Influence of environment fluctuations on incoherent neutron scattering functions

D. J. Bicout
Institut Laue-Langevin, Theory Group 6, Rue Jules Horowitz, BP 156, 38042 Grenoble Cedex 9, France
(Received 18 December 2000; published 20 June 2001)

In extending the conventional dynamic models, we consider a simple model to account for the environment fluctuations of particle atoms in a protein system and derive the elastic incoherent structure factor (EISF) and the incoherent scattering correlation function $C(Q,t)$ for both the jump dynamics between sites with fluctuating site interspacing and for the diffusion inside a fluctuating sphere. We find that the EISF of the system (or the normalized elastic intensity) is equal to that in the absence of fluctuations averaged over the distribution of site interspacing or sphere radius a. The scattering correlation function is $C(Q,t)=\Sigma_n\langle e^{-\lambda_n(a)t}\rangle\,\psi(t)$, where the average is taken over the Q-dependent effective distribution of relaxation rates $\lambda_n(a)$, and $\psi(t)$ is the correlation function of the length a. When $\psi(t)=1$, the relaxation of $C(Q,t)$ is exponential for the jump dynamics between sites [since $\lambda_n(a)$ is independent of a] while it is nonexponential for diffusion inside a sphere.

DOI: 10.1103/PhysRevE.64.011910 PACS number(s): 87.15.He, 02.50.Ey, 66.10.Cb

By analyzing the incoherent scattering function, $S(\mathbf{Q},\omega)$, where $\mathbf{Q}$ is the scattering wave vector and $\hbar\omega$ the energy transfer, techniques of quasielastic neutron scattering from hydrogen atoms (the main neutron scatterers in a typical protein) allow us to study motions of particles (atoms, molecules, chemical species, etc.) in biological systems [1]. For this purpose, there are many physical situations of interests such as molecules at surfaces, in micellar systems or in vesicles and structural cages, in which the system is modeled by the jump of particles among sites or by diffusion inside a confining geometry [2–5]. For instance, when the problem can be described by the jump dynamics of a particle between two nonequivalent sites separated by a distance a, the elastic part of $S(Q,\omega)$ [i.e., the elastic incoherent structure factor (EISF)], is given by

$$A_0(Qa)=1-2p\,(1-p)[1-j_0(Qa)], \tag{1}$$

where $j_l(z)$ is the spherical Bessel function of the first kind of order l, and p is the probability of finding the particle in one of the sites. The incoherent scattering correlation function $C(Q,t)$ [i.e., the inverse Fourier transform of the quasielastic part of $S(Q,\omega)$] is a single exponential independent of Q given by $C(t)=e^{-\Gamma t}$ where Γ (related to mean residence times of the particle in either site) is the relaxation rate of the probability of finding the particle in either site. This jump model has been used to study the internal molecular motions and to interpret the dynamical transition in proteins [6,7].

Likewise, when the problem can be described by the isotropic diffusion inside a sphere with impermeable surface [2], one finds that for Q small, the quasielastic part of $S(Q,\omega)$ is well described by a single Lorentzian with the linewidth $\Gamma_0=4.33D/a^2$, where a is the sphere radius and D, the diffusion constant of the particle. Equivalently, $C(Q,t)\simeq e^{-\Gamma_0 t}$ where Γ_0^{-1} is the typical time for a particle to diffuse over the entire sphere. For times of order or larger than Γ_0^{-1} (i.e., in the $\omega\ll\Gamma_0$ limit) the EISF is given by

$$A_0(Qa)=|F(Qa)|^2=\left|\frac{3j_1(Qa)}{Qa}\right|^2. \tag{2}$$

Such an analysis is used by several authors [4,8,9] to study, for instance, the internal dynamics, structure, and dynamics of surface molecules in proteins. In these studies, the particles (mainly hydrogen atoms) are assumed to diffuse within permanent spherical cages.

On the other hand, it is well known that proteins are fluctuating systems that undergo configurational fluctuations in their structure. In different conformational substates, a protein may have the same coarse structure but differs in local configurations leading to the fluctuations of the local environment of each protein atom. As a result, a distance between sites or a structural cage in a protein fluctuate in length or size (and shape) and have a finite lifetime due to local structural relaxation just like in the mode-coupling picture of liquids [10]. In this respect, neglecting the fluctuations of shapes for simplicity, the dynamics of each hydrogen atom in a typical protein can be described, in the first approximation, as a jump dynamics between sites separated by fluctuating distances or by diffusion inside a fluctuating sphere.

