behave as $A_n^l(Q) \sim Q^{2l}$. It thus follows that $A_n^1(Q)$ are the only amplitudes contributing to $C(Q,t)$ when $Q \to 0$ so that

$$\begin{aligned} C(Q=0,t) &= \sum_{n=0}^{\infty} \left\{ \lim_{Q \to 0} \left[\frac{A_n^1(Q)}{1 - A_0^0(Q)} \right] \right\} \exp\{-\Gamma_n^1 t\} \\ &= \sum_{n=0}^{\infty} C_n \exp\{-\Gamma_n^1 t\}, \end{aligned} \tag{3.12}$$

where

$$\begin{aligned} C_n = & \frac{5}{[R^5 + (e^{\beta\varepsilon} - \alpha_1) a^5] Z_n^1 (q_n^1)^8} \\ & \times |(e^{\beta\varepsilon} - \alpha_1)[3(q_n^1 a)^2 j_1(q_n^1 a) - (q_n^1 a)^3 j_0(q_n^1 a)] \\ & + \alpha_1 [3(q_n^1 R)^2 j_1(q_n^1 R) - (q_n^1 R)^3 j_0(q_n^1 R)] \\ & + \alpha_2 [3(q_n^1 R)^2 j_{-2}(q_n^1 R) + (q_n^1 R)^3 j_{-1}(q_n^1 R)] \\ & - \alpha_2 [3(q_n^1 a)^2 j_{-2}(q_n^1 a) + (q_n^1 a)^3 j_{-1}(q_n^1 a)]|^2. \end{aligned} \tag{3.13}$$

The single exponential approximation consists of replacing the multiexponential expansion (3.12) by

$$C(0,t)\simeq\exp\{-k(0)t\}\quad\text{with}\quad k(0)=\left[\sum_{n=0}^{\infty}\frac{C_n}{\Gamma_n^1}\right]^{-1},\tag{3.14}$$

i.e., the inelastic part of $S_{\mathrm{inc}}(Q\to 0,\omega)$ is a Lorentzian. This appears to be a good approximation of Eq. (3.12) when $\Gamma_0^1 \ll\Gamma_1^1<\Gamma_2^1<\cdots$ and $C_0\simeq 1\gg C_1>C_2>\cdots$, so that only the leading term contributes to $C(0,t)$. In this case, the (position) relaxation rate can be approximated by

$$k(0)\simeq\Gamma_0^1=\begin{cases}(q_0^1)^2D, & \text{continuous diffusion}\\ \gamma[1-\mathrm{e}^{-(q_0^1b)^2/2}], & \text{jump diffusion,}\end{cases}\tag{3.15}$$

where $(q_0^1)^2$ is the least (in magnitude) eigenvalue of the operator $\mathrm{H}_1(r)$ defined in Eq. (2.6). It follows from this that the position relaxation rate or the reciprocal of the time scale for the particle to diffuse over the entire allowed space is Γ_0^1. An approximate expression for q_0^1, and hence for Γ_0^1, can be derived by using the WKB approach to give

$$\lambda_0^1=(q_0^1R)^2\simeq\frac{2}{\sqrt{3}}\left\{\frac{[2(a/R)^{\nu}+(\nu-1)(a/R)^{2\nu}-\nu-1](1-\mathrm{e}^{-\beta\varepsilon})+2\nu}{[2\nu(a/R)^{\nu+2}-(\nu+1)(a/R)^{2\nu}-\nu+1](1-\mathrm{e}^{-\beta\varepsilon})+2\nu(2-\nu)}\right\},\tag{3.16}$$

with $\nu=\sqrt{3}$. As a check, when $\beta\varepsilon=0$ (which corresponds to diffusion inside a sphere of radius R), Eq. (3.16) predicts that $\lambda_0^1\simeq 4.309$ which has to be compared with the exact value 4.333.

D. Biexponential approximation

For small values of Q but $Q\neq 0$, an expression of $C(Q,t)$ can also be derived by considering the Taylor expansion of $A_n^l(Q)$ as a function of Q. The leading terms contributing to $C(Q,t)$ are $A_0^1(Q)\sim Q^2$, $A_0^2(Q)\sim Q^4$ and $A_1^0(Q)\sim Q^4$. But since $\Gamma_0^1\ll\Gamma_0^2$ and Γ_1^0 may be smaller than Γ_0^2, we only keep $A_0^1(Q)$ and $A_1^0(Q)$ in the expansion of $C(Q,t)$ to give

$$\begin{aligned}C(Q,t)&\simeq\frac{A_0^1(Q)}{1-A_0^0(Q)}\exp\{-\Gamma_0^1t\}+\frac{A_1^0(Q)}{1-A_0^0(Q)}\exp\{-\Gamma_1^0t\}\\&\simeq(1-Q^2A)\exp\{-\Gamma_0^1t\}+Q^2A\exp\{-\Gamma_1^0t\},\\&\qquad Q\to 0,\end{aligned}\tag{3.17}$$

where the constant A is given by

$$\begin{aligned}A&=\lim_{Q\to 0}\left\{\frac{A_1^0(Q)}{Q^2[1-A_0^0(Q)]}\right\}\\&=\frac{5}{12[R^5+(\mathrm{e}^{\beta\varepsilon}-\alpha_1)a^5]Z_1^0(q_1^0)^{10}}\\&\quad\times|(e^{\beta\varepsilon}-\alpha_1)\{2(q_1^0a)^3j_0(q_1^0a)+[(q_1^0a)^2-6]j_1(q_1^0a)\}\\&\quad+\alpha_1\{2(q_1^0R)^3j_0(q_1^0R)+[(q_1^0R)^2-6]j_1(q_1^0R)\}\\&\quad+\alpha_2\{2(q_1^0R)^2j_{-1}(q_1^0R)-[(q_1^0R)^2-6]j_{-2}(q_1^0R)\}\\&\quad-\alpha_2\{2(q_1^0a)^2j_{-1}(q_1^0a)-[(q_1^0a)^2-6]j_{-2}(q_1^0a)\}|^2.\end{aligned}\tag{3.18}$$

The inelastic part of $S_{\mathrm{inc}}(Q,\omega)$ is thus a bi-Lorentzian in this approximation.

