Orientational relaxation in a dispersive dynamic medium: Generalization of the Kubo-Ivanov-Anderson jump-diffusion model to include fractional environmental dynamics

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(Received 12 October 2007; published 25 March 2008)

The Ivanov-Anderson model (and an earlier treatment by Kubo) envisages a decay of the orientational correlation by random but large amplitude molecular jumps, as opposed to infinitesimal small jumps assumed in Brownian diffusion. Recent computer simulation studies on water and viscous liquids have shown that large amplitude motions may indeed be more of a rule than exception. Existing theoretical studies on jump diffusion mostly assume an exponential (Poissonian) waiting time distribution for jumps, thereby again leading to an exponential decay. Here we extend the existing formalism of Ivanov and Anderson to include an algebraic waiting time distribution between two jumps. As a result, the first ($\ell=1$) and second ($\ell=2$) rank orientational time correlation functions show the same long time power law, but their short time decay behavior is quite different. The predicted Cole-Cole plot of dielectric relaxation reproduces various features of non-Debye behavior observed experimentally. We also developed a theory where both unrestricted small jumps and large angular jumps coexist simultaneously. The small jumps are shown to have a large effect on the long time decay, particularly in mitigating the effects of algebraic waiting time distribution, and in giving rise to an exponential-like decay, with a time constant, surprisingly, less than the time constant that arises from small amplitude decay alone.

DOI: 10.1103/PhysRevE.77.031505 PACS number(s): 64.70.P−, 05.40.Jc, 66.20.−d, 66.10.−x

I. INTRODUCTION

Because orientational relaxation of molecules is relatively easily accessed by a variety of experimental techniques (NMR, IR, fluorescence depolarization, optical Kerr effect, to name a few) [1–6], many theoretical models and microscopic studies have addressed various aspects of molecular rotation in dense liquids and glasses [6–11]. The most celebrated of these studies is the one carried out by Debye many years ago, in terms of a simple rotational diffusion equation [3,4]. The theory assumes that rotational correlation in liquids decay by small amplitude rotational Brownian motion, with a rotational diffusion coefficient, D_R. The theory makes the simple prediction that the decay of the correlation functions of all ranks of Legendre function is exponential and is given by

$$C_\ell(t) \equiv \langle P_\ell[\cos\theta(t)]\rangle = \exp[-\ell(\ell+1)D_R t], \qquad (1)$$

where $\theta(t)$ is the azimuthal angle at time t. The Debye model of rotational diffusion has played a pivotal role in most of the discussions on rotational diffusion in the condensed phases. Many theoretical studies have attempted to improve upon the Debye model, using for example, a generalized Langevin equation approach which ultimately leads to a time or frequency dependent diffusion coefficient. But all these approaches use the general assumption of infinitesimal rotation of Brownian motion.

Recent experimental and theoretical studies on viscous liquids and surprisingly, liquid water, have shown a marked departure from the classical Debye behavior [11–17]. In these cases, rotational diffusion is found to occur by large amplitude jumps. In liquid water, the nonexponentiality, at room temperature, is weak but relaxation becomes progressively nonexponential at low temperatures [17]. The rotational relaxation (and also translational diffusion) seems to occur primarily through rare but large amplitude jumps. A quantitative understanding of the origin of such jumps has remained a subject of great interest, though largely unsolved.

A model of rotational jump diffusion was actually proposed in the past, most notably by Kubo [18,19] and Ivanov [7]. In Kubo's model of jump diffusion, the rotator was restricted to jump in a circle, that is restricted to two dimension. [See Fig. 1(a).] Ivanov's model was more general where jumps were isotropically distributed in three dimension. [See Fig. 1(b).] Ivanov's model has found increasing use in describing experimental results. In this model, the waiting time between jumps obey an exponential distribution and as a result, the decay is single exponential, with the first and second rank correlation functions which are given by

$$C_1(t) = \exp[-(1-\cos\Delta)t/\tau], \qquad (2)$$

$$C_2(t) = \exp\left[-\frac{3}{2}(1-\cos^2\Delta)t/\tau\right], \qquad (3)$$

where Δ is the constant amplitude of jump and τ is the average time interval between any two jumps. The probability that there are n jumps in a time interval t is assumed to be given by Poisson distribution

$$P(n,t) = \frac{(t/\tau)^n}{n!}\exp(-t/\tau). \qquad (4)$$

For small jumps, Eqs. (2) and (3) go over to the Debye behavior, with $\tau_1/\tau_2=3$, where τ_1 and τ_2 are the decay time

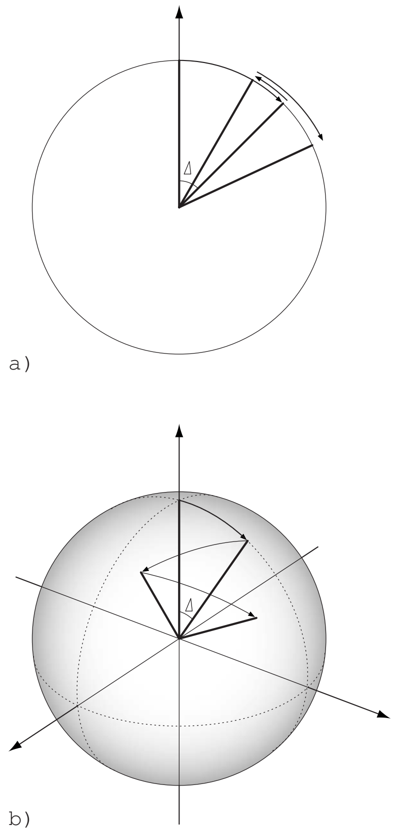

FIG. 1. (a) Schematic illustration of the Kubo model. Jumps are restricted on a circle. (b) Schematic illustration of the Ivanov-Anderson model. Jumps are isotropically distributed on a sphere.

constants of $C_1(t)$ and $C_2(t)$, respectively. However, the relaxation pattern is different for long jumps. The difference is most acute when the jump angle Δ is close to π. A jump by $\Delta \sim \pi$ relaxes $C_1(t)$ but not $C_2(t)$. Therefore, τ_1/τ_2 becomes much smaller than three and approaches zero. Interestingly, for intermediate values of jump length parameter ($\Delta \approx \pi/2$), the ratio of the two time constants approach unity. In the original models, reorientations were assumed to be isotropic. Recently, they have been extended to include anisotropic molecular reorientations [20,21]. In a notable development, recently Déjardin and Jadzyn have extended the Debye rotational diffusion model to a fractional rotational diffusion case to treat events that are nonlocal in time due to the existence of extensive memory effect [22]. Under fractional rotational Brownian motion, the decay of the relevant orientationalcorrelation functions is no longer exponential (or, sum of a few exponential terms). It was shown that the decay can be described as a combination of Mittag-Leffler temporal pattern, behaving like a stretched exponential at short times and an inverse power law in the long time limit. Fractional equations provide an anomalously slow decay at long times, often referred to as subdiffusive regime. As pointed out by many, the fractional Fokker-Planck or Smoluchowski equation is a natural generalization of normal diffusion to disordered systems with scale free memory effects [23–26]. Déjardin and Jadzyn obtained analytic expressions of the frequency (ω) dependent electric birefringence spectrum, $\chi(\omega)$. They plotted the Cole-Cole diagram for various cases to demonstrate the effects of fractional diffusion. Fractional diffusion gives rise to markedly non-Debye Cole-Cole plot which now varies from Cole-Davidson skewed arc behavior to Cole-Cole depressed circle. The treatment of Déjardin and Jadzyn is still based on rotational diffusion equation, and does not contain the effects of finite jumps. However, as already discussed, in many complex systems, rotational relaxation occurs by large amplitude jumps. For example, in liquid water, it has recently been discussed how much of the relaxation of orientational correlation occurs by jumps which are of the order of 60° [17]. Such motions cannot be treated as a Brownian diffusion. In addition, in many complex systems, the waiting time distribution between jumps may not be approximated by Poissonian distribution [23–28]. In the present work we have extended the theory of Kubo, Ivanov, and Anderson to treat jump diffusion with an algebraic waiting time distribution. Since the treatments of Kubo are different from that of Ivanov and Anderson, separate solutions have been obtained. As is usually the case for relaxation with fractional diffusion, an analytical solution of the orientational time correlation function has been obtained only in the frequency domain. However, we have been able to obtain asymptotic solution in all the cases. The decay of the correlation of the first and the second rank harmonic follow power law. This signifies a breakdown of Debye behavior in dispersive medium. We have also developed a theory where the large amplitude jumps simultaneously coexist with small amplitude jumps. Interestingly, the exponential kinetics is recovered even under the small fraction of small amplitude jumps but the decay is accelerated by large amplitude jumps.

