

Lattice model for translational and rotational motions based on generalised diffusion equations: I. General formalism

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Abstract. A simple lattice model based on generalised diffusion equations and Gaussian statistics, aimed at describing diffusive translational and rotational motions, is presented. It is shown that it allows the generation of correlation functions relevant to spectroscopic techniques that are very similar to those experimentally observed in a large variety of complex systems. For some ranges of values of the model parameters, these functions, which can be expressed in closed mathematical forms, can be approximately represented by the sum of two exponentials or by “stretched” exponentials.

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1 Introduction

Spectroscopic techniques (neutron and light scattering, NMR...) when used in complex condensed systems such as supercooled liquids, colloidal dispersions, polymers, gels, fluids in restricted geometries generally reveal strongly non-exponential behaviours for the relevant correlation functions. This observation is often associated with non-Arrhenius behaviour for the temperature dependence of mass transport coefficients, mainly translational and rotational diffusion coefficients and shear viscosity. A microscopic theory of these phenomena, based on first principles, is still lacking, even in the simplest cases such as the glass transition of pure systems composed of relatively small molecules [1]. A number of phenomenological theories such as the mode coupling theory, and models including lattice models have been developed to explain these results (for a review, see for example [2,3]). However, these approaches are limited only to the description of particular aspects of phenomena observed in complex systems. Lattice models have long been used in statistical physics, for example the “lattice gas” model (equivalent to the so-called “Ising model”) for describing second order phase transitions [4], or the “Flory-Huggins model” for describing static properties of polymers [5]. In these models, the concept of lattice is rather abstract and does not necessarily require the existence of a real translational regularity as it is the case in true crystals. A true regular lattice may however be assumed as in recent works related to orientational glass transition [6,7]. However, even in these cases,

the model cannot be taken too literally since the elongated objects that are located at the lattice points are assumed as having no radial dimension. Nevertheless, all these models turn out to be useful since they can describe at least qualitatively different classes of phenomena. In this paper, we propose an original approach for calculating correlation functions for both translational and rotational motions by using a simple “lattice-like” model based on generalised diffusion equations and on Gaussian statistics. We show that the proposed model (i) provides rather simple, closed form expressions for correlation functions (ii) can account rather accurately for the observed behaviour and (iii) may be used to reduce spectroscopic data to a small number of model parameters. The values of these parameters may then help to obtain new insights concerning the system studied, for example by revealing (hidden) characteristic distances or times, intermediate between molecular and macroscopic. Since diffusion is a concept associated with long time behaviour, the calculated correlation functions are expected to be valid only for longer times than a characteristic time t_{\min} , below which the description breaks down. This model is currently applied in our laboratory to the analysis of spectroscopic data from various “complex” systems. As a first example of application of this model, we have chosen a problem where the current models are not completely satisfactory, namely the simulation of NMR line shapes of amorphous polymers. Detailed results concerning the fluorine NMR spectra of polytetrafluoroethylene as a function of temperature will be presented in a forthcoming publication [8].

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2 The model for translational motion

The system is assumed to be composed of a large number of (possibly rigid) objects submitted to thermal motion. The position of the mass centre of these objects, as well as their orientation, fluctuate around equilibrium positions. At mechanical equilibrium, *i.e.* in the absence of macroscopic motions (flow), it is assumed that the average positions form a regular lattice that is chosen cubic for simplicity (this assumption can be removed, see Sect. 5). Let a be the average distance between objects, which is identified in this model with the cubic lattice spacing and $u_\alpha(t)$, $\alpha = x, y, z$ the components of the displacement of an object at time t from its average position (a lattice point). The assumptions concerning these latter quantities are the following, for example for component x :

- (i) they are independent random Gaussian variables with zero average. Their (common) mean square averages (or variance) are noted $\langle u_x^2 \rangle$. The probability density function $p(u_x)$ is:

$$p(u_x) = \frac{1}{[2\pi\langle u_x^2 \rangle]^{1/2}} \exp\left[-\frac{u_x^2}{2\langle u_x^2 \rangle}\right] \quad (1)$$

- (ii) their time correlation functions are simple exponentials characterised by a correlation time τ_0 . We have:

$$\langle u_x(t)u_x(0) \rangle = \langle u_x^2 \rangle \exp\left(-\frac{t}{\tau_0}\right) \quad (2)$$

- (iii) the random process is stationary, that is:

$$\langle u_x^2(t) \rangle = \langle u_x^2(t') \rangle \quad \forall t, t' \quad (3)$$

- (iv) all objects are dynamically equivalent.

With the variance $\langle u_x^2 \rangle$ and time τ_0 , a local self-diffusion coefficient D_t can be defined along x as:

$$D_t = \frac{\langle u_x^2 \rangle}{\tau_0} \quad (4)$$

3 Correlation and distribution functions

Let's assume that the centre of mass of the objects can be considered as incoherent scatterers for thermal neutrons. In this case, owing to the equivalence, the normalised intermediate incoherent scattering law writes:

$$I_s(Q, t) = \langle \exp[iQ(u_x(t) - u_x(0))] \rangle \quad (5)$$

where Q is the neutron transfer momentum component along x and the brackets mean an average over all possible initial displacements $u_x(0) = u_{x0}$ at thermal equilibrium. The random variables $u_x(t)$ being Gaussian, the variable $X = u_x(t) - u_x(0)$ is also Gaussian, which means that

its probability density is given by (1) with variance $\langle X^2 \rangle$. Then it is easy to show that:

$$\begin{aligned} I_s(Q, t) &= \int_{-\infty}^{\infty} \exp(iQX)p(X)dX \\ &= \exp\left[-\frac{Q^2}{2}\langle [(u_x(t) - u_x(0))]^2 \rangle\right]. \end{aligned} \quad (6)$$

By expanding the square in the argument of the exponential, and by using by the stationary property, we obtain:

$$I_s(Q, t) = \exp\left[-Q^2\langle u_x^2 \rangle \left(1 - \exp\left(-\frac{t}{\tau_0}\right)\right)\right]. \quad (7)$$

This correlation function does not decay to zero at infinite time. This is due to the fact that the motion is restricted to a volume whose linear size is about the mean amplitude fluctuation. The elastic incoherent structure factor (EISF) of this unidimensional-restricted motion is the limit of this function at infinite time:

$$I_s(Q, \infty) = |\langle \exp(iQu_x) \rangle|^2 = \exp[-Q^2\langle u_x^2 \rangle]. \quad (8)$$

It can easily be verified that equation (7) can be calculated by:

$$\begin{aligned} I_s(Q, t) &= \int_{-\infty}^{\infty} \exp(-iQu_{x0})p(u_{x0})du_{x0} \\ &\quad \times \int_{-\infty}^{\infty} \exp(iQu_x)G_s(u_x, u_{x0}, t)du_x \end{aligned} \quad (9)$$

where the time dependent distribution function $G_s(u_x, u_{x0}, t)$ is given by:

$$\begin{aligned} G_s(u_x, u_{x0}, t) &= \frac{1}{\left[4\pi\langle u_x^2 \rangle \left(1 - \exp\left(-\frac{t}{\tau_0}\right)\right)\right]^{1/2}} \\ &\quad \times \exp\left[-\frac{(u_x - u_{x0})^2}{4\langle u_x^2 \rangle \left[1 - \exp\left(-\frac{t}{\tau_0}\right)\right]}\right]. \end{aligned} \quad (10)$$