Now, setting the expression (3.17) into Eq. (2.18), we find that the relaxation rate constant is given by

$$\frac{1}{k(Q)}=\left[\frac{A_0^1(Q)}{1-A_0^0(Q)}\right]\frac{1}{\Gamma_0^1}+\left[\frac{A_1^0(Q)}{1-A_0^0(Q)}\right]\frac{1}{\Gamma_1^0}.\tag{3.19}$$

The interesting feature of this approximation is to shed light on another important eigenvalue of the problem, say Γ_1^0. Indeed, for a smooth and barrierless potential surface the eigenvalues of $\mathrm{H}_l(r)$ are ordered as $q_0^0=0<q_0^1<\cdots<q_1^0<\cdots$, i.e., $\Gamma_0^1<\Gamma_1^0$. In this case, $A_1^0(Q)\ll A_0^1(Q)$, the relaxation rate has a plateaulike behavior $k(Q)\simeq\Gamma_0^1$, and $C(Q,t)$ reduces to a single exponential.

However, one may observe the inversion of eigenvalues, i.e., $q_0^1>q_1^0$, in the presence of barriers on the potential surface and under certain conditions of potential parameters. For the potential in Eq. (3.1), the potential of mean force or free energy, $F(r)$, along the coordinate r is $F(r)=V(r)-\mathrm{T}S(r)$, where the entropy is $S(r)=k_B\ln[(r/R)^2]$ plus a constant. Thus, the free-energy barrier Δ, separating the region between the two concentric spheres and the inner sphere (characterized by $\varepsilon\neq 0$) is

$$\Delta=F(a)-F(R)=2k_BT\ln(R/a).\tag{3.20}$$

When $\Delta>k_BT$ (i.e., $R/a>1.65$), the fluctuations of the particle populations in the inner and outer spheres relax to equilibrium exponentially with the rate given by Γ_1^0. In this case, the eigenvalue q_1^0 is smaller than q_0^1, i.e., $\Gamma_1^0<\Gamma_0^1$. As a result, $k(Q)$ starts from a plateau value close to Γ_0^1 for small Q where $A_1^0(Q)\ll A_0^1(Q)$, decreases to its minimum at Q_{m}, turns over and increases as Q gets larger. In this limit, $C(Q,t)$ decays at long times with rate Γ_1^0 such that

$$\begin{aligned}\Gamma_1^0&=\lim_{t\to\infty}\left\{-\frac{d}{dt}\ln[C(Q,t)]\right\}\\&=\begin{cases}(q_1^0)^2D, & \text{continuous diffusion}\\ \gamma[1-e^{-(q_1^0b)^2/2}], & \text{jump diffusion,}\end{cases}\end{aligned}\tag{3.21}$$

where $(q_1^0)^2$ is the least (in magnitude) eigenvalue of the operator $\mathrm{H}_0(r)$ defined in Eq. (2.6).

However, $C(Q,t)$ decays at short times as

$$-\left.\frac{dC(Q,t)}{dt}\right|_{t=0}=A_0^1(Q)\Gamma_0^1+A_1^0(Q)\Gamma_1^0. \tag{3.22}$$

This rate constant (which is greater than Γ_1^0 and dominated by Γ_0^1) can roughly be regarded as the position relaxation rate over length scales defined by $Q^{-1}\leqslant R$. It thus follows from this that within the biexponential approximation, $C(Q,t)$ decays faster at short times with the Q-dependent position relaxation rate, and it decays at long times with the population relaxation rate.

When $\Delta>k_BT$, an analytical expression of $(q_1^0)^2$ in term of quadratures can be derived by using the first passage time formalism [8,9]. After calculations, we find

$$\frac{1}{(q_1^0)^2}=\frac{a^2}{15}\left(\frac{K_{\mathrm{eq}}}{1+K_{\mathrm{eq}}}\right)+\frac{(R-a)^2(5R^3+6aR^2+3a^2R+a^3)}{15a(R^2+aR+a^2)}\left(\frac{1}{1+K_{\mathrm{eq}}}\right), \tag{3.23}$$

where $K_{\mathrm{eq}}=[\int_a^R r^2 \mathrm{e}^{-\beta V(r)}dr]/[\int_0^a r^2 \mathrm{e}^{-\beta V(r)}dr]=(R^3-a^3)e^{-\beta\varepsilon}/a^3$ is the equilibrium constant between the population of particles in the region comprised between the inner and outer spheres and that in the inner sphere. It is worthwhile to note that if τ_{in} and τ_{out} denote the average times a particle spends within and out the inner sphere, respectively, we have $K_{\mathrm{eq}}=\tau_{\mathrm{out}}/\tau_{\mathrm{in}}$ and $\Gamma_1^0\simeq\tau_{\mathrm{in}}^{-1}+\tau_{\mathrm{out}}^{-1}$.

IV. ILLUSTRATIVE NUMERICAL RESULTS

Now, we complete the analytical results derived above with some illustrations obtained from numerical calculations.

Elastic incoherent structure factor. Figure 1 displays the EISF [i.e., the amplitude $A_0^0(Q)$] for diffusion inside two concentric spheres of radii a and $R=5a$ for various values of the fraction ϕ. Excepted for $\phi=1$, it is seen that $A_0^0(Q)$ becomes very small at $Qa\simeq4.49$ for all fractions. When ϕ goes from $\phi=0$ to $\phi=1$ or conversely, the shape of the EISF changes and becomes very different from that of a single sphere as a result of interferences between the two spheres. For $\phi=0.5$, there is even a small window of Q within which the EISF shows a plateaulike behavior. These features cannot be fitted with neither a diffusion inside an effective single sphere [3] nor inside a cylinder [10]. The other amplitudes $A_n^l(Q)$ are shown in Fig. 2 for $R=5a$ and $\phi=0.5$. In contrast to a single sphere case [3], the maximum of the next amplitudes to $A_0^0(Q)$ are about 30% smaller than one.

Amplitudes $A_0^1(Q)$ and $A_1^0(Q)$. Comparison between $A_0^1(Q)$ and $A_1^0(Q)$ is shown in Fig. 3. It can be seen that the maximum of $A_0^1(Q)$, located at $Qa\simeq0.5$, increases as ϕ increases and bumps up to 0.5 for the single sphere case. $A_0^1(Q)\sim Q^2$ as $Q\to0$, and it becomes almost zero for $Qa\geqslant1.25$.