In this paper, we present a simple model analysis to account for fluctuations of the local environment. We focus on the derivation of the EISF and $C(Q,t)$ in situations in which the site interspacing a (for the jump between sites) or the sphere radius a (for the diffusion inside a sphere) is allowed to fluctuate in the course of time. To model simply the fluctuations of a, we consider the following dynamics for the system formed out of a particle atom jumping between two sites [or diffusing inside a sphere with impermeable surface): the particle keeps jumping between sites separated by $a(t)$ (or diffusing within the spherical cage of radius $a(t)$] until it suffer a *configurational collision* of zero duration that equilibrates both the site interspacing (or the sphere radius) and the particle position. That is to say that after a collision the update particle position and the site interspacing (or the sphere radius) are chosen according to the normalized equilibrium distribution,

$$P_{\rm eq}(\mathbf{r},a)=\frac{e^{-\beta[V(a)+U(\mathbf{r},a)]}}{\int_0^\infty da\, e^{-\beta V(a)}\int_0^{4\pi}d\Omega\int_0^\infty r^2\, e^{-\beta U(\mathbf{r},a)}dr}, \tag{3}$$

where $\mathbf{r}=(r,\Omega)$, r is the particle position, Ω stands for polar and azimuthal coordinates, $U(\mathbf{r},a)$ is the potential energy for the particle position for a fixed a, while $V(a)$ is the potential of free energy associated to the length (spherical cage of radius) a, and $\beta^{-1}=k_BT$ is the thermal energy. The reduced equilibrium distribution for the length a is defined as, $p_{\rm eq}(a)=\int_0^{4\pi}d\Omega\int_0^\infty r^2P_{\rm eq}(\mathbf{r},a)dr$. The waiting time between successive configurational collisions is a random variable with distribution $\phi(t)$ related to the stationary correlation function of site interspacing (or the sphere radius) by

$$\psi(t)=\frac{\langle a(t)a(0)\rangle}{\langle a^2\rangle}=\int_t^\infty \phi(\tau)\,d\tau. \tag{4}$$

Assuming that the environment fluctuations act on the particle dynamics in renormalizing just the residence times (for jump dynamics) or the diffusion constant (for diffusion dynamics), thus, the Green's function, i.e., the probability density of finding the particle at the position $\mathbf{r}$ with site interspacing a (inside a sphere of radius a) at time t given that it was initially at $\mathbf{r}_0$ with site interspacing a_0 (inside a sphere of radius a_0), is given by

$$G(\mathbf{r},a,t|\mathbf{r}_0,a_0)=G_0(\mathbf{r},t|\mathbf{r}_0;a)\,\delta(a-a_0)\psi(t) + P_{\rm eq}(\mathbf{r},a)\,[1-\psi(t)], \tag{5}$$

where $G_0(\mathbf{r},t|\mathbf{r}_0;a)$ is the Green's function for a particle with a fixed-site interspacing a (or diffusing inside a sphere of a fixed radius a).

The incoherent intermediate scattering function, $I(\mathbf{Q},t)$, (which is the inverse Fourier transform of $S(\mathbf{Q},\omega)$) is

$$I(\mathbf{Q},t)=\int da_0\int d\mathbf{r}_0\int da\int d\mathbf{r}\, e^{i\mathbf{Q}.\mathbf{r}}G(\mathbf{r},a,t|\mathbf{r}_0,a_0) \times e^{-i\mathbf{Q}.\mathbf{r}_0}P_{\rm eq}(\mathbf{r}_0,a_0).$$

Using into this relation the expression of the Green's function in Eq. (5), one can show that for an isotropic problem, the function $I(\mathbf{Q},t)$ splits into two parts as,

$$I(Q,t)=A(Q)+[1-A(Q)]C(Q,t), \tag{6}$$

where the elastic part, i.e., the EISF of the system, is

$$A(Q)=\left|\int_0^\infty da\int_0^{4\pi}d\Omega\int_0^\infty r^2\, e^{i\mathbf{Q}.\mathbf{r}}P_{\rm eq}(\mathbf{r},a)\,dr\right|^2, \tag{7}$$

and the incoherent scattering correlation function $C(Q,t)$ containing all information about the relaxation dynamics, is

$$C(Q,t)=\left\langle\sum_{n=1}^\infty g_n(Qa)\,e^{-\lambda_n(a)\,t}\right\rangle\psi(t), =\left[\sum_{n=1}^\infty\int_0^\infty da\,\overline{g_n}[\beta V(a),Qa]\,e^{-\lambda_n(a)\,t}\right]\psi(t), \tag{8}$$

where the average of any function $f(a)$ is defined as $\langle f(a)\rangle=\int_0^\infty p_{\rm eq}(a)\,f(a)\,da$. The $g_n(Qa)$ is the Q-dependent bare distribution of relaxation rates $\lambda_n(a)$ in the absence of fluctuations, while $\overline{g_n}[\beta V(a),Qa]$ is the Q-dependent effective distribution of relaxation rates that accounts for distribution of a. To be specific, we assume that the effective potential of free energy associated to the length a is given by

$$V(a)=\begin{cases}\sigma a^2-\varepsilon-2k_BT\ln(a) & ;\quad a\geqslant R,\\ \infty & ;\quad a<R.\end{cases} \tag{9}$$

where $\varepsilon=\sigma R^2$, R (of order of the Van der Waals contact length) is the minimum value of a, σ is the force constant, and the repulsive logarithmic term represents the entropic contribution that accounts for the increase in configuration space as a increases. As a result of the balance between the attractive harmonic and repulsive entropic terms, the length a has an equilibrium value at finite temperature T given by $a_{\rm eq}=\max[R,(k_BT/\sigma)^{1/2}]$. We note in passing that such a harmonic potential in Eq. (9), without the entropic term, has been used to study the hydrophobic effect in the volume fluctuations of globular proteins [11].