II. GENERALIZATION OF JUMP MODEL

A. Kubo model

We consider a two-dimensional rotator which makes the series of jumps. The model was originally proposed by Kubo for rotational relaxation of spin under the presence of pulsed magnetic fields [18,19]. The angle changes by the jump with the amount Δ_n at time t_n. According to Kubo, we define

$$f^{(\ell)}(t) = \left\langle \sum_{n=0}^{\infty} \exp\left(i\,\ell \sum_{m=0}^{n} \Delta_m \right) P(n,t) \right\rangle, \tag{5}$$

where $P(n,t)$ represents the probability of having n jumps up to time t and $\langle \cdots \rangle$ denotes the ensemble average of scattering angles. The correlation functions are obtained by

$$C_\ell(t) = \mathrm{Re}[f^{(\ell)}(t)], \tag{6}$$

where $\ell = 1, 2$. It should be noticed here that the ℓth rank correlation function is defined in terms of $\cos \ell\,\theta(t)$ for the two-dimensional rotator. Even when the second rank correlation function is defined in terms of the Legendre function of the three-dimensional isotropic rotator, the right-hand side of Eq. (6) is equal to $[C_\ell(t) - C_\ell(\infty)]/[C_\ell(0) - C_\ell(\infty)]$, which still expresses the decay of correlation function. We calculate $\mathrm{Re}[f^{(\ell)}]$ and represents it by $C_\ell(t)$ of the two-dimensional rotator for the Kubo model. The waiting time distribution of each time interval $\tau_n = t_n - t_{n-1}$, is assumed to be statistically independent and it is represented by $\psi(t)$. We also introduce

$\varphi(t)=\int_t^\infty dt_1\psi(t_1)$ as a probability that a molecular rotor will not make a jump for the time interval between 0 and t. The probability of having n jumps up to time t is given after the Laplace transformation, $\hat{P}(n,s)=\int_0^\infty \exp(-st)P(n,t)$, as [29]

$$\hat{P}(n,s)=\hat{\varphi}(s)\hat{\psi}^n(s), \tag{7}$$

where $\hat{\varphi}(s)=[1-\hat{\psi}(s)]/s$. The amount of each jump is also assumed to be statistically independent,

$$\left\langle \exp\left(i\sum_n \Delta_n\right)\right\rangle = \exp(in\Delta). \tag{8}$$

Then, we have

$$C_\ell(t)=\mathrm{Re}\left[\sum_{n=0}^{\infty}\exp(i\,\ell\,n\Delta)P(n,t)\right]. \tag{9}$$

By substituting Eq. (7) into Eq. (9), the Laplace transform of it becomes

$$\hat{C}_\ell(s)=\frac{1-\hat{\psi}(s)}{s}\,\mathrm{Re}\left[\frac{1}{1-\exp(i\,\ell\,\Delta)\hat{\psi}(s)}\right]. \tag{10}$$

The above equation holds for an arbitrary waiting time distribution function and an arbitrary jump amplitude. When the waiting time distribution decays exponentially with the characteristic time of the jump interval, τ, the well-known result for the Poisson noise is recovered, i.e.,

$$\begin{aligned} C_\ell(t) &= \exp\{-(t/\tau)[1-\cos(\ell\Delta)]\}\cos[(t/\tau)\sin(\ell\Delta)] \\ &= \exp[-t(2/\tau)\sin^2(\ell\Delta/2)]\cos[(t/\tau)\sin(\ell\Delta)]. \end{aligned} \tag{11}$$

Equation (10) is the generalization of the Kubo model to the case of an arbitrary waiting time distribution. Equation (11) was given by Kubo for the Poissonian waiting time distribution for $\ell=1$ [18,19]. In two-dimensional rotational diffusion, Eq. (1) is replaced by $\exp(-\ell^2 D_R t)$ [30] since the correlation function is defined by $\langle\cos[\ell\theta(t)]\rangle$. Equation (11) gives $\tau_1/\tau_2=4$ in the limit of a small amplitude jump, which is consistent with the result of a conventional two-dimensional rotator. Rotational motion of liquid crystal molecules about their long axis is often analyzed by a rotational jump diffusion model similar to the Kubo model, where a circular random walk is performed among N sites equally spaced on the periphery of a circle [31]. The relaxation rates are obtained as $(2/\tau)\sin^2(\ell\Delta/2)$, which corresponds to those of Eq. (11) with $\Delta=2\pi/N$.

B. Ivanov-Anderson model

For dielectric relaxation, however, the Ivanov-Anderson model is more popular to describe the random scattering of angle [7,8]. The Ivanov-Anderson model is, however, similar in spirit to the Kubo model. The Ivanov-Anderson model assumes for simplicity an isotropic reorientation by random angular jumps. If we denote the angular change by nth jump by Δ_n and assume that it is statistically independent as in the Kubo model, we have

$$L_1=\cos\Delta=\langle\cos\Delta_n\rangle, \tag{12}$$

$$L_2=(3\cos^2\Delta-1)/2=\langle[(3\cos^2\Delta_n-1)]/2\rangle. \tag{13}$$

It is known that the correlation function is expressed in the form similar to Eq. (9) as

$$C_\ell(t)=\sum_{n=0}^{\infty}L_\ell^n P(n,t). \tag{14}$$

By substituting the Laplace transform of Eq. (7), the Laplace transform of the correlation function, Eq. (14), becomes

$$\hat{C}_\ell(s)=\frac{1-\hat{\psi}(s)}{s}\frac{1}{1-L_\ell\hat{\psi}(s)}. \tag{15}$$

Equation (15) is valid for an arbitrary waiting time distribution. When the waiting time distribution between jumps decays exponentially with the characteristic time τ, Eq. (15) recovers the well known results of Eqs. (2) and (3). Here, the Ivanov-Anderson model is generalized to the case of an arbitrary waiting time distribution.