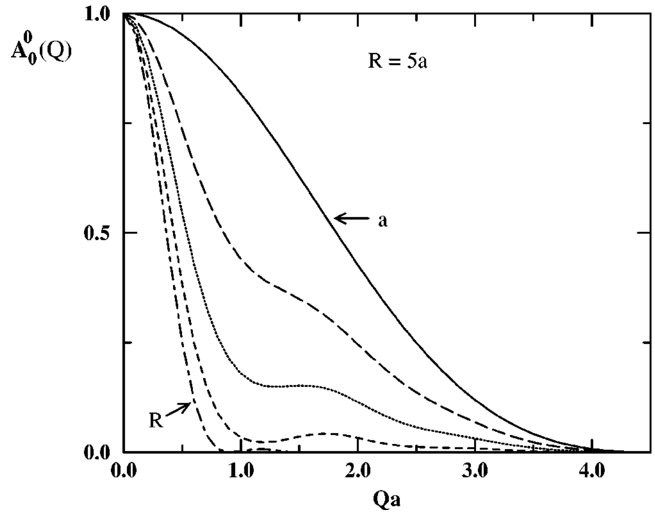

FIG. 1. The elastic incoherent structure factor (EISF) $A_0^0(Q)$ [given in Eq. (3.3)] as a function of Qa for various values of fractions: $\phi=0$ (solid line), $\phi=0.25$ (long-dashed line), $\phi=0.5$ (dotted line), $\phi=0.75$ (dashed line), and $\phi=1$ (dot-dashed line). The solid ($\phi=0$) and dot-dashed lines ($\phi=1$) correspond to the EISF for a sphere of radius a and R, respectively.

In contrast to $A_0^1(Q)$, when ϕ increases the maximum of $A_1^0(Q)$, located around $Qa\sim1$, decreases towards its single sphere value 0.075. Apart for small Q where $A_1^0(Q)\sim Q^4$, $A_1^0(Q)$ and $A_0^0(Q)$ have roughly the same shape and both become very small at $Qa\simeq4.49$ for $\phi<1$.

Moreover, we emphasize that when ϕ increases the maximum of $A_0^1(Q)$ decreases while the maximum of $A_1^0(Q)$ increases and the two maxima becomes of the same order of magnitude at $\phi=0.5$ for $R=5a$. This opposite behavior of the maximum of $A_0^1(Q)$ and $A_1^0(Q)$, also noticeable on the corresponding eigenvalues (see below), results from interferences between inner and outer spheres.

Inversion of least eigenvalues q_0^1 and q_1^0. The effect of the presence of a semipermeable inner sphere on the eigenvalue spectrum is illustrated in Table I. One can see that both the order and the orders of magnitude of eigenvalues are completely shuffled compared to the single sphere case (i.e., $\phi=1$). Let us focus now on the two first eigenvalues. As discussed above, the position relaxation time is related to the eigenvalue q_0^1 and the relaxation to equilibrium in fluctuations of the population between inner and outer spheres to the eigenvalue q_1^0.

Figure 4(a) shows the variation of $\lambda_0^1=(q_0^1R)^2$ as a function of the ratio of radii, a/R, for various fractions ϕ. It appears that λ_0^1 is very sensitive to the size of spheres for ϕ smaller or of order 0.5, and it is maximum around $a/R\sim0.6$, i.e., for barriers $\Delta\sim k_BT$. One can note that λ_0^1 is always larger or equal to the single sphere value 4.3, meaning that the position correlation function relaxes faster in the presence of an additional partially confining inner sphere. The dashed lines over numerical data on Fig. 4(a) indicates that the formula in Eq. (3.16) gives a reasonably good approximation to λ_0^1 for $\Delta>k_BT$ and $\phi\geqslant0.5$.

Comparison between q_0^1 and q_1^0 is shown in Fig. 4(b) where dashed lines separate two regions of relaxation dynamics. One is the region where $q_0^1<q_1^0$ (i.e., $\theta>1$) corre-

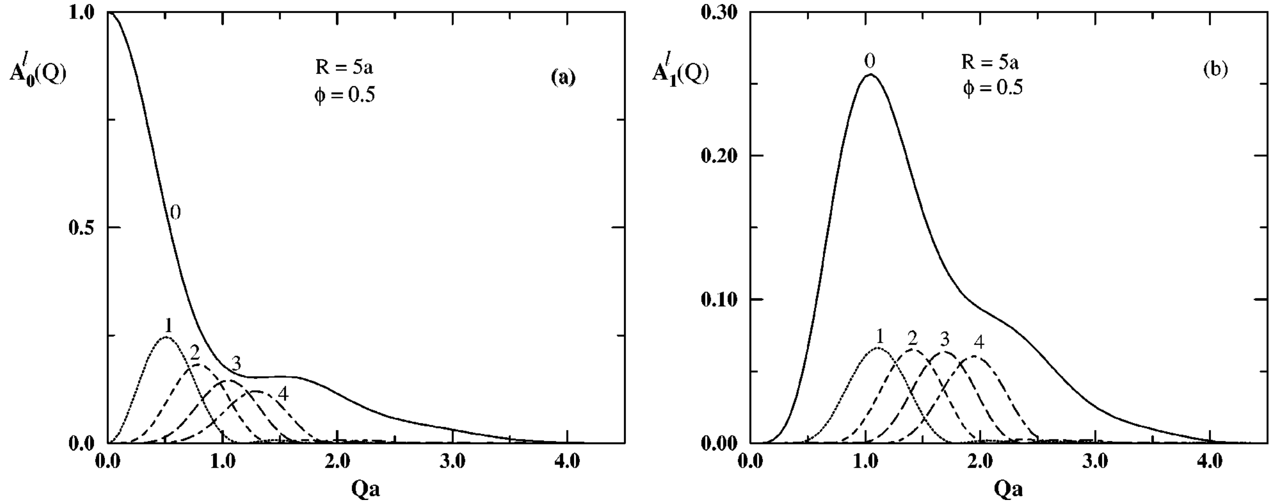

FIG. 2. The amplitudes $A_0^l(Q)$ [panel (a)] and $A_1^l(Q)$ [panel (b)] [given in Eqs. (3.11a) and (3.11b)], as a function of Qa for the fraction $\phi=0.5$. The quoted numbers correspond to values of l. Note the difference in the order of magnitude between $A_0^l(Q)$ and $A_1^l(Q)$.

sponding to either when the radii of spheres are comparable (i.e., $\Delta\sim k_BT$) or when the fraction of particles in the outer sphere is close to one (i.e., $\phi>0.5$). In this case the problem can be approximated by the diffusion inside an effective single sphere different from the outer sphere since it is still possible to have $q_0^1<q_1^0<q_2^0$ (see Table I). We call this the normal region because of the resemblance to the single sphere case. The amplitude $A_0^1(Q)$ is much larger than $A_1^0(Q)$ and the only characteristic time is the position relaxation time related to q_0^1.