In what follows, we derive in detail the EISF and the $C(Q,t)$ in Eqs. (7) and (8), respectively, for the jump dynamics between sites and diffusion inside a sphere.

FLUCTUATING SITE INTERSPACING

Consider the jump dynamics of a particle between two nonequivalent sites separated by a fluctuating distance a of stationary correlation function $\psi(t)$ and with τ_1 and τ_2 being the effective mean residence time of the particle in each site. For one site located at the origin, we have

$$e^{-\beta U(\mathbf{r},a)}=\begin{cases}p & ;\quad \mathbf{r}=\mathbf{0},\\ 1-p & ;\quad \mathbf{r}=\mathbf{a},\\ 0 & ;\quad \text{otherwise},\end{cases}\qquad ;\qquad p=\frac{\tau_1}{\tau_1+\tau_2}. \tag{10}$$

The distribution of relaxation rate is a delta function, $g_n(Qa)=\overline{g_n}[\beta\varepsilon,Qa]=\delta_{n,1}$ with $\lambda_1=\Gamma=\tau_1^{-1}+\tau_2^{-1}$. In this case, the normalized scattering intensity is given by Eq. (6) with the EISF and the scattering correlation function (independent of Q) given by

$$A(Q)=\langle A_0(Qa)\rangle\ \text{ and }\ C(t)=e^{-\Gamma t}\,\psi(t), \tag{11}$$

where $A_0(Qa)$ is given in Eq. (1). Since Γ is independent of the site interspacing, thus the effect of fluctuations on $C(t)$ is simply multiplicative as in Eq. (11). As a result of site inter-

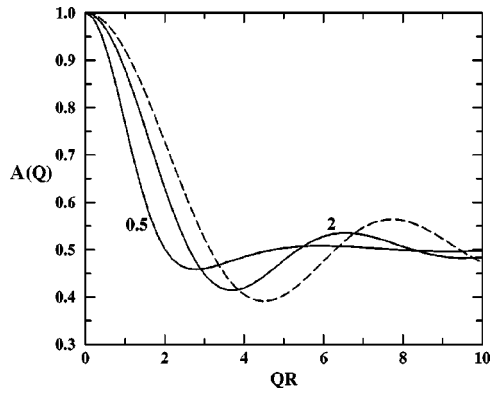

FIG. 1. The EISF $A(Q)$ in Eq. (11) as a function of QR for $p=0.5$ and $\varepsilon/k_BT=0.5,2$ as quoted on the figure. The dashed line represents $A_0(Q)$ in Eq. (1) for $a=R$ and $p=0.5$ for comparison.

spacing fluctuations, the structure factor $A(Q)$ (shown in Fig. 1) is the EISF for the jump dynamics between two sites separated by a fixed distance a averaged over the distribution of the distance. As $\beta\varepsilon$ gets smaller, the extrema of $A(Q)$ become less pronounced and are shifted to the left, compared to $A_0(Q)$. The mean-squared displacement of the particle is

$$\langle X^2\rangle = -3\left.\frac{d\ln[A(Q)]}{d(Q^2)}\right|_{Q=0} = p(1-p)\langle a^2\rangle = p(1-p)\left[\frac{3R^2}{2\beta\varepsilon}+\frac{R^2}{1+(\pi/2\beta\varepsilon)^{1/2}e^{\beta\varepsilon}\,\mathrm{erfc}(\sqrt{\beta\varepsilon})}\right]. \tag{12}$$

The solid line in Fig. 3(b) represents this function. When $\beta\varepsilon\to\infty$, we have $\langle X^2\rangle\simeq p(1-p)R^2$, like for nonfluctuating interspacing, while $\langle X^2\rangle\simeq 3p(1-p)k_BT/2\sigma$ as $\beta\varepsilon\to 0$, like for motions in a harmonic potential. This behavior is compatible and originates from jump dynamics between soft walls, the broadening of the point sites with temperature resulting from the environment fluctuations.