III. ALGEBRAIC WAITING TIME DISTRIBUTION OF JUMP

Now, we study the influence of the power law waiting time distribution $\psi(t)\sim 1/t^{\alpha+1}$ on the correlation functions. A well-known and popular waiting time distribution function which is normalizable is given by

$$\psi(t)=\frac{\alpha\gamma(\alpha+1,\gamma_r t)}{\gamma_r^\alpha t^{\alpha+1}}, \tag{16}$$

where $\gamma(z,p)\equiv\int_0^p e^{-t}t^{z-1}dt$ for ($\mathrm{Re}z>0$) is the incomplete Gamma function [32]. Equation (16) can be derived from a model in which the hopping rate depends on a parameter exponentially (for example activation energy) and the value of this parameter has an exponential distribution [33]. γ_r is a parameter characterizing the hopping frequency. The waiting time distribution of Eq. (16) can be written approximately in a more transparent form,

$$\psi(t)\approx\frac{\alpha\Gamma(\alpha+1)}{\gamma_r^\alpha t^{\alpha+1}}, \tag{17}$$

where $\Gamma(z)$ is the Gamma function [32]. The Laplace transform of the waiting time distribution is obtained as

$$\hat{\psi}(s)=1-{}_2F_1[1,\alpha,\alpha+1,-\gamma_r/s]. \tag{18}$$

Equation (18) is useful because the following property of the hypergeometric function is known [32],

$${}_2F_1[1,\alpha,\alpha+1,-\gamma_r/s]\approx\frac{\pi\alpha}{\sin\pi\alpha}\left(\frac{s}{\gamma_r}\right)^\alpha \quad \frac{s}{\gamma_r}<1. \tag{19}$$

By substituting Eq. (18) into Eq. (10), the extended Kubo model leads to,

$$\hat{C}_\ell(s)\approx\frac{{}_2F_1[1,\alpha,\alpha+1,-\gamma_r/s]}{s}\,\mathrm{Re}\left(\frac{1}{1-\exp(i\,\ell\,\Delta)}\right) \tag{20}$$

$$\approx \frac{\pi\alpha}{\sin \pi\alpha}\left[\frac{1-\cos(\ell\Delta)}{[1-\cos(\ell\Delta)]^2+\sin^2(\ell\Delta)}\right]\frac{1}{s^{1-\alpha}\gamma_r^\alpha}. \tag{21}$$

By performing the inverse Laplace transformation, we find the asymptotic time dependence for the extended Kubo model,

$$C_\ell(t) \approx \frac{\pi\alpha}{\sin \pi\alpha}\left[\frac{1-\cos(\ell\Delta)}{(1-\cos(\ell\Delta))^2+\sin^2(\ell\Delta)}\right]\frac{1}{\Gamma(1-\alpha)(\gamma_r t)^\alpha}. \tag{22}$$

We can obtain the solution of the extended Ivanov-Anderson model in a similar fashion. By substituting Eq. (19) into Eq. (18), Eq. (15) becomes

$$\hat{C}_\ell(s) = \frac{1}{L_\ell}\frac{s^{\alpha-1}}{s^\alpha + \dfrac{1-L_\ell}{L_\ell}\dfrac{\sin \pi\alpha}{\pi\alpha}\gamma_r^\alpha}. \tag{23}$$

In the long time limit,

$$(\gamma_r t)^\alpha > \frac{L_\ell}{1-L_\ell}\frac{\pi\alpha}{\sin(\pi\alpha)}, \tag{24}$$

we find, in the small s limit, the following asymptotic result:

$$\hat{C}_\ell(s) \approx \frac{\pi\alpha}{\sin \pi\alpha}\frac{1}{s^{1-\alpha}\gamma_r^\alpha}\frac{1}{1-L_\ell}. \tag{25}$$

By performing the inverse Laplace transformation, we find the asymptotic time dependence of the extended Ivanov-Anderson model as

$$C_\ell(t) \approx \frac{\pi\alpha}{\sin \pi\alpha}\frac{1}{(1-L_\ell)}\frac{1}{\Gamma(1-\alpha)(\gamma_r t)^\alpha}. \tag{26}$$

Both Kubo and Ivanov-Anderson models predict exactly the same time dependence of the correlation functions, which is described by the algebraic time dependence with the exponent α. As we can see from Eq. (24), the above asymptotic dependence is hardly attained when $L_\ell \approx 1$. This case can be examined more rigorously. By the inverse Laplace transformation of Eq. (23), we find the correlation functions expressed in terms of Mittag-Leffler function,

$$C_\ell(t) = E_\alpha\left[-\frac{1-L_\ell}{L_\ell}\frac{\sin \pi\alpha}{\pi\alpha}(\gamma_r t)^\alpha\right], \tag{27}$$

where the Mittag-Leffler function is defined by, $E_\alpha(z) = \Sigma_0^\infty z^k/\Gamma(\alpha k+1)$ and $L_\ell \approx 1$ is introduced. The Mittag-Leffler function is approximated by the stretched exponential function,

$$C_\ell(t) \approx \exp\left[-\frac{1-L_\ell}{\Gamma(1+\alpha)L_\ell}\frac{\sin(\pi\alpha)}{\pi\alpha}(\gamma_r t)^\alpha\right], \tag{28}$$

except the final component showing algebraic decay of Eq. (26) which appears at very long times when $L_\ell \approx 1$. $L_\ell \approx 1$ occurs when $\Delta \simeq 0$ for both $\ell=1$ and $\ell=2$. When $\Delta \simeq \pi$, $L_2 \approx 1$ but $L_1 < 1$. Therefore, when Δ is small, both $C_1(t)$ and $C_2(t)$ mainly decay according to stretched exponential law. As Δ is increased into the range, $0 \ll \Delta \ll \pi$, both $C_1(t)$ and $C_2(t)$ exhibit algebraic decay of Eq. (26). When Δ is closed to π, $C_2(t)$ mainly decays by the stretched exponential law and the final small components of both $C_1(t)$ and $C_2(t)$ are described by algebraic decay.

By the known identity of the Mittag-Leffler function for $\alpha=0.5$, Eq. (27) can be expressed as

$$C_\ell(t) = \exp\left[\left(\frac{2(1-L_\ell)}{\pi L_\ell}\right)^2\gamma_r t\right]\operatorname{erfc}\left[\frac{2(1-L_\ell)}{\pi L_\ell}\sqrt{\gamma_r t}\right], \tag{29}$$

for $\alpha=1/2$, where the complementary error function is defined by $\operatorname{erfc}(z)=(2/\sqrt{\pi})\int_z^\infty \exp(-y^2)dy$ [32]. We compare these analytical results with the numerical Laplace inversion of the exact results [Eqs. (10) and (15) with Eq. (18)] in Sec. V.

IV. SIMULTANEOUS COEXISTENCE OF LARGE AND SMALL AMPLITUDE JUMPS

In many situations, jumps with large amplitudes are rare and they are superimposed on the small amplitude jumps which occur frequently. We denote the waiting time distribution of large amplitude jump by, $\psi_a(t)$ and that of small amplitude jump by $\psi_b(t)$. Theoretically, they are related with each other. By denoting the waiting time distribution of large amplitude jump in the absence of small amplitude jump by, $\psi_a^{(0)}(t)$, and that of small amplitude jump in the absence of large amplitude jump by, $\psi_b^{(0)}(t)$, the waiting time distribution under the presence of both types of jumps is expressed as [34]

$$\psi_a(t) = \psi_a^{(0)}(t)\left(1-\int_0^t dt\psi_b^{(0)}(t)\right), \tag{30}$$

$$\psi_b(t) = \psi_b^{(0)}(t)\left(1-\int_0^t dt\psi_a^{(0)}(t)\right), \tag{31}$$

since the large amplitude jump occurs before the occurrence of small amplitude jump and vice versa.

First we consider the case of the Kubo model. The Laplace transform of the correlation function is generalized from Eq. (10) as

$$\hat{C}_\ell(s) = \frac{1-\hat{\psi}_a(s)-\hat{\psi}_b(s)}{s}\operatorname{Re}\left[\sum_{n=0}^\infty(\exp(i\ell\Delta_a)\hat{\psi}_a(s) + \exp(i\ell\Delta_b)\hat{\psi}_b(s))^n\right] \tag{32}$$

$$= \frac{1-\hat{\psi}_a(s)-\hat{\psi}_b(s)}{s}\times\operatorname{Re}\left[\frac{1}{1-\exp(i\ell\Delta_a)\hat{\psi}_a(s)-\exp(i\ell\Delta_b)\hat{\psi}_b(s)}\right], \tag{33}$$

where we assume that each jump belonging to either large or small amplitude is statistically independent and the average is denoted by, $\exp(i\ell\Delta_j)$, where $j=a,b$.