By opposition to the normal region, second is the inverted region where $q_0^1>q_1^0$ (i.e., $\theta<1$) corresponding to the situation in which either the radii of spheres are very different from each other (i.e., $\Delta>k_BT$) or a large fraction of particles is contained in the inner sphere (i.e., $\phi<0.5$). Figure 4(b) shows that $(q_1^0/q_0^1)^2\propto e^{-\beta\Delta}$ in this range. In this case, the amplitude $A_1^0(Q)$ is greater than or of order than $A_0^1(Q)$ and the relaxations of position and population between spheres compete as a function of Q to the overall relaxation [i.e., depending on the value of Q, $C(Q,t)$ may be either a single exponential or a biexponential function of time, see Fig. 5].

Scattering correlation function and relaxation rate. Figures 5(a) and 5(b) show a comparison of the incoherent scattering correlation function, $C(Q,t)$, for diffusion inside a single sphere and two concentric spheres. For $QR\leqslant 0.1$ (i.e., for large length scales), $C(Q,t)$ for the single sphere case decays exponentially with the rate constant $k(Q)\simeq\Gamma_0^1$ since dominated by the relaxation of the position. As QR increases, $C(Q,t)$ in the single sphere case becomes multiexponential as a result of an increasingly number of harmonics contributing to $C(Q,t)$. This latter tends to a single exponential again at higher QR (very short length scales) where the number contributing harmonics tends to infinity.

In the case of two concentric spheres, $C(Q,t)$ also decays exponentially with the rate constant $k(Q)\simeq\Gamma_0^1$ for $QR\leqslant 0.1$ because the amplitudes other than $A_0^1(Q)$ are too small to contribute so that the single exponential approximation is justified. On the other hand, $C(Q,t)$ exhibits a biexponential decay as a function of time for intermediate values of QR where the amplitudes like $A_1^0(Q)$ are of the same order of

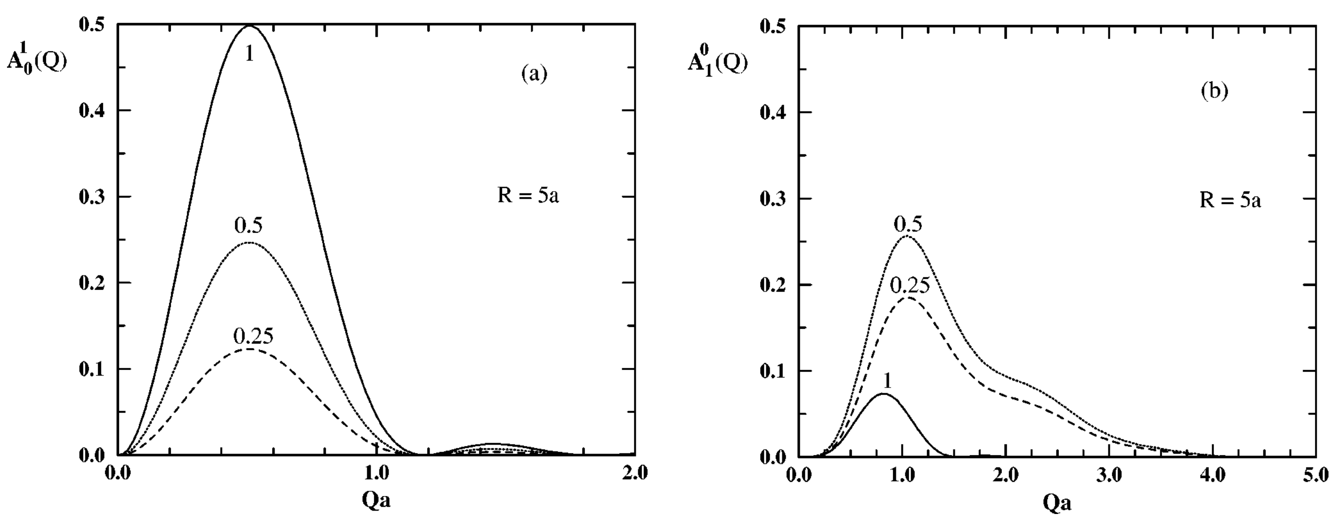

FIG. 3. The amplitudes $A_0^1(Q)$ [panel (a)] and $A_1^0(Q)$ [panel (b)] as a function of Qa. The quoted numbers correspond to values of ϕ. Note the different scales of the x axis between the two panels.

TABLE I. The first 11 roots in ascending order of Eq. (3.8) for $R=5a$ (i.e., for $\Delta=3.22k_BT$) and $\phi=0.5$ (i.e., for $\varepsilon=4.84k_BT$), where $(q_n^l)^2$ are the eigenvalues of the diffusion operator. From Eqs. (3.16) and (3.23) we find that $\lambda_0^1=5.07$ and $\lambda_1^0=1.81$, respectively. The column $\phi=1$ corresponds to eigenvalues for diffusion inside a sphere of radius R; the number in parentheses gives their order. Note the inversion of order for $\phi=0.5$, i.e., $q_0^1\simeq 2.6q_1^0$.

n	l	$\lambda_n^l=(q_n^lR)^2$	
		$\phi=0.5$	$\phi=1$
0	0	0.0000	0.0000(0)
1	0	1.7558	20.191(3)
0	1	4.5394	4.3330(1)
0	2	11.185	11.170(2)
0	3	20.342	20.377(4)
0	4	31.822	31.885(5)
2	0	32.534	59.680(9)
1	1	39.880	35.288(6)
0	5	45.559	45.650(7)
1	2	54.473	53.143(8)
0	6	61.516	61.639(10)

magnitude than $A_0^1(Q)$. The short-time decay rate is given by the position relaxation rate over length scales under consideration and the long-time decay rate by the population relaxation rate Γ_1^0. This corresponds to the inverted region on Fig. 4(b) where $\Gamma_1^0<\Gamma_0^1$, i.e., the relaxation of the position for these length scales occurs faster than the relaxation to equilibrium in fluctuations of population between spheres. As a consequence, for the same length scales under consideration, the overall decay of $C(Q,t)$ for two concentric spheres is smaller than that for the single sphere case.