One observes that $G_s(u_x, u_{x0}, t)$ is a Gaussian function of the variable $u_x - u_{x0}$ whose variance is:

$$2\langle u_x^2 \rangle \left[1 - \exp\left(-\frac{t}{\tau_0}\right)\right]. \quad (10a)$$

The function G_s is the solution of the following generalised diffusion equation:

$$\frac{\partial G_s(u_x, u_{x0}, t)}{\partial t} = D(t) \frac{\partial^2 G_s(u_x, u_{x0}, t)}{(\partial u_x)^2} \quad (11)$$

where the time dependent diffusion coefficient $D(t)$ is given by:

$$D(t) = \frac{\langle u_x^2 \rangle}{\tau_0} \exp\left(-\frac{t}{\tau_0}\right) = D_t \exp\left(-\frac{t}{\tau_0}\right). \quad (12)$$

To summarise, these last four equations allow us to describe, in the framework of Gaussian statistics, the random translational motion of a particle on a linear segment whose size is of the order of magnitude of the mean amplitude of u_x , and relation (7) is the corresponding intermediate incoherent scattering law for neutrons.

So far, the fact that an object can reach a neighbouring site at distance a has not been taken particularly into account. Since this neighbouring site is also an (equivalent) equilibrium site, the object can remain in this site. The possibility to reach efficiently this neighbouring site depends crucially on the relative values of the mean fluctuation amplitude and of the lattice spacing a . It is natural to characterise the facility for an object to move efficiently (*i.e.* to reach and stay) on a neighbouring site by the ratio R_t of the probability densities of the variable u_x at distance a and at the origin 0. According to (1), we have:

$$R_t = \frac{p(a)}{p(0)} = \exp\left(-\frac{a^2}{2\langle u_x^2 \rangle}\right) = \exp\left(-\frac{a^2}{2D_t\tau_0}\right). \quad (13)$$

The quantity R_t is close to 1 for large fluctuations compared to the lattice spacing (presumably at sufficiently high temperature), but due to the exponential dependence, it may be very small for small fluctuations (presumably at sufficiently low temperature). One thus expects a significant change in the behaviour of R_t with temperature when the magnitude of the fluctuations crosses the value of the lattice spacing.

Since τ_0 has been used to define a local diffusion coefficient, τ_0/R_t may be used in the same way to define a long range (or macroscopic) diffusion coefficient D_M . We have:

$$D_M = D_t R_t = \frac{\langle u_x^2 \rangle}{\tau_0} \exp\left(-\frac{a^2}{2\langle u_x^2 \rangle}\right). \quad (14)$$

As far as R_t is non zero, at sufficiently long time, the object has escaped from its initial site and can be found at any distance from its origin. This is the characteristic feature of standard diffusion in an infinite medium. The solution of the corresponding diffusion equation is a Gaussian function of $u_x - u_{x0}$ whose variance is $2D_M t$.

Assuming that the two diffusive processes (local and long range) are additive, the diffusion coefficient $D_{\text{tot}}(t)$ for the whole process is simply the sum of the two diffusion coefficients. We have:

$$D_{\text{tot}}(t) = D_t \exp\left(-\frac{t}{\tau_0}\right) + D_M = D_t \left[\exp\left(-\frac{t}{\tau_0}\right) + R_t \right]. \quad (15)$$

The time dependent distribution function for the displacement of an object becomes:

$$G_s(u_x, u_{x0}, t) = \frac{1}{\left[4\pi\langle u_x^2 \rangle \left(1 - \exp\left(-\frac{t}{\tau_0}\right) + R_t \frac{t}{\tau_0}\right)\right]^{1/2}} \times \exp\left[-\frac{(u_x - u_{x0})^2}{4\langle u_x^2 \rangle \left[1 - \exp\left(-\frac{t}{\tau_0}\right) + R_t \frac{t}{\tau_0}\right]}\right]. \quad (16)$$

This function is the solution of the following diffusion equation:

$$\frac{\partial G_s(u_x, u_{x0}, t)}{\partial t} = \left[\frac{\langle u_x^2 \rangle}{\tau_0} \left(\exp\left(-\frac{t}{\tau_0}\right) + R_t \right) \right] \times \frac{\partial^2 G_s(u_x, u_{x0}, t)}{(\partial u_x)^2}. \quad (17)$$

In this equation, one retrieves the fact that at sufficiently long time, the local motion can be neglected, and one recovers the usual diffusion equation in an infinite medium, characterised by long range diffusion coefficient D_M .

The corresponding intermediate incoherent scattering law is obtained from (9) by using (16). One obtains:

$$I_s(Q, t) = \exp\left[-Q^2\langle u_x^2 \rangle \left(1 - \exp\left(-\frac{t}{\tau_0}\right) + R_t \frac{t}{\tau_0}\right)\right]. \quad (18)$$

This relation reduces to (7) in the absence of long range motion ($R_t = 0$). One observes in (18) that the assumption of additivity of the diffusion coefficients is equivalent to the assumption that the local and long range diffusion are independent processes, since the intermediate scattering law is the product of the two individual intermediate scattering laws.

To summarise, the present model for motion of rigid objects on a lattice provides general expressions for translational self-correlation functions relevant to spectroscopic techniques. It is a three-parameter model. In condensed matter, two of them can logically be considered as almost fixed, namely the lattice spacing a and the correlation time τ_0 . The third parameter $\langle u_x^2 \rangle$ is likely to be (possibly strongly) temperature-dependent. In fact, these functions are relevant to incoherent scattering only. For coherent scattering, pair-correlation functions must be calculated. This will be done in a forthcoming paper [11], but preliminary results show that the general shapes of these functions are qualitatively similar to the self-correlation ones. If the normalised structure factor $I(Q)$ of the system can be represented by the product of a form factor of the objects $P(Q)$ and an interference term $S(Q)$, the so-called ‘‘incoherent approximation of coherent scattering’’ consists in replacing the actual variance $\langle u_x^2 \rangle$ by an effective (coherent) variance given by $\langle u_x^2 \rangle / S(Q)$. Equivalently, the diffusion coefficient D_t should be replaced by an effective diffusion coefficient given by a similar law if

one assumes that τ_0 is a constant. In fact, in the philosophy of the present model, τ_0 should probably be identified with the average time required for a thermal fluctuation to cross a typical (experimental) distance. With a typical sample size of 1 mm, and a heat celerity (thermal diffusivity divided by a molecular distance) of 10^5 cm/s (this celerity is expected to be only weakly temperature dependent in condensed matter), one obtains τ_0 in the order of magnitude of some microseconds. These results concerning the incoherent approximation of coherent scattering will be tested in detail in the framework of the present model, extended to coherent scattering [11].