For the Ivanov-Anderson model, the Laplace transform of the correlation function is generalized from Eq. (15) as

$$\hat{C}_\ell(s) = \frac{1-\hat{\psi}_a(s)-\hat{\psi}_b(s)}{s}\left[\sum_{n=0}^{\infty}(L_\ell^{(a)}\hat{\psi}_a(s)+L_\ell^{(b)}\hat{\psi}_b(s))^n\right] \tag{34}$$

$$= \frac{1-\hat{\psi}_a(s)-\hat{\psi}_b(s)}{s}\left[\frac{1}{1-L_\ell^{(a)}\hat{\psi}_a(s)-L_\ell^{(b)}\hat{\psi}_b(s)}\right], \tag{35}$$

where we again assume that each jump belonging to either large or small amplitude is statistically independent and the average is denoted by

$$L_1^{(j)} = \cos\Delta_j, \tag{36}$$

$$L_2^{(j)} = (3\cos^2\Delta_j - 1)/2, \tag{37}$$

where $j=a,b$.

When both amplitude jumps occur according to the exponential waiting time distribution,

$$\psi_a(t) = \frac{1}{\tau_a}\exp(-t/\tau_a - t/\tau_b) \tag{38}$$

$$\psi_b(t) = \frac{1}{\tau_b}\exp(-t/\tau_a - t/\tau_b), \tag{39}$$

Kubo's result of Eq. (11) is generalized to

$$C_\ell(t) = \exp\left[-\sum_{j=a,b}(t/\tau_j)(1-\cos(\ell\Delta_j))\right] \times\cos\left[\sum_{j=a,b}(t/\tau_j)\sin(\ell\Delta_j)\right]. \tag{40}$$

While, Ivanov-Anderson's results, Eqs. (2) and (3) are generalized to

$$C_1(t) = \exp\left[-\sum_{j=a,b}(1-\cos\Delta_j)(t/\tau_j)\right], \tag{41}$$

$$C_2(t) = \exp\left[-\sum_{j=a,b}\frac{3}{2}(1-\cos^2\Delta_j)(t/\tau_j)\right], \tag{42}$$

as expected from the Markovian kinetics.

When the large amplitude jump obeys the algebraic waiting time distribution,

$$\psi_a^{(0)}(t) = \frac{\alpha\gamma(\alpha+1,t/\tau_a)}{t(t/\tau_a)^\alpha}, \tag{43}$$

and the small amplitude jump obeys the exponential kinetics,

$$\psi_b^{(0)}(t) = \frac{1}{\tau_b}\exp(-t/\tau_b), \tag{44}$$

the waiting time distributions under the presence of both types of jumps are given by

$$\psi_a(t) = \psi_a^{(0)}(t)\exp(-t/\tau_b), \tag{45}$$

$$\psi_b(t) = \frac{1}{\tau_b}\exp(-t/\tau_b)\int_t^\infty dt_1\psi_a^{(0)}(t_1). \tag{46}$$

The Laplace transform is obtained as

$$\hat{\psi}_a(s) = \hat{\psi}_a^{(0)}(s+1/\tau_b), \tag{47}$$

$$\hat{\psi}_b(s) = \frac{1/\tau_b}{s+1/\tau_b}[1-\hat{\psi}_a^{(0)}(s+1/\tau_b)], \tag{48}$$

where $\hat{\psi}_a^{(0)}(z)$ is expressed as

$$\hat{\psi}_a^{(0)}(z) = 1 - {}_2F_1[1,\alpha,\alpha+1,-1/(\tau_a z)]. \tag{49}$$

By substituting Eqs. (47) and (48) into Eqs. (33) and (35), the exact solutions are obtained in the Laplace domain. However, the inverse Laplace transform is too complicated for analytical calculation and will be performed numerically.

Since we are interested in the case where the characteristic time of small amplitude jump is much shorter than that of large amplitude jump, the approximate solutions can be obtained by taking the limit, ${}_2F_1\{1,\alpha,\alpha+1,-1/[\tau_a(s+1/\tau_b)]\} \approx {}_2F_1[1,\alpha,\alpha+1,-\tau_b/\tau_a]$, which leads to $\hat{\psi}_a^{(0)}(s+1/\tau_b) \approx \hat{\psi}_a^{(0)}(1/\tau_b)$. In the approximation, the s dependence in the Laplace transform of waiting time distribution is dropped out. The s dependence can be ignored when we are interested in the time scale larger than that of small amplitude jumps. The quantity is just the time integration over waiting time distribution of large amplitude jumps and represents the probability of occurrence of large amplitude jumps, i.e., the escape probability from small amplitude jumps by a large amplitude jump. By introducing the approximation, we find that the correlation functions decay exponentially,

$$C_1(t) = \exp\left[-(t/\tau_b)\left(1-\frac{\cos(\Delta_b)\hat{\psi}_b(0)}{1-\cos(\Delta_a)\hat{\psi}_a(0)}\right)\right], \tag{50}$$

$$C_2(t) = \exp\left[-3(t/\tau_b)\frac{1-\cos(2\Delta_a)\hat{\psi}_a(0)-\cos(2\Delta_b)\hat{\psi}_b(0)}{3+\hat{\psi}_b(0)-3\cos(2\Delta_a)\hat{\psi}_a(0)}\right]. \tag{51}$$

When Δ_a is close to $\Delta_b \simeq 0$, we recover Eqs. (2) and (3) with $\Delta=\Delta_b$ and $\tau=\tau_b$ by substituting $\hat{\psi}_b(0)\approx 1$ and $\hat{\psi}_a(0)\approx 0$ into the above expressions. The exponential kinetics of Eqs. (50) and (51) even under the algebraic waiting time distribution of the rare but large amplitude jumps is the important result of this article.

V. NUMERICAL RESULTS

Figure 2 shows the relaxation of correlations of Ivanov-Anderson model for $\Delta=60°$. For this value of Δ, $C_2(t)$ decays faster than $C_1(t)$ for any values of α. Compared to the decay by normal diffusion, decay of both $C_2(t)$ and $C_1(t)$ is slowed down when the waiting time distribution has an al-

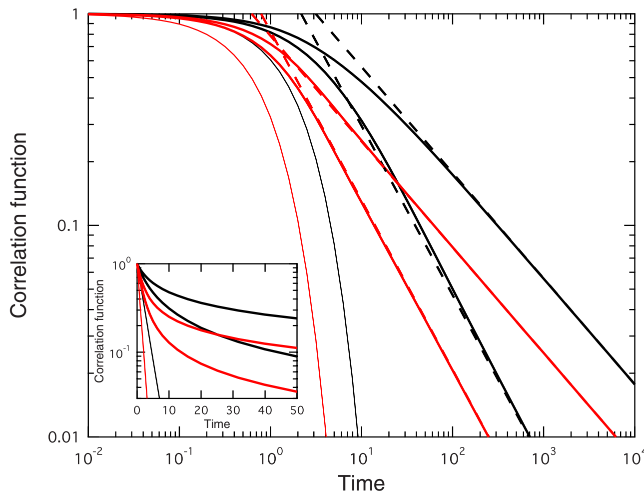

FIG. 2. (Color online) Correlation functions of the Ivanov-Anderson model with $\Delta = 60°$ against dimensionless time, $\gamma_r t$. Red lines represent $C_2(t)$ and black lines represent $C_1(t)$. $\alpha = 0.5$ and 0.8 from top to bottom. Thin lines indicate the results of the normal diffusion. Dashed lines represent asymptotic algebraic time dependence of Eq. (26). The log linear plot is shown in the inset.

gebraic time dependence. At long times, all decay curves are well represented by the algebraic decay of Eq. (26) with the exponent α. The long time tail in the decay of correlation originates from the algebraic time dependence of the waiting time distribution. The exponent is the same for both $\ell = 2$ and $\ell = 1$ components.