Likewise, comparison of the relaxation rate, $k(Q)$, for diffusion inside a single sphere and two concentric spheres is shown in Fig. 6. Apart from oscillations resulting from interferences, the value of $k(Q)$ at low QR is slightly greater for the two concentric spheres than that for the single sphere case. The plateaulike behavior of $k(Q)$ for the two concentric spheres goes further in QR values similar to diffusion inside a cylinder [10]. For the cylinder, this extension of $k(Q)$ is attributed to the anisotropy of the cylindrical shape. For the two concentric spheres, the anisotropy arises from cross transitions between the inner and outer spheres. In addition to this, $k(Q)$ for the two concentric spheres has a turnover behavior as a function of Q with a minimum at Q_m as an indication of the inversion of the least eigenvalues. This inversion of least eigenvalues is also noticeable on $C(Q,t)$ since, as for the example shown in Fig. 5(b), $C(Q,t)$ is exponential for $QR=0.1$ and biexponential for $QR=5$ while the relaxation rate $k(Q)$ is exactly the same for the two values of QR (with $Q_mR\simeq 3.2$). The analysis shows that for intermediate values of QR, $C(Q,t)$ is well described by a single exponential for $Q<Q_m$ while it is a biexponential function of time for $Q>Q_m$.

As expected, for the two cases of single sphere and two concentric spheres, the differences in $C(Q,t)$ and $k(Q)$ between the continuous and jump-diffusion models appear only at higher Q, i.e., for very short length scales.

V. SUMMARY

As an extension to the diffusion inside a sphere model we have considered the problem of diffusion inside two concentric spheres as a model for diffusing motions within a closed region or cage containing another semipermeable cage that divides the system into two subregions. Our aim has been to derive the EISF and the incoherent scattering correlation function $C(\mathbf{Q},t)$ for this model of diffusion inside two concentric spheres. The main results of calculations, which have been done for both continuous and jump diffusions, can be summarized as follows.

The EISF [i.e., the amplitude $A_0^0(Q)$] is characterized by three parameters: the radius a of the semipermeable inner sphere, the radius R of the outer sphere, and the degree of permeability ϕ which describes the fraction of equivalent particles diffusing in the outer sphere. As a result of interferences between spheres, we find that the EISF is a weighted coherent summation over amplitudes corresponding to inner and outer spheres.

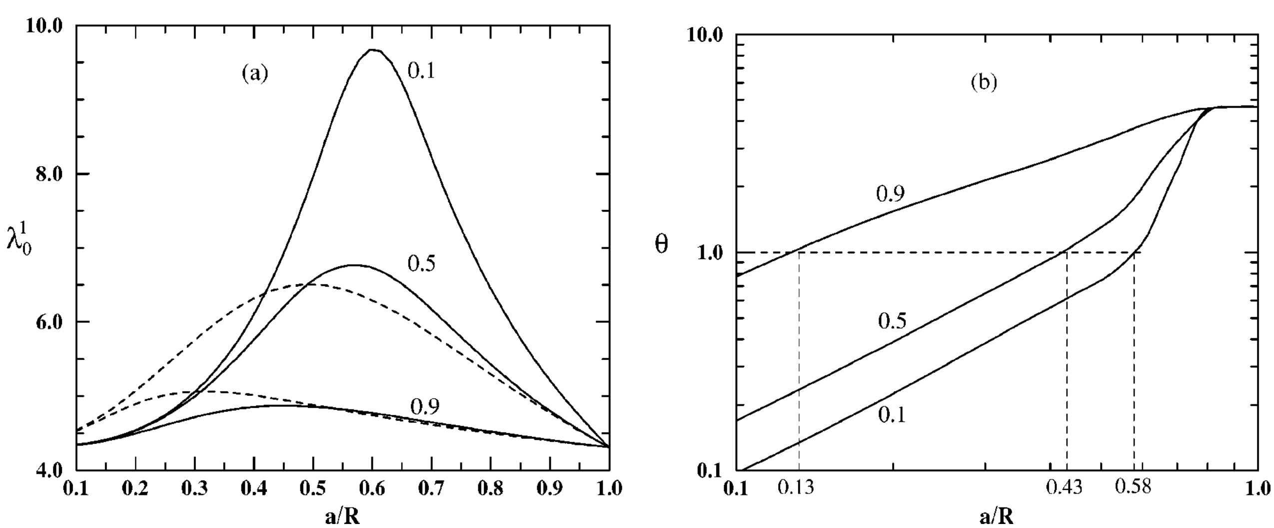

FIG. 4. Eigenvalue $\lambda_0^1=(q_0^1R)^2$ [panel (a)] and the log-log plot of the ratio $\theta=(q_0^1)^2/(q_1^0)^2$ as a function of a/R. The quoted numbers correspond to values of ϕ. The dashed lines in panel (a) represent the approximation in Eq. (3.16) for $\phi=0.5$ and 0.9.