Introducing the scaling diffusion coefficient defined as $D_{sc} = a^2/\tau_0$, one can express the macroscopic diffusion coefficient D_M as a function of the reduced variable $s = \langle u_x^2 \rangle / a^2$:

$$\frac{D_M}{D_{sc}} = s \exp\left(-\frac{1}{2s}\right). \quad (19)$$

It can be noted that if the temperature dependence of $\langle u_x^2 \rangle$ (or s) is linear (this is probably a realistic situation at sufficiently high temperature), then the exponential term corresponds to an Arrhenius-type dependence. We have D_M being proportional to $T \exp(-T_a/T)$, where T_a is some characteristic temperature (energy). Consequently, from the Stokes-Einstein functional form relating diffusion coefficient to viscosity (valid in condensed fluid media under standard conditions), one finds that, in this high temperature limit, the temperature dependence of the viscosity is just $\exp(T_a/T)$.

Since all sites are occupied by rigid (impenetrable) objects, a particular object can move on a neighbouring site only if the object on this site has also moved away. The present model is thus expected to apply in systems where the translational motions of neighbouring objects are (strongly) coupled. In other words, the model implicitly assumes that the motions are essentially collective, as it is the case in condensed matter where the density is near close-packing. The collective aspect thus suggests the need of introducing the notion of translational coherence length ξ , defined as the mean distance beyond which the motions of objects are no more coupled. This distance ξ , which is expected to increase when the width of the (translational) ‘‘thermal cloud’’ $\langle u_x^2 \rangle$ decreases, is irrelevant for calculating incoherent scattering laws, *i.e.* self-correlation functions, but is of primary importance for calculating coherent scattering laws, *i.e.* the pair-correlation functions $I_p(Q, t)$, and the structure factor $I(Q) = I_p(Q, 0)$ [11].

4 Extension of the model to rotational motion

4.1 Motion on a circle

A similar kind of model can be developed for rotational motion among N equidistant sites on a circle. One particular object, located at one lattice point of the previous (translational) lattice is pictured as an uniaxial object

whose orientation can fluctuate around an axis perpendicular to it. This rotation axis is fixed in the laboratory frame. The orientation of the object axis in the rotation plane is described by an angle φ , considered as a random variable. The circle with its N sites now represents the ‘‘lattice’’ for the rotational motion. The angle $\alpha = 2\pi/N$ plays the role of a rotational lattice ‘‘distance’’. Let’s consider first the motion around one particular site, located by convention at $\varphi = 0$, in the absence of the other sites. The symmetry of the problem implies that all relevant functions have periodicity 2π , and can thus be expanded in Fourier series. We start the discussion of this problem from the diffusion equation. By analogy with (11, 12), we assume that the time dependent distribution function G_s of angle φ satisfies the following generalised diffusion equation:

$$\frac{\partial G_s(\varphi, \varphi_0, t)}{\partial t} = D_r \exp\left(-\frac{t}{\tau_0}\right) \frac{\partial^2 G(\varphi, \varphi_0, t)}{(\partial \varphi)^2} \quad (20)$$

where D_r is a rotational diffusion coefficient and τ_0 a characteristic time. The solution of this equation can be written:

$$G(\varphi, \varphi_0, t) = \frac{1}{2\pi} \times \sum_{n=-\infty}^{\infty} \exp\left[-n^2 D_r \tau_0 \left[1 - \exp\left(-\frac{t}{\tau_0}\right)\right]\right] \exp[in(\varphi - \varphi_0)]. \quad (21)$$

The distribution at infinite time is:

$$G(\varphi, \varphi_0, \infty) = \frac{1}{2\pi} \sum_{n=-\infty}^{\infty} \exp[-n^2 D_r \tau_0] \exp[in(\varphi - \varphi_0)]. \quad (22)$$

The equilibrium distribution function $p(\varphi_0)$ can also be developed in Fourier series. We write

$$p(\varphi_0) = \frac{1}{2\pi} \sum_{n=-\infty}^{\infty} S_n \exp(in\varphi_0) \quad (23)$$

where the coefficients S_n can be defined as an infinite number of local orientational order parameters.

By calculating in two different ways the average value of $\exp[im(\varphi - \varphi_0)]$ at infinite time, either using (22, 23), or directly by assuming that the angles at zero and infinite times are not coupled and have the same distribution p (this calculation is valid only because both this function and $G(\varphi, \varphi_0, t)$ depend on $(\varphi - \varphi_0)$ only, and not on φ and φ_0 separately), one can easily show that:

$$S_n = \langle \exp(in\varphi) \rangle = \exp\left[-\frac{n^2 D_r \tau_0}{2}\right]. \quad (24)$$

The equilibrium distribution can thus be written:

$$p(\varphi_0) = \frac{1}{2\pi} \sum_{n=-\infty}^{\infty} \exp\left[-\frac{n^2 D_r \tau_0}{2}\right] \exp(in\varphi_0). \quad (25)$$

Finally, since any function of φ with period 2π can be expanded in series of $\exp(in\varphi)$, it is sufficient to know the inter-correlation functions $C_{m,n}(t) = \langle \exp[im\varphi(t)] \exp(-in\varphi_0) \rangle$ to be able to calculate any correlation function. Using the above relations, we obtain:

$$C_{m,n}(t) = \exp \left[-m^2 D_r \tau_0 \left(1 - \exp \left(-\frac{t}{\tau_0} \right) \right) \right] \times \exp \left[-\frac{(m-n)^2 D_r \tau_0}{2} \right]. \quad (26)$$

Now we show that, for practical purposes, this random process on a circle is isomorphous to the Gaussian random process for translation on a straight line described previously, despite the fact that in the first case, it involves imaginary exponential functions of the variable instead of Gaussian functions. In fact, the two models have different topologies, since in the translational case, the variable is allowed to explore the interval $-\infty$ to ∞ , while in the rotational case, it is restricted to a 2π interval. Since the moving particle can make physically many turns on the circle, the probability to make an angle φ at time t is not the same as the probability to make $\varphi + n\pi$. Thus, in principle, the angular interval should also range between $-\infty$ and ∞ . In order to connect the periodic description with the more physical non-periodic one, one must forget the strict 2π symmetry. In this case, the above distribution functions should be considered as Fourier integrals rather than Fourier series. This means that the sums over n in (21, 23, 25) should be replaced by integrals over n , now considered as a continuous variable. For example, for the time dependent distribution function, we have:

$$G(\varphi, \varphi_0, t) = \int_{-\infty}^{\infty} \exp \left[-n^2 D_r \tau_0 \left[1 - \exp \left(-\frac{t}{\tau_0} \right) \right] \right] \times \exp[in(\varphi - \varphi_0)] dn. \quad (27)$$

The integral can be performed exactly, and one obtains the following Gaussian function:

$$G(\varphi, \varphi_0, t) = \frac{1}{\left[4\pi D_r \tau_0 \left[1 - \exp \left(-\frac{t}{\tau_0} \right) \right] \right]^{1/2}} \times \exp \left[-\frac{(\varphi - \varphi_0)^2}{4D_r \tau_0 \left[1 - \exp \left(-\frac{t}{\tau_0} \right) \right]} \right]. \quad (28)$$

Similarly, we have

$$p(\varphi_0) = \frac{1}{[2\pi D_r \tau_0]^{1/2}} \exp \left[-\frac{\varphi_0^2}{2D_r \tau_0} \right]. \quad (29)$$

From these relations, one can define the angular variance $\langle \varphi^2 \rangle$ for this Gaussian process by:

$$\langle \varphi^2 \rangle = D_r \tau_0. \quad (30)$$

Note that, since $\langle \varphi^{2n+1} \rangle = 0$, the expansion in series of the two members of (24) around 0, implies relation (30).