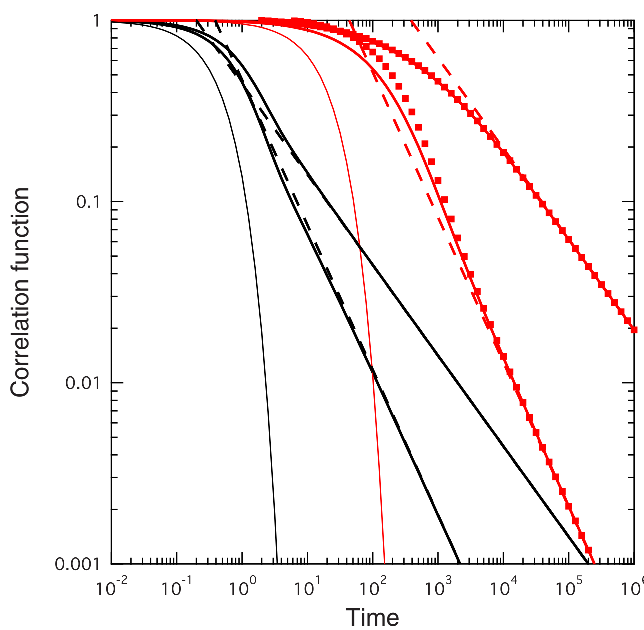

FIG. 3. (Color online) Correlation functions of the Ivanov-Anderson model with $\Delta = 170°$ against dimensionless time, $\gamma_r t$. Red lines represent $C_2(t)$ and black lines represent $C_1(t)$. $\alpha = 0.5$ and 0.8 from top to bottom. Thin lines indicate the results of the normal diffusion. Dashed lines represent asymptotic algebraic time dependence of Eq. (26). Dots represent the results of Mittag-Leffler function of Eq. (27).

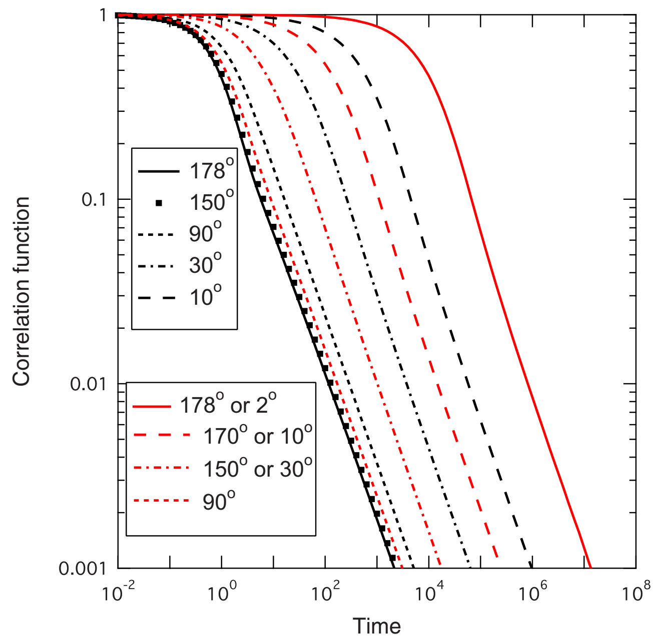

FIG. 4. (Color online) Correlation functions of the Ivanov-Anderson model for $\alpha = 0.8$ with various values of jump amplitude against dimensionless time, $\gamma_r t$. Red lines represent $C_2(t)$ and black lines and symbols represent $C_1(t)$.

When Δ is increased to $\Delta = 170°$, $C_2(t)$ decays slower than $C_1(t)$ for any values of α as shown in Fig. 3. As α is decreased, the relaxation becomes slower. Long time asymptotic decay is again represented by the algebraic decay of Eq. (26). $C_2(t)$ decays according to Mittag-Leffler function at intermediate times and the fitting becomes better as α is lowered. Since the Mittag-Leffler function is approximated by the stretched exponential decay of Eq. (28) in this time range, $C_2(t)$ is well fitted by the stretched exponential function. The stretched exponential decay appears when Δ is close to 180° for $C_2(t)$ and Δ is close to 0° for both $C_2(t)$ and $C_1(t)$. For other values of Δ the analytical form of the decay is not obtained but as we can see from the inset of Fig. 2 the decay curves are very different from the single exponential decay when $\alpha < 1$. Only when $\alpha = 1$, the correlations decay fast with exponential time dependence which is shown by the straight line in the log-linear plot.

The results for different values of Δ with α kept constant are summarized in Fig. 4. For any value of Δ, asymptotic time dependence is described by the algebraic time dependence with the exponent α. The relaxation of $C_1(t)$ slows down monotonically as Δ is decreased. Since $C_2(t)$ is given by the square of $\cos\Delta$, the decay is the same when Δ is changed to $\pi - \Delta$. As Δ is increased from 0°, the decay of $C_2(t)$ becomes faster. The fastest decay is obtained for $\Delta = 90°$. When Δ is further increased from $\Delta = 90°$, the decay is slowed down.

In order to facilitate comparison with dielectric relaxation experiments in dispersive medium, we investigated the behavior of the Cole-Cole diagram as a function of system parameters (like jump angle and value of the power law exponent). The Cole-Cole diagram is obtained from the complex dielectric function, $\epsilon(\omega)$, which satisfies [19,35]

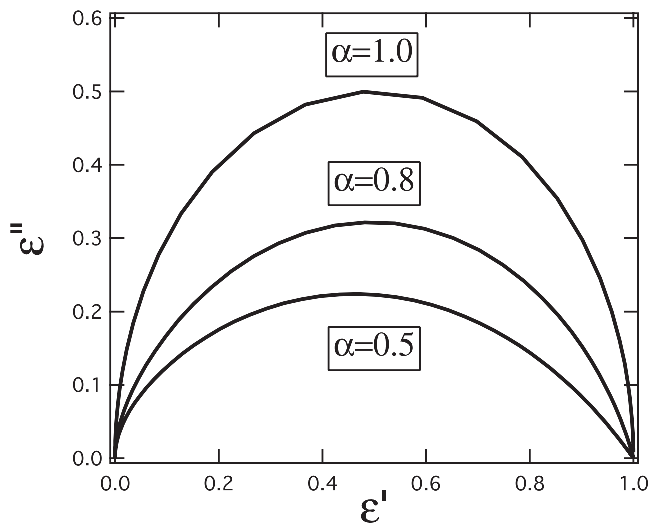

FIG. 5. Cole-Cole diagram of the Ivanov-Anderson model for $\Delta=30°$.

$$\frac{\epsilon(\omega)-\epsilon_\infty}{\epsilon_{st}-\epsilon_\infty}=1+i\omega\hat{C}_1(-i\omega), \tag{52}$$

where ϵ_{st} is the static dielectric constant and ϵ_∞ is the optical dielectric constant. The semi-circle of Debye relaxation is obtained for normal diffusion. As α is decreased, the maximum of ϵ'' is decreased and the Cole-Cole diagram is depressed. When Δ is relatively small, the Cole-Cole diagram is symmetric, as shown in Fig. 5 for any value of α. Such change of the Cole-Cole diagram by decreasing α has been already noticed, but without paying much attention to the influence of the jump amplitude [36,37].

Now, we investigate the influence of the jump amplitude on the Cole-Cole diagram. For the same value of α, the Cole-Cole diagram is skewed and becomes asymmetric as the jump amplitude Δ is increased, as shown in Figs. 6 and 7. The asymmetry is larger for smaller values of α.