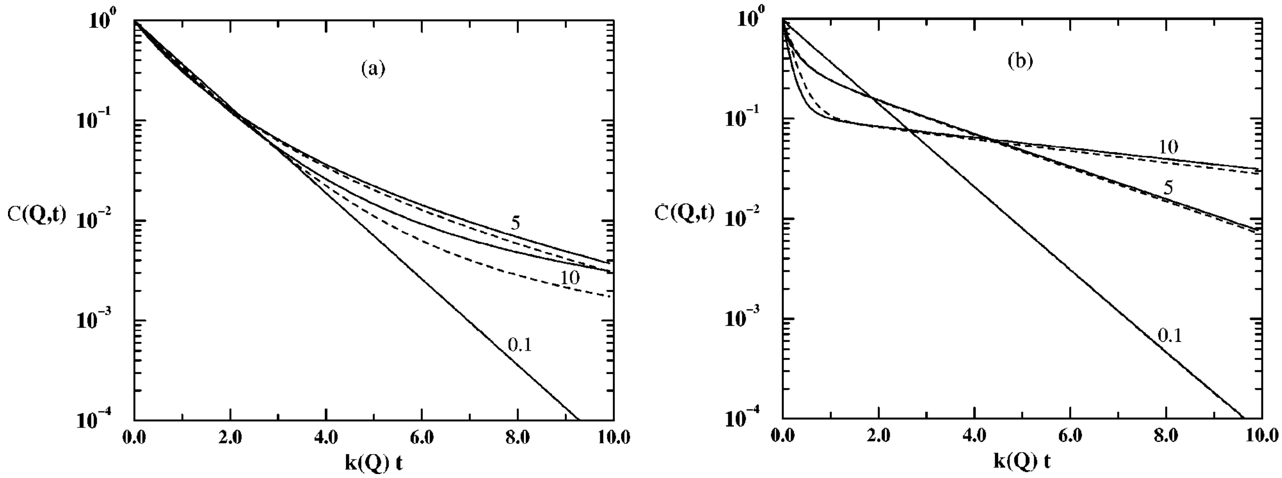

FIG. 5. Correlation function $C(Q,t)$ as a function of the reduced time $k(Q)t$, where $k(Q)$ is the relaxation rate constant. The quoted numbers correspond to values of the scattering wave vector QR. $k(Q)=Dk_{\mathrm{cd}}/R^2$ for the continuous diffusion (solid lines) with diffusion coefficient D, and $k(Q)=\gamma k_{\mathrm{jd}}$ for the jump diffusion (dashed lines) with the jump length $b=0.15R$ and jump frequency $\gamma=2D/b^2 \simeq 89D/R^2$. (a) Diffusion inside a sphere of radius R with the relaxation rate constants $(QR,k_{\mathrm{cd}},k_{\mathrm{jd}}) = \{(0.1,4.36,4.25);(5,16.55,15.08);(10,80.35,52.45)\}$. (b) Diffusion inside two concentric spheres of radii a and $R=5a$ for $\phi=0.5$. The relaxation rate constants are $(QR,k_{\mathrm{cd}},k_{\mathrm{jd}})=\{(0.1,4.74,4.61);(5,4.73,4.60);(10,14.49,13.21)\}$. For comparison, the position and population relaxation rates are $(\Gamma_0^1,\Gamma_1^0)\simeq(4.54,1.76)\times D/R^2$ for both continuous and jump diffusions. The equilibrium constant between inner and outer populations is $K_{\mathrm{eq}}=\tau_{\mathrm{out}}/\tau_{\mathrm{in}}=0.98$ and the inner residence time is $\tau_{\mathrm{in}}\simeq 1.15\times R^2/D \sim 30\times a^2/D$.

When $Q\to 0$ (i.e., for $QR<0.1$), the incoherent scattering correlation function decays exponentially as a function of time with the rate given by the position relaxation rate $k(0)=\Gamma_0^1$ [see Eq. (3.15)]. In the opposite $Q\to\infty$ limit (i.e., for $QR>10$), $C(Q,t)$ has also an exponential decay as a function of time as given in Eq. (2.17). For intermediate values of QR, however, there are two types of decay for $C(Q,t)$ depending upon the ratio of radii R/a [i.e., the entropic barrier, Δ, see Eq. (3.20)] and the fraction ϕ.

In the normal region (i.e., $R/a\sim 1.6 \Rightarrow \Delta\sim k_BT$ and/or $\phi \sim 1$), the problem can be approximated by a diffusion inside an effective single sphere which the radius can be determined from the EISF. In this case, $C(Q,t)$ can be approximated by a single exponential with the rate $k(Q)\sim\Gamma_0^1$ for $QR<\pi$. For higher values of QR, $C(Q,t)$ becomes multiexponential because of the contribution of higher harmonics.

In the inverted region (i.e., $R/a>1.6 \Rightarrow \Delta > k_BT$ and/or $\phi \leqslant 0.75$) on the other hand, $k(Q)$ shows a turnover behavior as a function of Q with a minimum at Q_m. For $Q<Q_m$, the correlation function $C(Q,t)$ is well described by a single exponential whereas it is a biexponential function of time for $Q>Q_m$. In this latter case, the short-time decay rate of $C(Q,t)$ is controlled by the position relaxation rate over length scales Q^{-1} and the long-time decay rate by the population relaxation rate Γ_1^0 [see Eq. (3.21)]. For these values of QR, the relaxation of the position occurs faster than the re-