By analogy with the translational case (relation (2)), relation (30) suggests that the characteristic time τ_0 should be identified with the correlation time of the random variable φ , the corresponding correlation function being exponential.

One thus recovers formally all the results of the unidimensional translational Gaussian model. Indeed, the calculation shows that one obtains exactly the same expressions for the order parameters and for the correlation functions by using the Gaussian functions, where the angle φ is allowed to vary between $-\infty$ and ∞ , than with the periodic functions where the angle φ is restricted to a 2π interval. Thus, for practical purposes, that is for calculating measurable quantities, the two formalisms are strictly equivalent since order parameters and correlation functions are the only quantities that can be determined from experiments.

It is interesting to mention that, although equivalent for experimental predictions, the two formalisms are not identical. It can indeed be verified that the numerical values of $G(\varphi, \varphi_0, t)$ or $p(\varphi_0)$ are not the same when they are calculated either by (21, 25) or by (28, 29). This is easily understood since in the first case, the probabilities are summed over an infinite number of angles differing by an integer number of 2π , while in the second case, only one value is considered.

The problem is now to decide which formalism should be used for extending this single site model to the many site model (neighbouring sites separated by angle $\alpha = 2\pi/N$) since the calculation of R_r , which is the analogue of R_t in the translational model, relation (13), involves the probability density $p(\varphi_0)$ through the relation $R_r = p(\alpha)/p(0)$. It is clear that the Gaussian formalism should be used since the physics changes when the particle reaches a neighbouring site, and such a site is defined by a single value of the angle α . The angles $\alpha + m\pi$ with m integer positive or negative correspond to different sites in the Gaussian formalism, and to the same site in the periodic formalism. Consequently, in order to calculate the factor R_r , relation (29) must be used rather than relation (25). One thus obtains an expression very similar to (13), namely:

$$R_r = \exp \left(-\frac{\alpha^2}{2\langle \varphi^2 \rangle} \right) = \exp \left(-\frac{\alpha^2}{2D_r \tau_0} \right). \quad (31)$$

With this expression, the expression for the inter-correlation functions, formally identical to those of the unidimensional translational case may finally be written:

$$C_{m,n}(t) = \exp \left[-m^2 \langle \varphi^2 \rangle \left[1 - \exp \left(-\frac{t}{\tau_0} \right) + R_r \frac{t}{\tau_0} \right] \right] \times \exp \left[-\frac{(m-n)^2 D_r \tau_0}{2} \right]. \quad (32)$$

In fact, this is not the correct expression since the origin has been chosen at one particular site. Since all sites are equivalent, one must average over all of them. Calling

$\varphi_p = \alpha(p-1) = 2\pi(p-1)/N$ the angular position of site p with respect to site 1 taken as origin on the circle, all the above expressions are valid when one replaces the current angle φ by $\varphi - \varphi_p$ and the initial angle φ_0 by $\varphi_0 - \varphi_p$, and one averages over p . Since $\exp i\varphi = \exp i\varphi_p \exp i(\varphi - \varphi_p)$, the macroscopic inter-correlation function is written:

$$C_{m,n}(t) = \frac{1}{N} \sum_{p=1}^N \exp[i(m-n)\varphi_p] \exp \left[-m^2 \langle \varphi^2 \rangle \right] \times \left[1 - \exp \left(-\frac{t}{\tau_0} \right) + R_r \frac{t}{\tau_0} \right] \exp \left[-\frac{(m-n)^2 D_r \tau_0}{2} \right]. \quad (32a)$$

One observes that the self-*(i.e. m = n)* correlation functions are independent of the particular values of the φ_p s, that is to say of the origin chosen. As in the translational case, they are independent from the number of (rotational) sites, and they depend only on the distance between two neighbouring sites through the value of R_r . Physically speaking, the origin of the orientational order comes from the presence of an (identical) object located on a neighbouring (translational site). Because of the close-packing, one object can rotate only if the neighbouring objects have also rotated with the same angle. As in the translational case, the many site rotational model also implies a coupling of the rotations of neighbouring objects and consequently requires the introduction of the notion of (rotational) coherence length, which is expected to increase as the width of the (rotational) “thermal cloud” $\langle \varphi^2 \rangle$ decreases (see the previous discussion on this aspect for translational motion).

In the many site model, one can define “long (angular) range” orientational order parameters $S_{n,M}$ (index M for “macroscopic”, as in the translational case) by averaging $\langle \exp(in\varphi) \rangle$ over all rotational sites taking into account the fact that $S_n = \langle \exp[in(\varphi - \varphi_p)] \rangle$. We obtain:

$$S_{n,M} = S_n \frac{1}{N} \sum_{p=1}^N \exp \frac{2\pi i(p-1)}{N}. \quad (32b)$$

For the two site model ($N = 2$), one finds that all odd $S_{n,M}$ order parameters are zero whereas all the even ones are equal to the corresponding local even order parameters. This result means that, for n even, jumps among the two sites do not affect the value of the function $\exp(in\varphi)$. In other words, jumps among sites are irrelevant so that the even correlation functions do not decay to zero at infinite time. Consequently, in the expression of the corresponding macroscopic correlation function, the coefficient R_r should be omitted.

4.2 Rotational motion in an uniaxial medium

The problem is similar to the previous one, except that the rotation axis is no more fixed in the laboratory frame, but have any direction in the plane perpendicular to the object

axis. The rotational problem is now a bi-dimensional one, since the orientation of the object axis on the unit sphere is described by two angles symbolised by Ω , namely polar angle θ and azimuthal angle ϕ . The number of sites N on the sphere may be arbitrary, provided it forms a regular mapping. The simplest problem is when N is restricted to 2 with the two sites located at the north and south poles, defined by $\theta = 0$ and π (the values of ϕ are irrelevant there). In this case, the model may now be adequate, for example, to describe orientational fluctuations in uniaxial phases.

We follow the method used for the one-dimensional case. We solve first the problem with one site located at the north pole. The diffusion equation is similar, except that the second member of the equation is the angular part of the Laplacian Δ , and also that D_r is now a two-dimensional rotational diffusion coefficient. We have:

$$\frac{\partial G_s(\Omega, \Omega_0, t)}{\partial t} = D_r \exp \left(-\frac{t}{\tau_0} \right) \Delta_\Omega [G_s(\Omega, \Omega_0, t)]. \quad (33)$$

The solution of this equation can be written:

$$G_s(\Omega, \Omega_0, t) = \frac{1}{4\pi} \sum_{l=0}^{\infty} \exp \left[-l(l+1)D_r\tau_0 \left[1 - \exp \left(-\frac{t}{\tau_0} \right) \right] \right] \times \sum_{m=-l}^l Y_m^l(\theta, \varphi) Y_m^{l*}(\theta_0, \varphi_0), \quad (34)$$

where the Y_m^l are the spherical harmonics, and the subscript * symbolises the complex conjugate. The distribution at infinite time is:

$$G_s(\Omega, \Omega_0, \infty) = \frac{1}{4\pi} \sum_{l=0}^{\infty} \exp[-l(l+1)D_r\tau_0] \times \sum_{m=-l}^l Y_m^l(\theta, \varphi) Y_m^{l*}(\theta_0, \varphi_0). \quad (35)$$