The results of the Kubo model are quite similar to those of Ivanov-Anderson model. In the Kubo model, however, an oscillation is observed, in addition to the algebraic or stretched exponential decay, as shown in Figs. 8 and 9. In the Kubo model of the oscillator [18,19], it has been pointed out that the jump contributes both to the damping and the oscillation of correlation functions. Dipoles rotate in a direction with an average amplitude Δ, which gives rise to oscillation in correlation functions. In the case of magnetic resonance as originally studied by Kubo, the oscillation corresponds to the shift of resonant frequency found in the more elaborate theory. In the case of electric dipoles, oscillation is due to the rather unphysical modeling of the rotator, which has a preferable direction of rotation.

The oscillation disappears by decreasing α values. When the jump amplitude is small, $C_1(t)$ oscillates more than $C_2(t)$. For $\Delta=60°$, $C_1(t)$ oscillates even when α is decreased to $\alpha=0.8$. In the case of $\Delta=170°$, $C_2(t)$ oscillates for normal diffusion while other decay curves exhibit essentially monotonic decay.

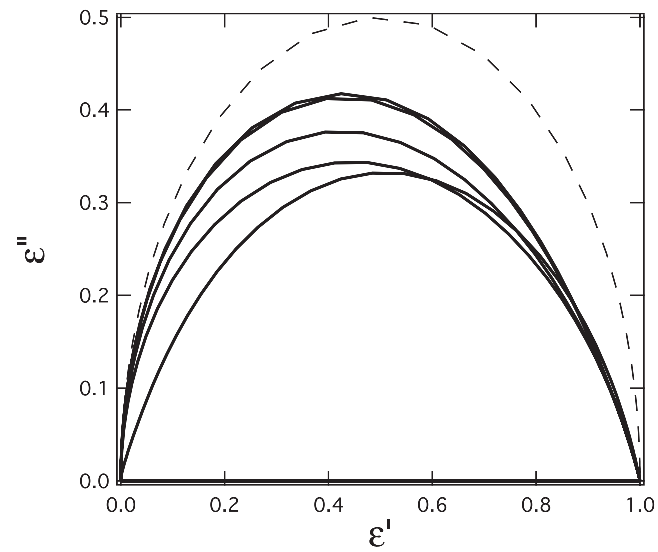

FIG. 6. Cole-Cole diagram of the Ivanov-Anderson model for $\alpha=0.8$. Solid lines indicate $\Delta=10°$, 60°, 90°, 150°, and 180° (almost overlaps with the line of $\Delta=150°$) from bottom to top at $\epsilon'=0.2$. Dashed line represents the Debye relaxation of $\alpha=1.0$.

So far, we have investigated the effect of long algebraic waiting time on the rotational relaxation with large jump amplitude. Large amplitude jumps are normally superimposed by small amplitude jumps. Therefore, we study the case when both large and small amplitude jumps are simultaneously present. As shown in Fig. 10, in this case the kinetics is found to be almost exponential and the decay is well represented by Eq. (50) for $C_1(t)$ and Eq. (51) for $C_2(t)$. The exponential kinetics is also confirmed from the Cole-Cole diagram, where semi-circle of Debye relaxation can be seen (not shown). The decay curves obtained by multiplying Eqs.

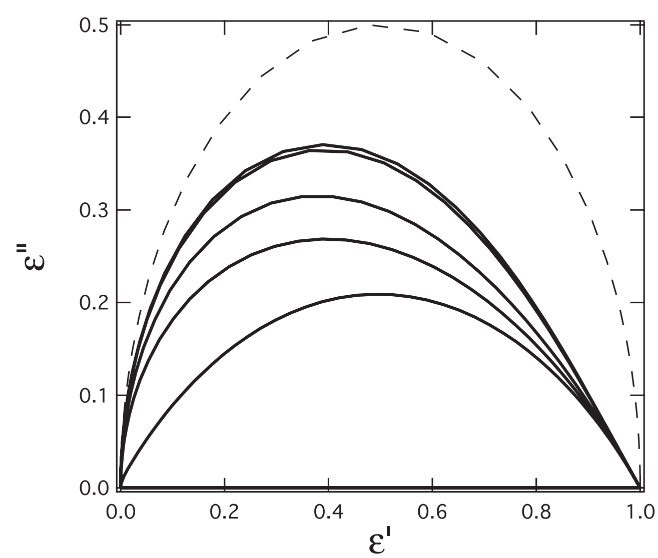

FIG. 7. Cole-Cole diagram of the Ivanov-Anderson model for $\alpha=0.5$. Solid lines indicate $\Delta=10°$, 60°, 90°, 150°, and 180° (almost overlaps with the line of $\Delta=150°$) from bottom to top. Dashed line represents the Debye relaxation of $\alpha=1.0$.

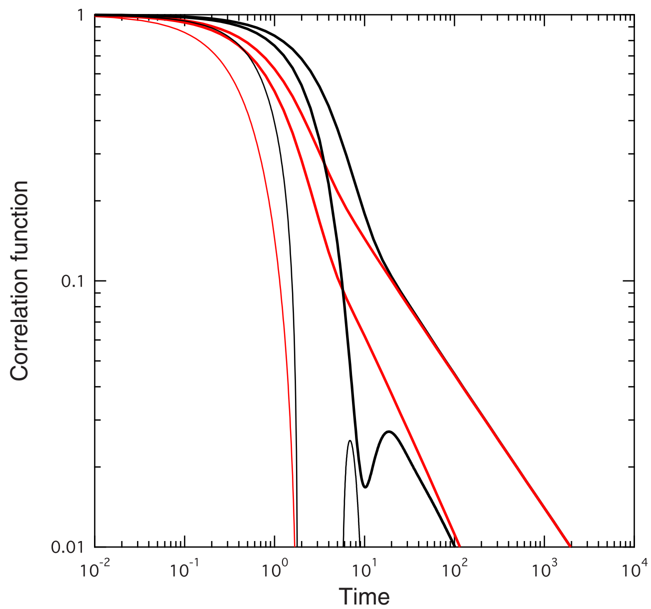

FIG. 8. (Color online) Correlation functions of the Kubo model with $\Delta=60°$ against dimensionless time, $\gamma_r t$. Red lines represent $C_2(t)$ and black lines represent $C_1(t)$. $\alpha=0.5$, 0.8 from top to bottom. Thin lines indicate the results of normal diffusion.

(2) and (3) for small amplitude jump with the inverse Laplace transform of Eq. (15), where Eq. (18) for large amplitude jump is introduced, are different from the exact numerical results. The exponential kinetics is of course different from the algebraic decay or stretched exponential decay found for the large amplitude jump alone. The small amplitude jumps are more frequent than the large amplitude jumps. The former gives rise to an exponential decay but in the presence of large amplitude jump the correlation functions decay almost exponentially with the time constant much smaller than that for the small amplitudes alone. Thus, although the large amplitude jumps are rare, they contribute a lot to the relaxation. The waiting time distribution of large amplitude jumps in the absence of small amplitude jumps has an algebraic asymptotic time dependence which is easily interrupted by the more frequent small amplitude jumps. The decay is exponential as a result of cumulative small amplitude jumps, but the decay is accelerated by the large amplitude jumps.