Generalization of Eqs. (11) and (12) to the case of jump dynamics among N equivalent sites on a fluctuating circle of radius a is straightforward. In this case, the normalized scattering intensity still writes like in Eq. (6) with the EISF given by $A(Q)=\langle A_0(Qa)\rangle$ and the Q-dependent scattering correlation function by

$$C(Q,t)=\left[\sum_{l=1}^{N}\frac{\langle A_l(Qa)\rangle}{1-\langle A_0(Qa)\rangle}\exp\left\{-\left(\frac{2t}{\tau}\right)\sin^2\left(\frac{l\pi}{N}\right)\right\}\right]\psi(t), \tag{13}$$

where the amplitude

$$A_l(Qa)=N^{-1}\Sigma_{n=1}^{N}j_0[2Qa\sin(n\pi/N)]\cos(2\,ln\pi/N)$$

for $l=0,1,\ldots,N$, and τ is the effective mean residence time in each site. Interestingly, the mean-squared displacement of the particle is simply $\langle X^2\rangle=\langle a^2\rangle$, where $\langle a^2\rangle$ is obtained from Eq. (12).

FLUCTUATING SPHERE

The potential for diffusion inside a sphere of radius a with impermeable surface is

$$U(r,a)=\begin{cases}0 & ; \quad r\leqslant a,\\ \infty & ; \quad r>a.\end{cases} \tag{14}$$

In this case, the normalized scattering intensity is given by Eq. (6) with the scattering correlation function given by

$$C(Q,t)=\left\{\sum_{n,l=0}^{\infty}\int_0^{\infty}da\,\underbrace{p_{\mathrm{eq}}(a)\left[\frac{[A_n^l(Qa)-A(Q)\delta_{0l}\,\delta_{0n}]}{[1-A(Q)]}\right]e^{-(x_n^l)^2Dt/a^2}}_{\bar{g}_n^l(Qa,a)}\right\}\psi(t), \tag{15}$$

where the $A_n^l(Qa)$ are given by [2,12]:

$$A_n^l(Qa)=\frac{6(2l+1)(x_n^l)^2}{(x_n^l)^2-l(l+1)}\left[\frac{Qa\,j_{l+1}(Qa)-lj_l(Qa)}{(Qa)^2-(x_n^l)^2}\right]^2. \tag{16}$$

$\bar{g}_n^l(Qa,a)$ is the Q-dependent effective distribution of relaxation times $\tau_n^l(a)=a^2/(x_n^l)^2D$, D is the effective diffusion constant, and x_n^l are the roots of equation [2,12], $x_n^l\,j_{l+1}(x_n^l)=lj_l(x_n^l)$. For the potential in Eq. (9), the structure factors $\langle A_0^0(Q)\rangle$ (i.e., the EISF for a sphere of radius a averaged over the distribution of radii) and the EISF of the system $A(Q)$ are therefore:

$$\langle A_0^0(Q)\rangle=\langle|F(Q)|^2\rangle=\frac{9\int_1^{\infty}x^3[j_1(xQR)]^2\,e^{-\beta\varepsilon x^2}\,dx}{(QR)^2\int_1^{\infty}x^5\,e^{-\beta\varepsilon x^2}\,dx}, \tag{17a}$$

$$A(Q)=|\langle F(Q)\rangle|^2=\left|\frac{3\int_1^{\infty}x^4\,j_1(xQR)\,e^{-\beta\varepsilon x^2}dx}{QR\int_1^{\infty}x^5\,e^{-\beta\varepsilon x^2}\,dx}\right|^2. \tag{17b}$$