It is also convenient to introduce the Legendre polynomials P_l defined by:

$$P_l(\cos \theta) = \left(\frac{4\pi}{2l+1} \right)^{1/2} Y_0^l(\theta, \phi). \quad (36)$$

If γ is the angle between the directions defined by Ω and Ω_0 , we have the identity:

$$P_l(\cos \gamma) = \frac{4\pi}{2l+1} \sum_{m=-l}^l Y_m^l(\theta, \varphi) Y_m^{l*}(\theta_0, \varphi_0). \quad (37)$$

This relation shows that $G_s(\Omega, \Omega_0, t)$ depends only on the angle γ , and not on Ω and Ω_0 separately. The equilibrium distribution function $p(\Omega_0)$ having uniaxial symmetry, it can be developed in series of Legendre polynomials. We write:

$$p(\Omega_0) = \frac{1}{4\pi} \sum_{l=0}^{\infty} (2l+1) S_l P_l(\cos \theta_0) \quad (38)$$

where the coefficients $S_l = \langle P_l(\cos \theta_0) \rangle = \int P_l(\cos \theta_0) \times p(\Omega_0) d\Omega_0$ can be considered as an infinite number of local orientational order parameters.

As for the one-dimensional case, by calculating in two different ways the average value of $P_l(\cos \gamma)$ at infinite time, either by using (35), or directly by using (37) assuming that the solid angles at zero and infinite times are not coupled and have the same distribution $p(\Omega_0)$, it can be shown that:

$$S_l = \langle P_l(\cos(\theta_0)) \rangle = \exp \left[-\frac{l(l+1)D_r\tau_0}{2} \right]. \quad (39)$$

Note that the demonstration of this result is much less straightforward than in the one-dimensional case, and requires the use of explicit forms of the quantities $C_{m,m'}^{l,l'}(0)$ defined below. The equilibrium distribution can thus be written:

$$p(\Omega_0) = \frac{1}{4\pi} \sum_{l=0}^{\infty} (2l+1) \exp \left[-\frac{l(l+1)D_r\tau_0}{2} \right] P_l(\cos(\theta_0)). \quad (40)$$

For high orientational order, that is for θ_0 restricted to small values around 0, or equivalently, small values of $D_r\tau_0$, one can expand the two members of (39) and limit them to the first two terms. Since the development of P_l is $P_l(\cos \theta) = 1 - l(l+1)\theta^2/4$, it is natural to define the mean square fluctuation of angle θ by:

$$\langle \theta^2 \rangle = 2D_r\tau_0. \quad (41)$$

The factor 2 in this expression, which does not appear in the one-dimensional case, relation (30), comes from the fact that diffusion occurs here in two dimensions (on the surface of a sphere). As in the one-dimensional case, this relation suggests that τ_0 should be identified with the correlation time of the random variable θ , the correlation function being exponential.

Finally, since any function of Ω can be expanded in series of spherical harmonics, for practical purposes, it is sufficient to know the inter-correlation functions $C_{m,m'}^{l,l'}(t) = \langle Y_m^l(\Omega(t)) Y_{m'}^{l'*}(\Omega_0) \rangle$ to be able to calculate any correlation function. Using the above relations, it is easy to show that we have:

$$C_{m,m'}^{l,l'}(t) = C_{m,m}^{l,l'}(0) \delta_{m,m'} \times \exp \left[\frac{-l(l+1)}{2} \langle \theta^2 \rangle \left(1 - \exp \left(-\frac{t}{\tau_0} \right) \right) \right] \quad (42)$$

with

$$C_{m,m}^{l,l'}(0) = \int Y_m^l(\Omega_0) Y_{m'}^{l'*}(\Omega_0) p(\Omega_0) d\Omega_0. \quad (43)$$

We give below the values of the coefficients $C_{m,m}^{l,l'}(0)$ for the self-correlation functions of the spherical harmonics of order 0, 1 and 2, which are relevant to most spectroscopic

techniques:

$$C_{0,0}^{0,0}(0) = \frac{1}{4\pi} \quad (44)$$

$$C_{0,0}^{1,1}(0) = \frac{1}{4\pi} (1 + 2S_2) \quad (45)$$

$$C_{1,1}^{1,1}(0) = C_{-1,-1}^{1,1}(0) = \frac{1}{4\pi} (1 - S_2) \quad (46)$$

$$C_{0,0}^{2,2}(0) = \frac{1}{4\pi} \frac{7 + 10S_2 + 18S_4}{7} \quad (47)$$

$$C_{1,1}^{2,2}(0) = C_{-1,-1}^{2,2}(0) = \frac{1}{4\pi} \frac{7 + 5S_2 - 12S_4}{7} \quad (48)$$

$$C_{2,2}^{2,2}(0) = C_{-2,-2}^{2,2}(0) = \frac{1}{4\pi} \frac{7 - 10S_2 + 3S_4}{7}. \quad (49)$$

Finally, one must calculate the factor R_r to take into account the jump on the neighbouring site, here the south pole. As for the one-dimensional case, the periodic function $p(\Omega_0)$ given by equation (40) cannot be used in this calculation, because this function takes into account an infinite number of π jumps. It is not clear whether this periodic model can be transformed into a two-dimensional non-periodic model since the spherical harmonics are, in principle, not defined when l and m are real numbers. In other words, the sums over l and m cannot *a priori* be transformed into integrals, contrarily to Fourier series which can be transformed into Fourier integrals. However, the spherical harmonics can be expressed in terms of Legendre functions $P_l^m(\cos \theta)$, themselves related to hypergeometric functions [9], which can be defined for any real or complex value of l and m , so that there is some hope that the present one site rotational model on a sphere may be related to a two-dimensional (Gaussian?) model where angles θ and ϕ are allowed to vary between $-\infty$ and ∞ . This problem will not be explored here. In order to guess the form of the factor R_r for our problem, we shall assume that an argument similar to that used in the previous unidimensional model holds, and that we have, for the two-site model:

$$R_r = \exp \left(-\frac{\pi^2}{2\langle \theta^2 \rangle} \right) = \exp \left(-\frac{\pi^2}{4D_r\tau_0} \right). \quad (50)$$

With this expression, one finally obtains the following expression for the inter-correlation functions:

$$C_{m,m'}^{l,l'}(t) = C_{m,m}^{l,l'}(0) \delta_{m,m'} \times \exp \left[-\frac{l(l+1)}{2} \langle \theta^2 \rangle \left(1 - \exp \left(-\frac{t}{\tau_0} \right) + R_r \frac{t}{\tau_0} \right) \right]. \quad (51)$$

As for the one-dimensional case, the self-correlation functions are independent of the number of sites and only depend on the distance between neighbouring sites through the value of R_r . The expressions for the inter-correlation functions, which are expected to depend explicitly on the number and on the relative locations of the various sites, are more complex and will not be given here. As for the one-dimensional case, the present many-site, bi-dimensional model implies that the orientational motions

are essentially collective, requiring the introduction of the notion of orientational coherence length ξ . Further, the model also implies coupling with translational motions since it is impossible to rotate simultaneously two adjacent thick, impenetrable objects, with their centres of mass being fixed in the laboratory frame. Thus, collective rotational motions of anisotropic objects in dense media necessarily imply a coupling with translational motions.