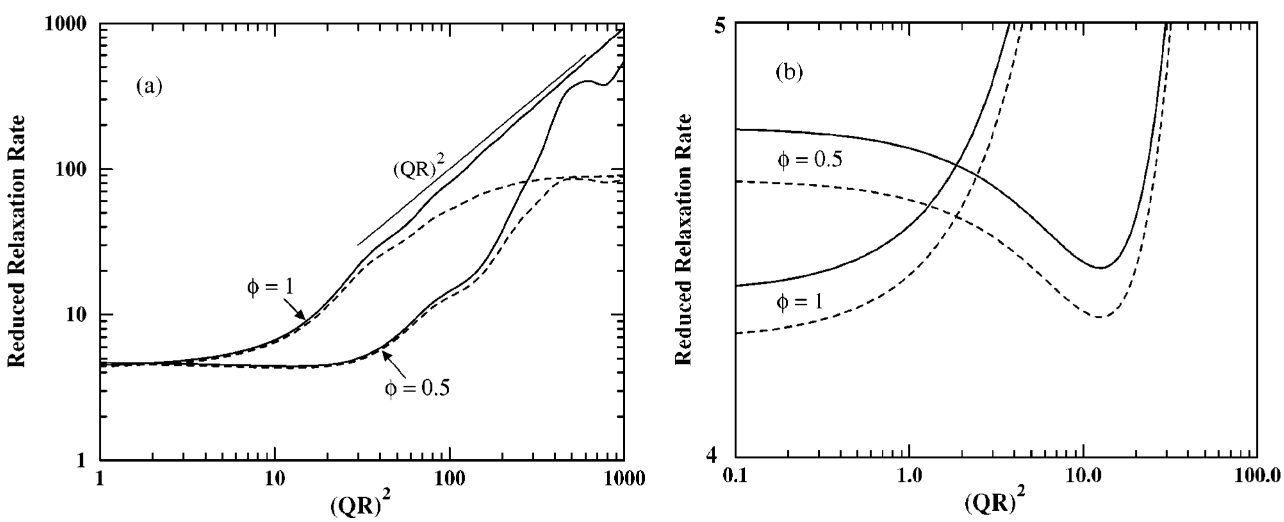

FIG. 6. Reduced relaxation rate constants $R^2k(Q)/D$ (continuous diffusion, solid lines) and $k(Q)/\gamma$ (jump diffusion, dashed lines) as a function of $(QR)^2$. (a) Diffusion inside a sphere of radius R (i.e., $\phi=1$) and inside two concentric spheres of radii a and $R=5a$ ($\phi=0.5$). For the jump diffusion, the jump length is $b=0.15R$ and the jump frequency $\gamma=2D/b^2\simeq 89D/R^2$. (b) Zoom of panel (a) showing the turnover behavior of $k(Q)$ for $\phi=0.5$. The coincidence between quoted curves (i.e., solid-solid and dashed-dashed lines) occurs at $QR=1.36$ where $R^2k(Q)/D=4.65$ and $k(Q)/\gamma=4.53$, and the minimum is located at $Q_mR\simeq 3.25$.

laxation to equilibrium in fluctuations of population between spheres. The biexponential behavior of $C(Q,t)$ takes place up to higher values of QR like, for example, $QR \sim 10$ for $R=5a$ (i.e., $\Delta = 3.2 k_B T$) and $\phi = 0.5$ [see Fig. 5(b)].

Finally, the model discussed in this paper is essentially a simple example of motions in a confining potential with barrier crossing. The foregoing analysis outlines what kind of information one can get by using the incoherent neutron scattering technique to study this problem. The model can be extended to include, for example, anisotropic effects, multidomain systems, or to deal with situations where the diffusion rates are different in each subregion. In addition, although the discussion was presented for the translational diffusion this model can properly be adapted and applied as well to other degrees of freedom like rotation and vibration. It may be instructive to investigate also in these directions.

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APPENDIX: GREEN'S FUNCTIONS FOR CONTINUOUS AND JUMP-DIFFUSION MODELS

In this appendix we derive formal expressions for Green's functions, $G(\mathbf{r},t|\mathbf{r}_0)$, describing the particle diffusion in a potential $V(\mathbf{r})$. To this end, we consider the two diffusion models commonly used for the derivation of $G(\mathbf{r},t|\mathbf{r}_0)$.

1. Continuous diffusion model

When the particle motion can be described as a continuous diffusion, the probability density, $G(\mathbf{r},t|\mathbf{r}_0)$, satisfies the Smoluchowski equation

$$\frac{\partial G}{\partial t} = \boldsymbol{\nabla} \cdot \mathbf{D}(\mathbf{r}) e^{-\beta V(\mathbf{r})} \cdot \boldsymbol{\nabla} e^{\beta V(\mathbf{r})} G, \tag{A1}$$

where $\mathbf{D}(\mathbf{r})$ is the diffusion tensor which we will assume to be a constant tensor independent of $\mathbf{r}$. When both the potential and the diffusion are isotropic, $G(\mathbf{r},t|\mathbf{r}_0)$ can be expanded in terms of spherical harmonic functions $Y_l^m(\Omega)$ as

$$G(\mathbf{r},t|\mathbf{r}_0) = \sum_{l=0}^{\infty} g_l(r,t|r_0) \sum_{m=-l}^{m=+l} Y_l^m(\Omega) Y_l^{*m}(\Omega_0), \tag{A2}$$

where the function $g_l(r,t|r_0)$ satisfies the Smoluchowski equation in the presence of an angular momentum sinklike term,

$$\frac{\partial g_l}{\partial t} = \left[\frac{1}{r^2} \frac{\partial}{\partial r} r^2 D e^{-\beta V(r)} \frac{\partial}{\partial r} e^{\beta V(r)} - \frac{l(l+1)}{r^2} \right] g_l . \tag{A3}$$

Using the transformation, $g_l(r,t) = e^{-(q^l)^2 D t} e^{-\beta V(r)/2} \psi^l(r)/r$, Eq. (A3) reduces to the eigenvalue problem

$$\mathrm{H}_l(r) \psi^l(r) = -(q^l)^2 \psi^l(r), \tag{A4}$$

where the autoadjoint operator $\mathrm{H}_l(r)$ is given by

$$\mathrm{H}_l(r) = \frac{e^{\beta V(r)/2}}{r} \frac{d}{dr} r^2 e^{-\beta V(r)} \frac{d}{dr} \frac{e^{\beta V(r)/2}}{r} - \frac{l(l+1)}{r^2}. \tag{A5}$$

Let q_n^l and $\psi_n^l(r)$ be the eigenvalues and eigenfunctions of the operator $\mathrm{H}_l(r)$, the Green's function of the diffusion equation (A3) is thus given by

$$g_l(r,t|r_0) = \frac{e^{-\beta[V(r)-V(r_0)]/2}}{r r_0} \sum_{n=0}^{\infty} \psi_n^l(r) \psi_n^{*l}(r_0) \times \exp\{-(q_n^l)^2 D t\}, \tag{A6}$$

with $q_0^0 = 0$ and $r^2 p_{\mathrm{eq}}(r) = |\psi_0^0(r)|^2$. As a result, for a purely isotropic diffusion problem with a constant diffusion coefficient, the Green's function $G(\mathbf{r},t|\mathbf{r}_0)$ is given by Eq. (A2) with $g_l(r,t|r_0)$ defined in Eq. (A6).