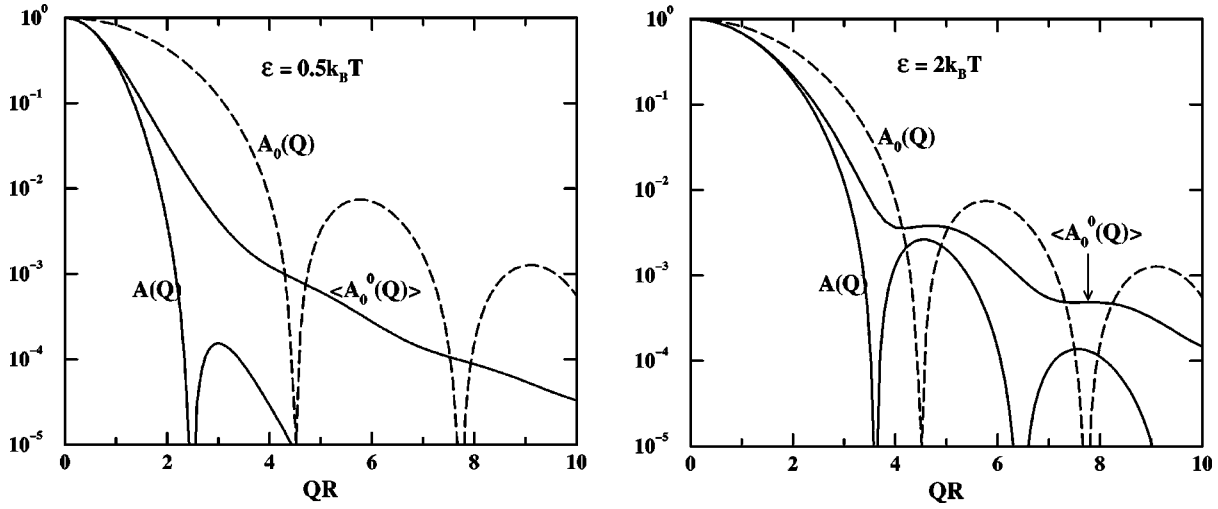

FIG. 2. The amplitudes $\langle A_0^0(Q)\rangle$ and $A(Q)$ in Eqs. (17a) and (17b), respectively, as a function of QR for two values of the reduced energy $\varepsilon/k_BT=0.5,2$ as quoted in the figures. The dashed lines represent $A_0(Q)$ in Eq. (2) for $a=R$ for comparison. Note that $QR \in [0.1,6]$ in the typical neutron-scattering experiment.

Figure 2 shows that $A(Q) \leqslant \langle A_0^0(Q)\rangle$ for all QR, and the difference between the two functions increases with increasing the temperature, i.e., as $\beta\varepsilon$ gets smaller. The location of minima of $A(Q)$ and $\langle A_0^0(Q)\rangle$ do not coincide and their values are equal to zero for $A(Q)$ while they are different from zero for $\langle A_0^0(Q)\rangle$. Like in Fig. 1, the location of minima are shifted to the left, compared to $A_0(Q)$ and tend to disappear as $\beta\varepsilon$ gets smaller. To assess to what extent $A(Q)$ and $\langle A_0^0(Q)\rangle$ contribute to the elastic intensity, we turn back to Eq. (15). The shortest relaxation time of this expansion is Γ^{-1}, where $\Gamma=(x_1^0)^2 D/R^2$ is the typical time for a particle to diffuse over the entire sphere of radius R. When $t\sim\Gamma^{-1}$, the second term containing the exponential time-dependence in Eq. (15) can be neglected. In this case the incoherent intermediate scattering function reduces to:

$$I(Q,\psi)=\psi(\Gamma)\,\langle A_0^0(Q)\rangle+[1-\psi(\Gamma)]A(Q). \qquad (18)$$

This expression, which would represent the elastic part of $S(Q,\omega)$ for the resolution time of about Γ^{-1}, contrasts with the case in the absence of fluctuations, where the incoherent intermediate scattering function relaxes to the EISF for time scales of order or greater than Γ^{-1}. Figure 3(a) displays $I(Q,\psi)$ versus QR for various values of $\psi(\Gamma)$. Manifestly, $I(Q,\psi)$ is different from the EISF $A(Q)$, even for $\psi(\Gamma)=0.1$. It is obvious that $I(Q,\psi)$ will eventually be equal to the EISF in the $\psi(\Gamma)\to 0$ limit when the particle diffusion is very slow compare to fluctuations of the sphere radius. In the opposite limit, when the particle diffusion is fast compared to sphere radius fluctuations, i.e., $\psi(\Gamma)\sim 1$, the $I(Q,\psi)$ is essentially given by $\langle A_0^0(Q)\rangle$. The mean-squared displacement of the particle is