Concerning the “long (angular) range” order parameters $S_{l,M}$ one must average over the two sites. Since the north and south poles can be exchanged by replacing (θ, ϕ) by $(\pi - \theta, \phi + \pi)$ and that $P_l[\cos(\pi - \theta)] = (-1)^l P_l(\cos \theta)$, it follows that all odd macroscopic order parameters are zero whereas all even ones are equal to the corresponding even local order parameters. For the same reasons as in the one-dimensional case, the coefficient R_r should be omitted in the expression of the macroscopic correlation functions with l even.

Of particular interest is the case $l = l' = 2$ relevant to light scattering, NMR and other spectroscopic techniques associated with second rank tensors. Since l is even, we have:

$$C_{m,m'}^{2,2}(t) = C_{m,m}^{2,2}(0)\delta_{m,m'} \times \exp \left[-3\langle\theta^2\rangle \left(1 - \exp \left(-\frac{t}{\tau_0} \right) \right) \right]. \quad (52a)$$

On the contrary, for the case $l = l' = 1$ relevant to dielectric or infrared absorption spectroscopies, the factor R_r should be kept. We have:

$$C_{m,m'}^{1,1}(t) = C_{m,m}^{1,1}(0)\delta_{m,m'} \times \exp \left[-\langle\theta^2\rangle \left(1 - \exp \left(-\frac{t}{\tau_0} \right) + R_r \frac{t}{\tau_0} \right) \right]. \quad (52b)$$

5 Typical shapes of spectroscopic correlation functions

The above calculations show that all correlation functions have the same functional form. The following two parameter (F and G) function $Y(t, \tau_0, F, G)$:

$$Y(t, \tau_0, F, G) = \exp \left[-F \left[1 - \exp \left(-\frac{t}{\tau_0} \right) + G \frac{t}{\tau_0} \right] \right] \quad (53)$$

allows the generation of all possible shapes as a function of the reduced variable $x = t/\tau_0$.

Let's discuss first the translational problem. In this case, two situations must be considered:

- (i) large F values mean large Q values (typical for neutron scattering) and/or large fluctuation amplitudes (compared to $1/Q$), whereas small F values are typical for light scattering, whatever the amplitude (because Q is generally very small in practice).

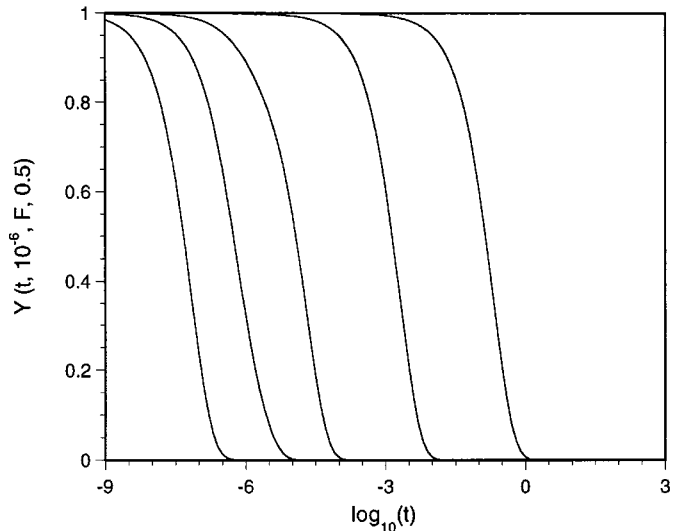


Fig. 1. Equation (53) for $\tau_0 = 10^{-6}$ s, $G = 0.5$ and $F = 10, 1, 0.1, 10^{-3}, 10^{-5}$ (from left to right).

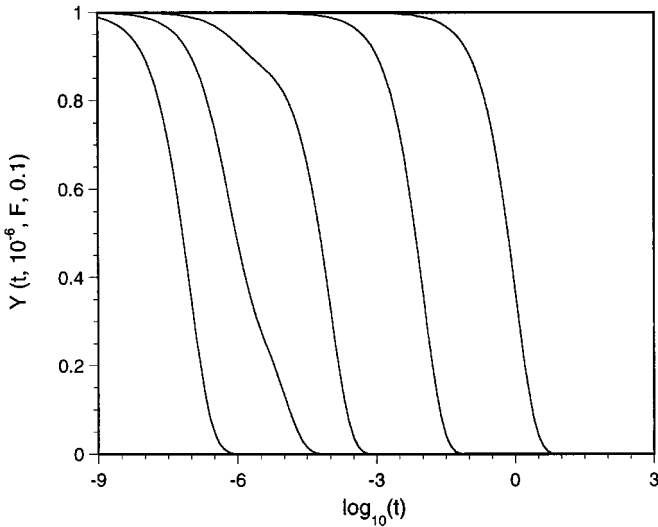
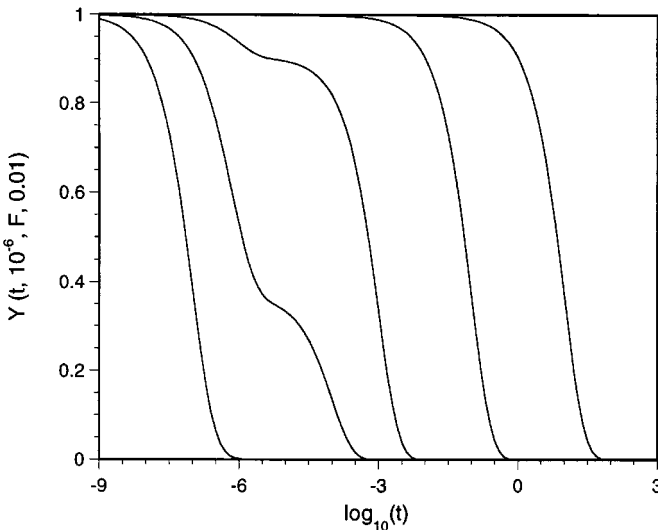
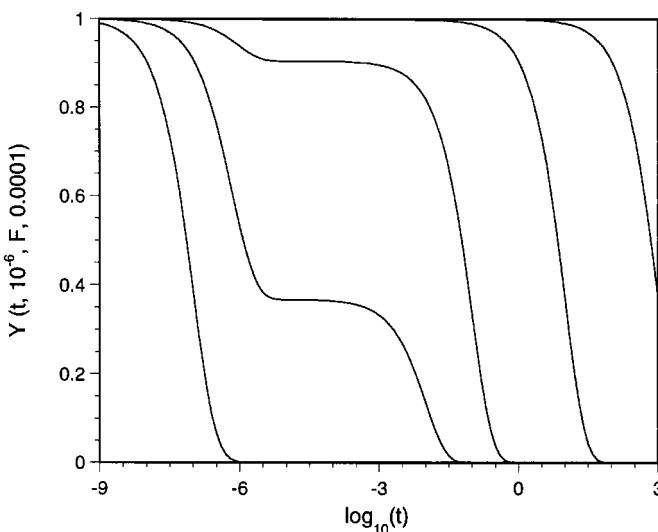
- (ii) values of G close to 1 means large (now compared to the lattice spacing a) fluctuation amplitudes, whereas $G \ll 1$ means small fluctuation amplitudes. Of particular interest is the situation around $R = 1/e$ (*i.e.* when fluctuation amplitudes are comparable to the lattice spacing) since one expects for the functions an important behaviour change when this value is crossed (for example by varying the temperature).