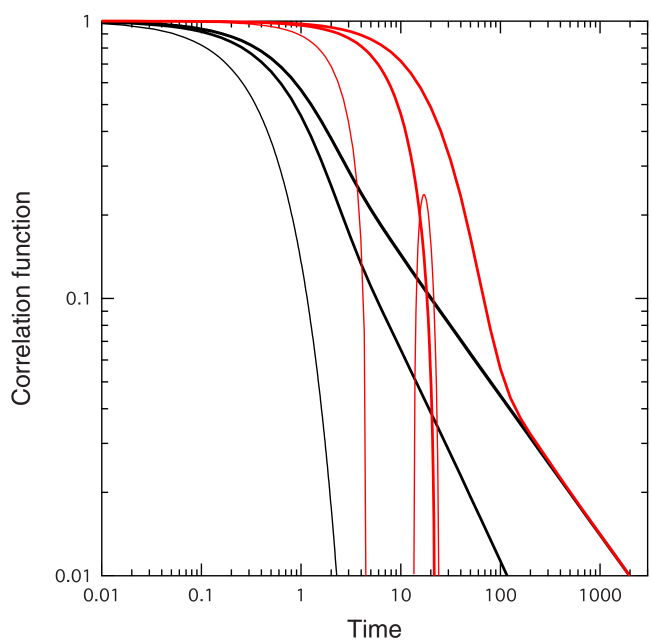

FIG. 9. (Color online) Correlation functions of the Kubo model with $\Delta=170°$ against dimensionless time, $\gamma_r t$. Red lines represent $C_2(t)$ and black lines represent $C_1(t)$. $\alpha=0.5$, 0.8 from top to bottom. Thin lines indicate the results of normal diffusion.

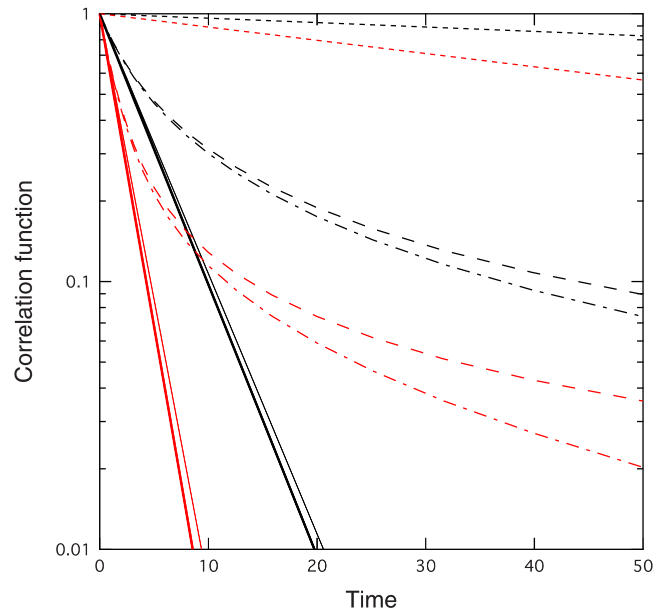

FIG. 10. (Color online) Correlation functions of the Ivanov-Anderson model for $\alpha=0.8$ against dimensionless time, t/τ_a. The large amplitude jump of $\Delta_a=60°$ and the small amplitude jump of $\Delta_b=5°$ coexist. The frequency of the small amplitude jump is 5 times larger than that of the large amplitude jump, $\tau_a/\tau_b=5$. Red lines represent $C_2(t)$ and black lines represent $C_1(t)$. Thick lines indicate the exact numerical results. Thin lines indicate the approximate results of Eqs. (50) and (51). Short-dashed lines indicate the result of the small amplitude jump alone. Long-dashed lines indicate the result of the large amplitude jump alone. The dashed-dotted lines are the results assuming independent superposition of two processes as explained in the text.

As explained, the exponential kinetics of correlation functions, $C_1(t)=\exp(-t/\tau_1)$ and $C_2(t)=\exp(-t/\tau_2)$, results from the interplay between the frequent small amplitude jumps and the rare events of large amplitude jumps having algebraic waiting time distribution. Although the results are not shown, substantially the same results are obtained even when α is lowered to 1/2. For $\alpha<1$, τ_1 and τ_2 are obtained from Eq. (50) and Eq. (51), respectively, while the results of normal diffusion are given by, Eqs. (41) and (42).

We now investigate the jump amplitude dependence of the ratio of the correlation times, τ_1/τ_2. As shown in Fig. 11, the result for $\alpha=0.8$ and that for normal diffusion are almost the same, although the apparent functional forms are seemingly very different. When Δ_a is small, the ratio is close to 3

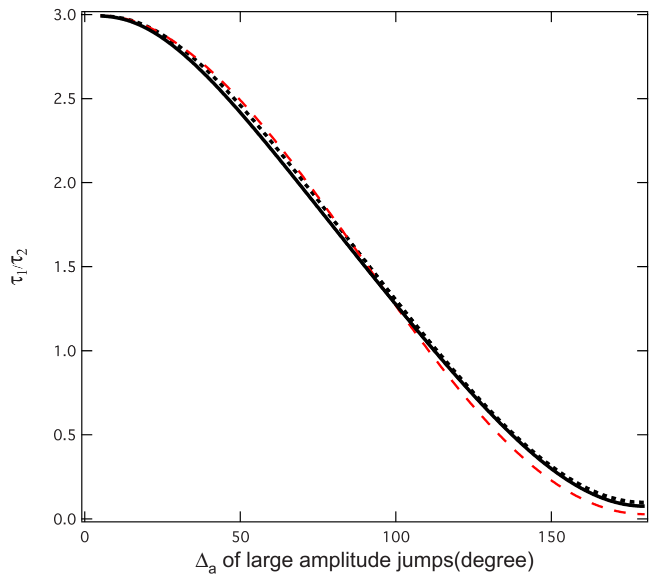

FIG. 11. (Color online) τ_1/τ_2 against the amplitude of the large amplitude jumps for the fixed jump amplitude $\Delta_b=5°$ of the small amplitude jumps. The frequency of the small amplitude jump is 5 times larger than that of the large amplitude jump, $\tau_a/\tau_b=5$. The solid line indicates the results of $\alpha=0.8$. Dots indicate the results of $\alpha=0.5$. The red dashed line indicates the results for the normal diffusion of $\alpha=1.0$.

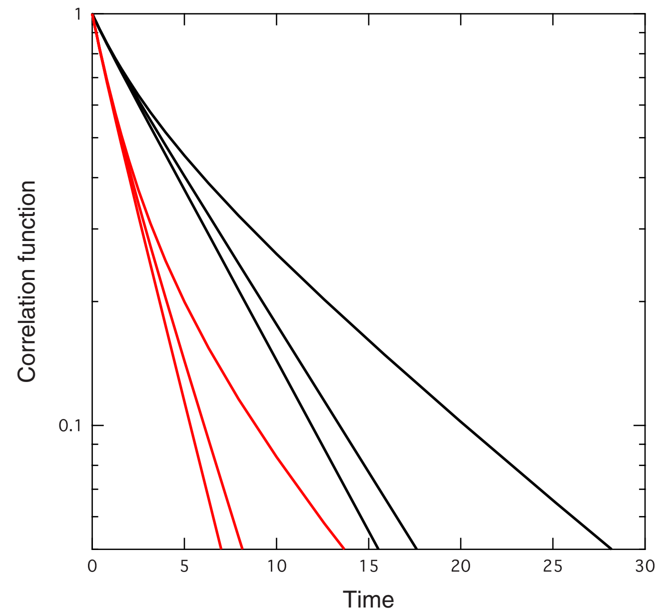

FIG. 12. (Color online) Correlation functions of the Ivanov-Anderson model for $\alpha=0.8$ against dimensionless time, t/τ_a. The large amplitude jump of $\Delta_a=60°$ and the small amplitude jump of $\Delta_b=5°$ coexist. The frequency of the small amplitude jump is changed. Red lines represent $C_2(t)$ and black lines represent $C_1(t)$. $\tau_a/\tau_b=0.1$, $\tau_a/\tau_b=0.5$, and $\tau_a/\tau_b=1.0$ from top to bottom.

and it decreases monotonically to zero as Δ_a is increased close to 180°. The small deviation between the two lines is increased as Δ_a is increased. Since the results among different values of α are very close, it could be difficult to judge from the correlation functions whether the long amplitude jumps have algebraic long time tail in the waiting time distribution.