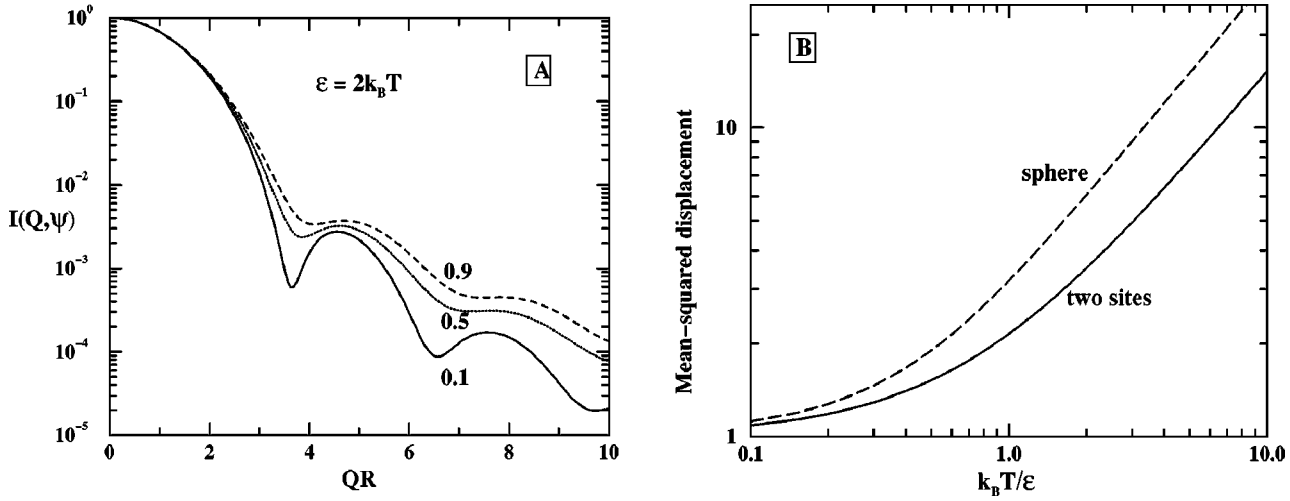

FIG. 3. **Panel A:** The intensity $I(Q,\psi)$ in Eq. (18) for diffusion inside a fluctuating sphere, versus QR for $\psi(\Gamma)=0.1,0.5,0.9$ as quoted in the figure. **Panel B:** Reduced mean-squared displacements $\langle X^2\rangle/p(1-p)R^2$ in Eq. (12) (solid line) for jump dynamics and $5\langle X^2\rangle/3R^2$ in Eq. (19) (dashed line) for diffusion, as a function of the reduced temperature k_BT/ε.

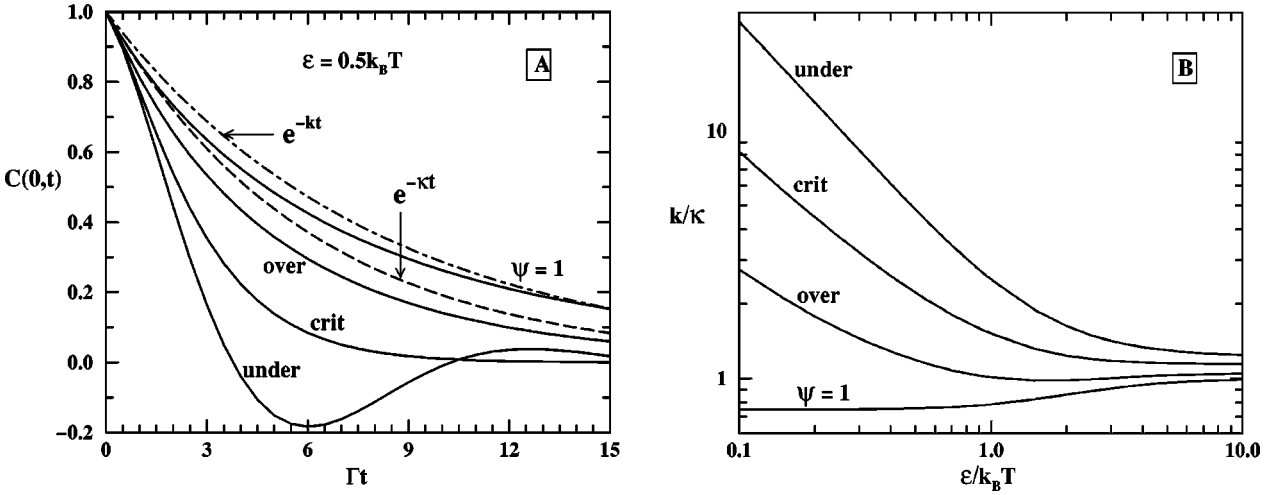

FIG. 4. **Panel A:** Correlation function $C(0,t)$ in Eq. (20) as a function of the reduced time Γt for the reduced energy $\beta\varepsilon=0.5$. The dashed and dot-dashed lines represent $e^{-\kappa t}$ and e^{-kt}, respectively, with $\kappa=13\Gamma/79$ and $k=79\Gamma/633$. **Panel B:** Reduced relaxation rate k/κ [ratio of Eqs. (23) and (22)] as a function of ε/k_BT. For the two panels, we have $\omega_0=\Gamma/2$ and the quotations ''under'' ($\gamma=\Gamma/4$), ''crit'' ($\gamma=\Gamma$), and ''over'' ($\gamma=4\Gamma$) correspond, respectively, to underdamped, critical, and overdamped regimes of $\psi(t)$ in Eq. (21).

$$\langle X^2\rangle=-3\frac{d\ln[I(Q,\psi)]}{d(Q^2)}\bigg|_{Q=0}=\langle r^2\rangle$$
$$=\frac{3R^2}{5}\left\{\frac{3}{\beta\varepsilon}+\left[1+\frac{2}{\beta\varepsilon}+\frac{2}{(\beta\varepsilon)^2}\right]^{-1}\right\}. \qquad (19)$$

Note that $\langle X^2\rangle$ is independent of $\psi(\Gamma)$ since, as is illustrated in Fig. 2, in the Gaussian scattering approximation the structure factors are, $A(Q)=A_0^0(Q)\simeq 1-3Q^2\langle r^2\rangle/5$ as $Q\to 0$. Figure 3(b) shows the temperature dependence of the particle mean-squared displacement. At low temperature $\langle X^2\rangle=3R^2/5$, like for diffusion inside a sphere of radius R while $\langle X^2\rangle\sim 9k_BT/5\sigma$ at higher temperature, like for motions in a harmonic potential. This behavior is compatible and originates from diffusion inside a sphere with a thick soft surface, the thickening of the spherical surface with temperature resulting from the environment fluctuations.