For the rotational problem, the situation is similar, except that there is no Q dependence so that:

- (i) large F values now means large angular fluctuations compared to about 1 radian, and
- (ii) large G values means that the fluctuation amplitudes are large compared to the angular distance α between sites. Note that this last situation is not relevant for the two site models when n or l are even, because $G = 0$.

Figures 1–4 show equation (53) for $G = 0.5, 0.1, 10^{-2}, 10^{-4}$ respectively, and several values of F between 0.5 and 10^{-5} , over twelve decades in time. To be closer to typical experimental values, we have somewhat arbitrarily chosen $\tau_0 = 10^{-6}$ s, so that t varies from 10^{-9} to 10^3 s. It is observed that all curves are qualitatively very close to typical functions that are observed in real experiments with complex systems, generally showing up a plateau when G is small. These functions correspond to either translational or rotational motions. For light scattering with VV polarisation, or unpolarised, the real spectra may be more complex, with two plateaux corresponding to a superimposition of translational and rotational motions [2, 3].

The overall shapes of these curves are never purely exponential. However, they can be represented by pure exponentials at long (compared to τ_0/G) times. It is interesting to note that in the range around $t = \tau_0$, curves for G between 0.5 and 0.1 can often be satisfactorily represented by a “stretched exponential” of the form $\exp[-(t/\tau_0)^\beta]$


 Fig. 2. *Idem* Figure 1 for $G = 0.1$.

 Fig. 3. *Idem* Figure 1 for $G = 10^{-2}$.

 Fig. 4. *Idem* Figure 1 for $G = 10^{-4}$.

(so-called KWW law) with $0.5 < \beta < 1$. Such function is extensively used in analysis of real data [2,3]. For very small values of G , case where a well-defined plateau exists, the full curve can often be approximated by a sum of two exponentials. In practice, it is sometimes observed that the terminal part of the correlation function (after the plateau) can also be represented by a “stretched” exponential. To explain this behaviour in the framework of the model, one can invoke some anisotropy of the motions. In other words, the amplitudes of the fluctuations are not the same in all directions of space, which means that some translational order exists in the system. An isotropic macroscopic sample must then be pictured as a “powder” of rather ordered domains. This implies that the lattice cannot be anymore considered as cubic, so that three different lattice distances along the three axes must be *a priori* considered. Obtaining the theoretical correlation function associated with the macroscopic sample requires a “powder” average on this function. Let’s assume for simplicity that the diffusion in the domains (and consequently the domains) have uniaxial symmetry, and let’s the two corresponding diffusion coefficients be D_1 (parallel to the symmetry axis) and D_2 (perpendicular to it). In this case, two lattice spacings a_1 and a_2 must be introduced. Let Θ be the angle between the symmetry axis and the momentum transfer vector Q . The diffusion coefficient along Q now depends on Θ . We have:

$$D_\theta = D_1 \cos^2 \Theta + D_2 \sin^2 \Theta. \quad (54)$$

The general form for the correlation functions in the presence of such anisotropic motions can be represented by (53) with F replaced by $F = F_1 \cos^2 \Theta + F_2 \sin^2 \Theta$, and averaged over Θ . Assuming that the powder is isotropic, and that the mean square fluctuations (or equivalently the diffusion coefficients) along directions 1 and 2 are proportional to the square of the corresponding lattice spacings a_1 and a_2 , so that G is independent of Θ , we obtain:

$$Y'(t, \tau_0, F_1, F_2, G) = \frac{1}{2} \int_0^\pi \exp \left[- (F_1 \cos^2 \Theta + F_2 \sin^2 \Theta) \right] \times \left[1 - \exp \left(-\frac{t}{\tau_0} \right) + G \frac{t}{\tau_0} \right] \sin \Theta d\Theta. \quad (55)$$

Such a function can be calculated, for example with the MATHEMATICA software. A closed form expression exists, involving the modified error function $\text{erfi}(z) = \text{erf}(iz)/i$. Figures 5 and 6 show results of the calculation as a function of F_2 varying between 1 and 0, for $F_1 = 1$ and $G = 1$ (no plateau) (Fig. 5) and $G = 10^{-5}$ (well-defined plateau) (Fig. 6). Decreasing values of F_2 from 1 to 0 means that the diffusion changes from isotropic to unidimensional. It is seen from Figure 5 (no plateau) that the effect of reducing the dimensionality of diffusion slows down the decrease of the function at long times. It turns out that all these curves can be satisfactorily represented by KWW laws with an exponent β varying from 0.9 (for $F_2 = 1$) to about 0.6 (for $F_2 \approx 0.2$). For F_2 between 0.2 and 0, the fit using KWW law is not so good. Figure 6 shows that the situation is more complex when a plateau

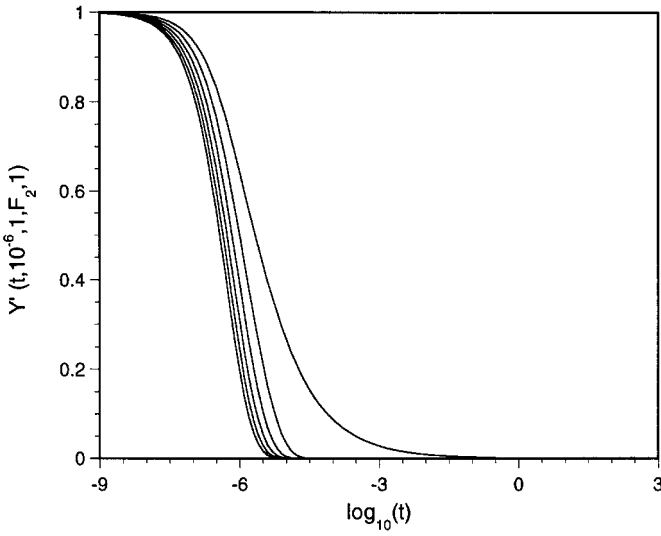


Fig. 5. Equation (55) for $\tau_0 = 10^{-6}$ s, $G = 1$, $F_1 = 1$ and $F_2 = 1, 0.8, 0.6, 0.4, 0.2, 0$ (from left to right).

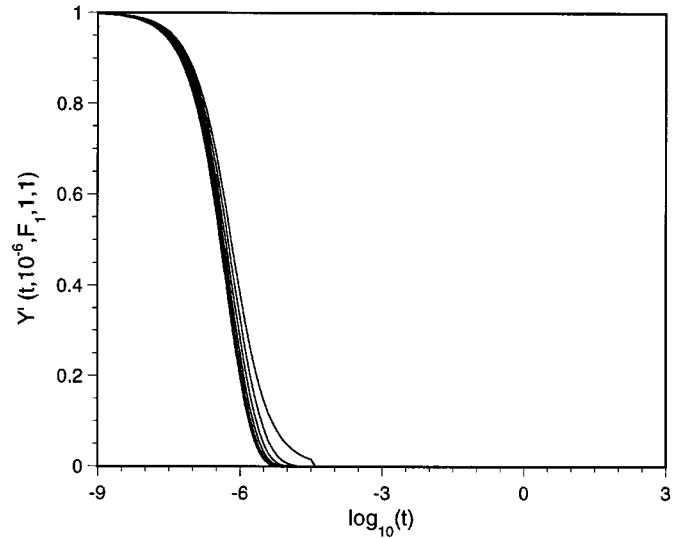


Fig. 7. Equation (55) for $\tau_0 = 10^{-6}$ s, $G = 1$, $F_2 = 1$ and $F_1 = 1, 0.8, 0.6, 0.4, 0.2, 0$ (from left to right).