The exponential kinetics is robust as shown in Fig. 12. Even when the frequency of the small amplitude jumps is the same as that of the large amplitude jumps, the decay is still exponential. However, when the small amplitude jumps occur 10 times less frequently than the large amplitude jumps, then nonexponential kinetics is observed in the short time regime, $t \leq \tau_b$.

VI. CONCLUSIONS

The models of Ivanov and of Kubo are well-known models of the decay of the orientational correlation by random but large amplitude molecular jumps. These models are expected to give rise to decay dynamics quite distinct from the Brownian diffusion by infinitesimal small jumps. When the waiting time distribution for large jumps is Poissonian, even the models of Ivanov and Kubo lead to exponential decay. The jump angle and its distribution are estimated from two-dimensional NMR spectroscopy by measuring quadrupole as well as dipole correlations [38].

However, if the waiting time distribution is not Poissonian, then the difference between large jumps and the Brownian diffusion can be significant. In the present work, we have extended the models of Ivanov and Kubo to include such cases. In particular, we have employed an algebraic waiting time distribution for large jumps, as such distributions can be useful to describe liquids, especially in restricted geometries. Recent computer simulation studies on water and viscous liquids have indeed shown that large amplitude motions may be more of a rule than exception.

In the present study, we have solved the theoretical models with algebraic waiting time distribution analytically to obtain the first ($\ell=1$) and second ($\ell=2$) rank orientational time correlation functions. As expected, the decay is nonexponential, with power law at longer times. The correlation functions for $\ell=1$ and $\ell=2$ show the same long time power law exponents, but the short time decay behavior is quite different for the two correlation functions.

In order to facilitate comparison with experiments on dielectric relaxation, we have calculated Cole-Cole plots generated by the orientational decay for a wide variety of parameters, such as jump amplitude and the power law exponent. The predicted Cole-Cole plot of dielectric relaxation reproduces various features of non-Debye behavior observed experimentally.

In addition, we have developed a theory where both unrestricted small jumps and large amplitude jumps coexist simultaneously. The small amplitude jumps are shown to have a large effect on the long time decay, particularly in mitigating the effects of algebraic waiting time distribution. Thus, in the limit of the appreciable number of small jumps, we find the decay to become single exponential. We find somewhat surprisingly that this exponential decay is much faster than that given by small jumps alone.

In this work, we have not made any specific application of our theory but shown that several features of the Cole-Cole plot resemble the ones observed experimentally in complex systems. Since algebraic waiting time distribution of jumps naturally gives rise to a Davidson-Cole kind of frequency dependence of dielectric function, the present formalism should find use in interpretation of existing experimental results. Work in this direction is under progress.

ACKNOWLEDGMENTS

B. B. thanks AIST, Tsukuba for kind hospitality during his stay and also DST (India) for partial research support. This work is partly supported by the Grant-in-Aid for Science Research in a priority area "Super-Hierarchical" of the MEXT.

[1] B. J. Berne and R. Pecora, *Dynamic Light Scattering with Applications to Chemistry, Biology, and Physics* (Wiley, New York, 1976).
[2] G. R. Fleming, *Chemical Applications of Ultrafast Spectroscopy* (Oxford University Press, New York, 1986).
[3] B. Bagchi and A. Chandra, Adv. Chem. Phys. **80**, 1 (1991).
[4] P. Debye, *Polar Molecules* (Dover, New York, 1929).
[5] A. J. Cross, D. H. Waldeck, and G. R. Fleming, J. Chem. Phys. **78**, 6455 (1983).
[6] R. S. Mong, M. D. Ediger, S. G. Boxer, and M. D. Fayer, J. Phys. Chem. **86**, 4694 (1982); H. Cang, V. N. Novikov and M. D. Fayer, J. Chem. Phys. **118**, 2800 (2003).
[7] E. N. Ivanov, Sov. Phys. JETP **18**, 1041 (1964).
[8] J. E. Anderson, Faraday Symp. Chem. Soc. **6**, 82 (1972).
[9] P. Madden and D. Kivelson, Adv. Chem. Phys. **56**, 467 (1984).
[10] A. Chandra and B. Bagchi, J. Chem. Phys. **92**, 6833 (1990).
[11] S. Kammerer, W. Kob, and R. Schilling, Phys. Rev. E **56**, 5450 (1997).
[12] R. A. L. Vallée, M. Van der Auweraer, W. Paul, and K. Binder, Europhys. Lett. **79**, 46001 (2007).
[13] C. DeMichele and D. Leporini, Phys. Rev. E **63**, 036702 (2001).
[14] M. Faetti, M. Giordano, D. Leporini, and L. Pardi, Macromolecules **32**, 1876 (1999).
[15] L. Andreozzi, F. Cianflone, C. Donati, and D. Leporini, J. Phys.: Condens. Matter **8**, 3795 (1996).
[16] V. Bercu, M. Martinelli, C. A. Massa, L. A Pardi, and D. Leporini, J. Chem. Phys. **123**, 174906 (2005).
[17] D. Laage and J. T. Hynes, Proc. Natl. Acad. Sci. U.S.A. **104**, 11167 (2007).
[18] R. Kubo, in *Fluctuation, Relaxation and Resonance in Magnetic Systems* (Oliver and Boyd, Edinburgh, 1962).
[19] R. Kubo, M. Toda, and N. Hashitsume, *Statistical Physics II: Nonequilibrium Statistical Mechanics* (Springer-Verlag, Berlin, 1991), p. 47.
[20] G. Diezemann and H. Sillescu, J. Chem. Phys. **111**, 1126 (1999).
[21] L. Alessi, L. Andreozzi, M. Faetti, and D. Leporini, J. Chem. Phys. **114**, 3631 (2001).
[22] J.-L. Déjardin and J. Jadzyn, J. Chem. Phys. **122**, 074502 (2005).
[23] E. Barkai, R. Metzler, and J. Klafter, Phys. Rev. E **61**, 132 (2000).
[24] E. Barkai and R. Silbey, J. Phys. Chem. B **104**, 3866 (2000).
[25] R. Metzler and J. Klafter, J. Phys. A **37**, R161 (2004).
[26] I. M. Sokolov, J. Klafter, and A. Blumen, Phys. Today **55**(11), 48 (2002).
[27] J. Klafter and I. M. Sokolov, Phys. World **18**, 29 (2005).
[28] K. Seki, B. Bagchi, and M. Tachiya, J. Phys. Chem. B (to be published).
[29] E. W. Montroll and G. H. Weiss, J. Math. Phys. **6**, 167 (1965).
[30] R. Zwanzig, *Nonequilibrium Statistical Mechanics* (Oxford University Press, New York, 2002).
[31] J. D. Barnes, J. Chem. Phys. **58**, 5193 (1973).
[32] M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions* (Dover, New York, 1972).
[33] M. Tachiya and A. Mozumder, Chem. Phys. Lett. **34**, 77 (1975).
[34] A. V. Barzykin and M. Tachiya, Phys. Rev. Lett. **73**, 3479 (1994).
[35] R. Zwanzig, Annu. Rev. Phys. Chem. **61**, 67 (1965).
[36] R. Metzler and J. Klafter, J. Non-Cryst. Solids **305**, 81 (2002).
[37] S. Gomi and F. Yonezawa, Phys. Rev. Lett. **74**, 4125 (1995).
[38] R. Böhmer and G. Hinze, J. Chem. Phys. **109**, 241 (1998).