Let us turn now to the quasielastic term of $S(Q,\omega)$. The dynamics involved can be characterized by considering the position correlation function $C(0,t)$ obtained in taking the $Q\to 0$ limit of $C(Q,t)$ in Eq. (15) to give:

$$C(0,t)=\left[\int_1^\infty \overline{g}(\beta\varepsilon,x)\,e^{-\Gamma t/x^2}\,dx\right]\psi(t);\ \overline{g}(\beta\varepsilon,x)$$
$$=\frac{x^7\,e^{-\beta\varepsilon x^2}}{\int_1^\infty x^7\,e^{-\beta\varepsilon x^2}\,dx}. \qquad (20)$$

The effective distribution $\overline{g}(\beta\varepsilon,x)$ of relaxation times x^2/Γ is maximum at $x_m=\max[1,(7/2\beta\varepsilon)^{1/2}]$. For the purpose of illustration we consider the situation where the fluctuation dynamics of the sphere radius is described by the Langevin oscillator with the correlation function

$$\psi(t)=e^{-\gamma t/2}\left[\cosh(\mu t)+\left(\frac{\gamma}{2\mu}\right)\sinh(\mu t)\right];\ \mu=\frac{\sqrt{\gamma^2-4\omega_0^2}}{2}, \qquad (21)$$

where γ and ω_0 are the collision frequency (related to the dissipation) and the frequency of the oscillator. The initial decay rate constant of $\psi(t)$ is zero and its relaxation time is γ/ω_0^2.

As shown in Fig. 4(a), because of the distribution of relaxation times due to fluctuations of the sphere radius, the $C(0,t)$ is no longer a single exponential. When $\psi(t)=1$, the short time behavior of $C(0,t)$ can be fitted by $e^{-\kappa t}$, where κ is the initial decay rate (see below) of $C(0,t)$, while e^{-kt}, where k is the relaxation rate (see below) of $C(0,t)$, is a poor approximation of $C(0,t)$ although they coincide around $\Gamma t=15$. In the presence of fluctuations when $\psi(t)\neq 1$, $C(0,t)$ is essentially dominated by $\psi(t)$.

The initial decay rate of $C(0,t)$ is,

$$\kappa=-\frac{dC(0,t)}{dt}\bigg|_{t=0}=\frac{3R^2}{5\langle r^2\rangle}\Gamma$$
$$\simeq\begin{cases}\Gamma & ;\quad \beta\varepsilon\to\infty\ \ (\text{low } T),\\ \beta\varepsilon\Gamma/3 & ;\quad \beta\varepsilon\to 0\ \ (\text{high } T).\end{cases} \qquad (22)$$

In this example, κ is independent of $\psi(t)$ and Γ/κ coincides with the mean-squared displacement. If one uses for the diffusion coefficient the relation $D=k_BT/m\xi$, where m is the particle mass and ξ the friction coefficient, we find that $\kappa\propto T$ at low T, while $\kappa\simeq(x_1^0)^2\sigma/m\xi$ independent of temperature for high T.

The relaxation rate, $k^{-1}=\int_0^\infty C(0,t)\,dt$, which depends on characteristics of $\psi(t)$, is

$$\frac{\Gamma}{k}=\left[\int_1^\infty x^7\,e^{-\beta\varepsilon x^2}\,dx\right]^{-1}\int_1^\infty dx\left[\frac{x^9\,(1+\gamma x^2/\Gamma)\,e^{-\beta\varepsilon x^2}}{1+\gamma x^2/\Gamma+(\omega_0/\Gamma)^2x^4}\right]. \tag{23}$$

The ratio k/κ as a function of inverse temperature is plotted in Fig. 4(b). Three types of decays of $C(0,t)$ can be noted: $k/\kappa<1$ the $C(0,t)$ has a nonexponential decay dominated by the distribution of relaxation times, $k/\kappa=1$ then $C(0,t)=e^{-\kappa t}$, and $k/\kappa>1$ where the nonexponential $C(0,t)$ [which originates from both the distribution of relaxation times and $\psi(t)$] may show oscillations and have long tail decay. These differences in the decay of $C(0,t)$ are more pronounced for $\beta\varepsilon\to 0$ (high T) where k/κ can be very large while $k/\kappa\to 1$ [i.e., $C(0,t)$ is almost a single exponential] when $\beta\varepsilon\to\infty$ (low T). Finally, it goes without saying, that when we are concerned with the jump diffusion in a fluctuating sphere, all the expressions derived above remain unchanged except that the $\exp\{-(x_n^l)^2Dt/a^2\}$ in Eq. (15) is replaced by $\exp\{-[1-e^{-(x_n^l b)^2/2a^2}]\,\gamma_j t\}$, where b and γ_j are the jump length and frequency [12], respectively.