2. Random jump-diffusion model

As introduced in this context by Hall and Ross [4], in this model one assumes that the particle undergoes successive uncorrelated jumps from site to site governed by the spatial probability distribution, $\rho(\mathbf{r},1|\mathbf{r}_0)$, of finding the particle at $\mathbf{r}$ after a single jump given that it was initially at $\mathbf{r}_0$. Jumps are assumed to be statistically independent events of zero duration and the time interval between successive jumps is a random variable obtained from the distribution, $\gamma e^{-\gamma t}$, where γ is the jump frequency. For this jump diffusion, the probability density, $G(\mathbf{r},t|\mathbf{r}_0)$, satisfies the integral equation

$$G(\mathbf{r},t|\mathbf{r}_0) = \rho(\mathbf{r},0|\mathbf{r}_0) e^{-\gamma t} + \int d\mathbf{r}' \int_0^t d\tau \gamma e^{-\gamma(t-\tau)} \rho(\mathbf{r},1|\mathbf{r}') G(\mathbf{r}',\tau|\mathbf{r}_0). \tag{A7}$$

This can be rewritten in an infinite series of the form

$$G(\mathbf{r},t|\mathbf{r}_0) = \sum_{m=0}^{\infty} \frac{(\gamma t)^m}{m!} e^{-\gamma t} \rho(\mathbf{r},m|\mathbf{r}_0), \tag{A8}$$

where $\rho(\mathbf{r},m|\mathbf{r}_0)$, the probability density of finding the particle at $\mathbf{r}$ after a m jumps given that it was initially at $\mathbf{r}_0$, is such that $\rho(\mathbf{r},m+1|\mathbf{r}_0) = \int d\mathbf{r}' \rho(\mathbf{r},1|\mathbf{r}') \rho(\mathbf{r}',m|\mathbf{r}_0)$. For the purpose of the model, it is convenient to assume that for large m, the spatial probability distribution $\rho(\mathbf{r},m|\mathbf{r}_0)$ satisfies the diffusion equation

$$\frac{\partial \rho}{\partial m} = \boldsymbol{\nabla} \cdot \mathbf{B}(\mathbf{r}) e^{-\beta V(\mathbf{r})} \cdot \boldsymbol{\nabla} e^{\beta V(\mathbf{r})} \rho, \tag{A9}$$

where $\mathbf{B}(\mathbf{r})$ is the jump length tensor which we will assume to be a constant tensor independent of $\mathbf{r}$. As for the continuous diffusion, when both the potential and the jump events are isotropic, the function $\rho(\mathbf{r},m|\mathbf{r}_0)$ can be expanded in terms of spherical harmonic functions $Y_l^m(\Omega)$ as

$$\rho(\mathbf{r},m|\mathbf{r}_0)=\sum_{l=0}^{\infty}\rho_l(r,m|r_0)\sum_{m=-l}^{m=+l}Y_l^m(\Omega)Y_l^{*m}(\Omega_0), \tag{A10}$$

where $\rho_l(r,m|r_0)$, satisfies the diffusion equation

$$\frac{\partial\rho_l}{\partial m}=\left[\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{b^2}{2}e^{-\beta V(r)}\frac{\partial}{\partial r}e^{\beta V(r)}-\frac{l(l+1)}{r^2}\right]\rho_l, \tag{A11}$$

in which we have used $2\mathbf{B}=b^2\delta_{ij}$, where b is the jump length. This equation is identical to Eq. (A3) with the correspondence $2Dt=b^2m$. It thus follows from what precedes that

$$\rho_l(r,m|r_0)=\frac{e^{-\beta[V(r)-V(r_0)]/2}}{rr_0}\sum_{n=0}^{\infty}\psi_n^l(r)\psi_n^{*l}(r_0)\times\exp\{-(q_n^lb)^2m/2\}, \tag{A12}$$

where q_n^l and $\psi_n^l(r)$ are the eigenvalues and eigenfunctions of the operator $\mathrm{H}_l(r)$ defined in Eq. (A4). Combining Eqs. (A10) and (A12) into Eq. (A8), we find that for the isotropic jump-diffusion model, the Green's function $G(\mathbf{r},t|\mathbf{r}_0)$ is still given by Eq. (A2) but with $g_l(r,t|r_0)$ given by

$$\begin{aligned}g_l(r,t|r_0)&=\sum_{m=0}^{\infty}\frac{(\gamma t)^m}{m!}e^{-\gamma t}\rho_l(r,m|r_0)\\&=\frac{e^{-\beta[V(r)-V(r_0)]/2}}{rr_0}\sum_{n=0}^{\infty}\psi_n^l(r)\psi_n^{*l}(r_0)\\&\quad\times\exp(-\{1-\exp[-(q_n^lb)^2/2]\}\gamma t).\end{aligned} \tag{A13}$$

In the $b\rightarrow 0$ limit, Eq. (A13) coincides with Eq. (A6) for $b^2\gamma=2D$.

[1] M. Bée, *Quasielastic Neutron Scattering* (Adam Hilger, Bristol, 1988).
[2] L. Van Hove, Phys. Rev. **95**, 249 (1954).
[3] F. Volino and A.J. Dianoux, Mol. Phys. **41**, 271 (1980).
[4] P.L. Hall and D.K. Ross, Mol. Phys. **42**, 673 (1981).
[5] M.-C. Bellissent-Funel, J. Teixeira, K.F. Bradley, and S.H. Chen, J. Phys. I **2**, 995 (1992); M.-C. Bellissent-Funel, J-M. Zanotti, and S.H. Chen, Faraday Discuss. **103**, 281 (1996).
[6] E. Cohen de Lare and R. Kahn, J. Phys. (Paris) **42**, 1029 (1981).
[7] *Handbook of Mathematical Functions*, edited by M. Abramowitz and I. A. Stegun (Dover, New York, 1972), see p. 445 for Riccati-Bessel functions and p. 484 for integrals of Bessel functions.
[8] K. Schulten, Z. Schulten, and A. Szabo, J. Chem. Phys. **74**, 4426 (1981).
[9] D.J. Bicout and A. Szabo, J. Chem. Phys. **106**, 10 292 (1997).
[10] A.J. Dianoux, M. Pineri, and F. Volino, Mol. Phys. **46**, 129 (1982).