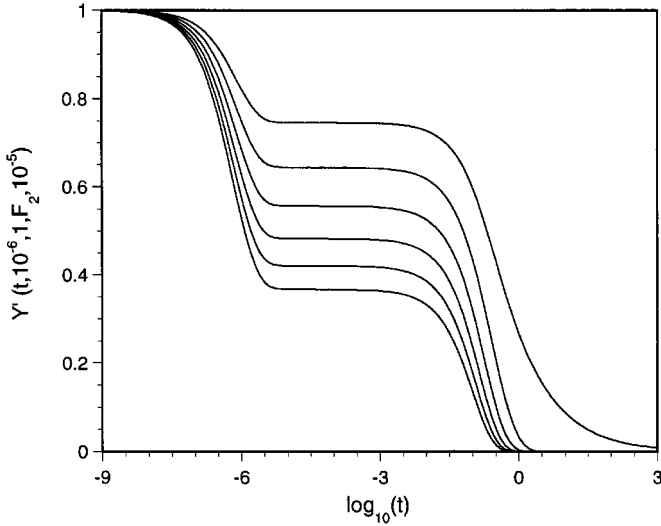


Fig. 6. *Idem* Figure 5 for $G = 10^{-5}$.

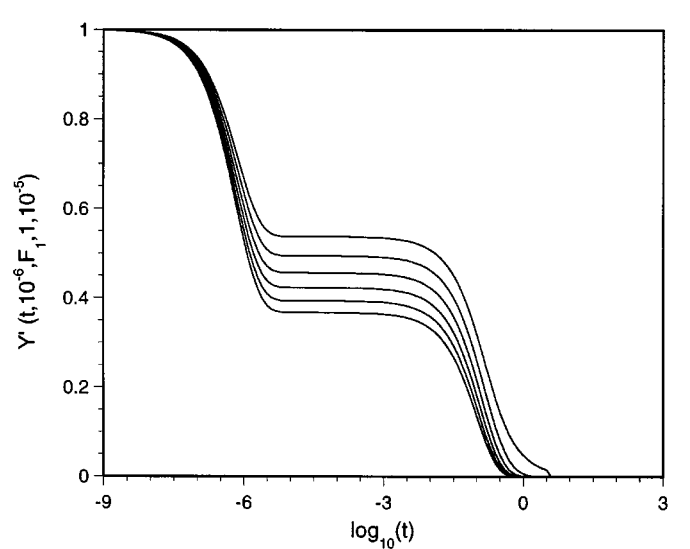


Fig. 8. *Idem* Figure 7 for $G = 10^{-5}$.

exists. When F_2 decreases, the level of the plateau increases and the terminal exponential stretches more and more, as found in the previous case. The terminal part of the function can also be represented satisfactorily by KWW laws with similar values of the exponent β . The case $F_2 = 1$ and F_1 varying from 1 to 0 has also been considered (diffusion changing from isotropic to planar). Effects are similar to the previous case, but variations are smaller, as expected (Figs. 7 and 8).

One of the main results of this model is to show that plateaux and stretched exponentials are ubiquitous in spectroscopic correlation functions, but the theoretical expressions are not the KWW law. Here, this law only appears as a good empirical representation of parts of these functions.

Finally, it must be said that the above discussion about anisotropic diffusion implicitly concerned translational motion. For anisotropic rotational motion in three

dimensions, the arguments are probably more complex, but since the rotational diffusion coefficients around three perpendicular axes attached to a non-spherical object, form a second rank tensor, it is likely that the net effects of anisotropy on the shape of rotational correlation functions are very similar to those predicted for translation.

Last but not least, it may be useful to explain why a value of $t_{\min} = 10^{-9}$ s rather than 0 was chosen for the minimum time in the figures. The reason is that all the correlation functions predicted by the model are pure exponentials at sufficiently small times and this is incompatible with the fact that they must have a horizontal slope at $t = 0$ in order to fulfil the stationary condition of random processes. This is in agreement with the general statement that a random motion can be considered as diffusive only at sufficiently large times. In real systems composed of polyatomic objects, internal degrees of freedom

such as bond vibrations, librations ... exist. Such motions are usually described in terms of more or less damped oscillations whose characteristic times are typically in the range 10^{-13} – 10^{-11} s (“infrared” and “far-infrared” time scales). Further, if the objects are assumed to be small with mass m and/or inertial momentum I , the behaviour is ballistic (correlation functions are then parabolic functions of time) for times shorter than $(\hbar Q^2/2m)^{-1}$ for translational motion or $(\hbar/2I)^{-1}$ for rotational motion. Typical values of these latter times for small molecules are in the same range as before. In other words, correlation functions associated with these short time motions exhibit oscillatory and/or parabolic behaviour until times about five to ten times these values, that is typically 10^{-12} – 10^{-10} s. In order to introduce these short time motions in the description, one must simply multiply the corresponding correlation function with that of the present model (assuming that the two kinds of motions are decoupled). In this way, it would be possible to reproduce experimental data until time as short as, say 10^{-13} s. An example of decomposition of experimental correlation functions into short time (molecular) motions and long time (diffusive) motions is given in [10] in the case of glass former ortho-terphenyl (OTP).

6 Conclusion

To summarise, a simple phenomenological model of diffusion on a lattice based on generalised diffusion equations and Gaussian statistics has been presented. It allows to generate spectroscopic time correlation functions whose general shapes are qualitatively very similar to the large variety of shapes (with plateaux and stretched exponentials) that are observed in the field of complex fluids (supercooled liquids, glass transition, colloids, gels ...). As such, this model is not a theory since it only provides (rather simple) formulae which allow reduction of the spectroscopic data to the values of a few parameters, mainly a , $\langle u_x^2 \rangle$ and τ_0 for translation and α , $\langle \varphi^2 \rangle$ or $\langle \theta^2 \rangle$ and τ_0 for rotation, that is a linear or angular distance, a mean square fluctuation amplitude and a correlation time. The aim of any further theoretical work, out of the scope of the model, would then be to explain the actual values of these parameters in terms of more microscopic quantities.

A preliminary version of this model has been used in [10] to analyse a number of spectroscopic data obtained with liquids in their normal and supercooled phases. A microscopic model has also been proposed in [10] to explain the values of the obtained parameters in terms of molecular quantities. As mentioned in the introduction, the present improved version of the model is successfully applied to simulate fluorine NMR line shapes of polytetrafluoroethylene [8]. It is hoped that all these results will incite at using this model to analyse data in similar systems, in order to test its validity and range of applicability.

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