SUMMARY

Let us summarize the main results derived above. We find that as a result of the environment fluctuations, the EISF of the system is given by Eq. (7) and the incoherent scattering correlation function $C(t)$, given in Eq. (8), is $C(Q,t)=\Sigma_n\langle e^{-\lambda_n(a)t}\rangle\,\psi(t)$, where the average is taken over the Q-dependent effective distribution of relaxation times and $\psi(t)$ is the correlation function of the fluctuating length.

For the jump dynamics between sites, Eq. (7) reduces to $\langle A_0(Qa)\rangle$, which is the EISF $A_0(Qa)$ [in Eq. (1)] in the absence of fluctuations averaged over the distribution of site interspacing. As the relaxation rate Γ (in the absence of fluctuations) is independent of the site interspacing, the incoherent scattering correlation function $C(t)$, given in Eq. (11), is equal to $C(t)$ in the absence of fluctuations times $\psi(t)$.

For the diffusion inside a fluctuating sphere, on the other hand, Eq. (7) reduces to $|\langle F(Qa)\rangle|^2$ where $F(Qa)$, given in Eq. (2), is the scattered amplitude for diffusion inside a sphere of fixed radius a and the average is taken over the distribution of radii. However, the normalized elastic intensity $I(Q,\psi)$, given by Eq. (18), involves two contributions depending on the relaxation of the sphere radius over time scales Γ^{-1}. When the particle diffusion is slow compared to the fluctuations of the sphere, $I(Q,\psi)$ is equal to $|\langle F(Qa)\rangle|^2$ while, in the opposite limit, it is is given by $\langle|F(Qa)|^2\rangle$. Since the relaxation time $\tau_n^l(a)$ for the diffusion in a sphere depend on the sphere radius, the fluctuations of the sphere radius generate an effective distribution of relaxation time so that $C(Q,t)$, in Eq. (15), is $C(Q,t)=\Sigma_{n,l=0}^\infty\langle e^{-t/\tau_n^l(a)}\rangle\,\psi(t)$, where the average is taken over the Q-dependent effective distribution of relaxation times and $\psi(t)$ is the correlation function of the sphere radius.

It worthwhile to mention that when $\psi(t)=1$, the situation resembles what is known as the heterogeneous scenario for the explanation of the stretched exponential or Kohlrausch-Williams-Watts relaxation [13]. Such a situation may be encountered in the case where the particle atoms in a protein system undergo jump dynamics between sites (or diffusion inside spherical cages) each of them with different site interspacing (radius), i.e., polydispersity in length scales. In this case, $C(Q,t)$ is exponential for jump dynamics between sites (provided that Γ is the same for each particle) while it is nonexponential for diffusion inside a sphere. The above results with $\psi(t)\neq 1$ are derived in the homogeneous scenario [13], which assumes that all particles are dynamically identical.

To conclude, we emphasize that the dynamics of particle atoms in a protein system is a multidimensional problem in which the particles and constituent elements of their environment undergo their own dynamics in their respective potentials. The speculative discussion outlined above is a quite simplified two-dimensional version (particle position **r** and site interspacing or sphere radius a) of the problem. Nonetheless, it is encouraging to see that the present analysis indicates that the form of the scattering intensity, for instance, is quite influenced by the fluctuations. This suggests at least reconsidering the way of fitting experimental data and revising the interpretation of parameters determined. In the same spirit, an analysis combining particle dynamics and fluctuations in both the size and shape of the confining geometries can be developed along these lines.

ACKNOWLEDGMENTS

The author thanks J. Dianoux and E. Kats for their comments on the manuscript.

[1] M. Bée, *Quasielastic Neutron Scattering* (Adam Hilger, Bristol, 1988).
[2] F. Volino and A.J. Dianoux, Mol. Phys. **41**, 271 (1980).
[3] P.L. Hall and D.K. Ross, Mol. Phys. **42**, 673 (1981).
[4] 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).
[5] *Hydration Processes in Biology: Theoretical and Experimental Approaches*, edited by M. -C. Bellissent-Funel (IOS Press, Amsterdam, 1999), Vol. 305.
[6] W. Doster, S. Cusack, and W. Petry, Nature (London) **337**, 754 (1989).
[7] J. Fitter, R.E. Lechner, G. Büldt, and N.A. Dencher, Proc. Natl. Acad. Sci. U.S.A. **93**, 7600 (1996).
[8] J. Perez, J.-M. Zanotti, and D. Durand, Biophys. J. **77**, 454 (1999).

[9] *Hydration Processes in Biology: Theoretical and Experimental Approaches*, edited by M. -C. Bellissent-Funel (IOS Press, Amsterdam, 1999), Vol. 305, pp. 195–217.
[10] W. Götze and L. Sjögren. Rep. Prog. Phys. **55**, 241 (1992).
[11] B. Lee, Proc. Natl. Acad. Sci. U.S.A. **80**, 622 (1983).
[12] D.J. Bicout, Phys. Rev. E **62**, 261 (2000).
[13] A. Arbe, J. Colmenero, M. Monkenbusch, and D. Richter, Phys. Rev. Lett. **81**, 590 (1998).