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# Viscoelastic effects on the dynamic susceptibility of a Brownian particle in an external potential

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The relaxation behavior of an assembly of noninteracting dipolar molecules acted on by an alternating electric field and moving in a viscoelastic liquid is studied by solving the corresponding Fokker-Planck-Kramers equation. Both inertial and viscoelastic effects are taken into account leading to an infinite hierarchy of differential-recurrence relations where the appropriate relaxation functions are characterized by three indices. An exact expression for the complex dielectric susceptibility is found by using a matrix formulation. Dispersion and absorption spectra together with Cole-Cole diagrams are then plotted exhibiting a resonant structure in the FIR region due to the forcing regime impressed by the electric field. From these curves, it is shown that inertia and elasticity are strongly coupled. This coupling effect becomes much more important as the elastic relaxation time characterizing the interactions of the molecules with the thermal bath becomes greater than the Debye relaxation time. [S1063-651X(98)13908-9]

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## I. INTRODUCTION

The rotational Brownian motion in a dielectric fluid consisting of molecules having permanent dipole moments was originally studied by Debye [1]. His theory based on Smoluchowski's equation [2] in configuration space only (long-time behavior or high friction limit) led him to calculate in the linear approximation the frequency-dependent orientational polarization arising from the application of an alternating electric field to the molecules. Unfortunately, the formula he obtained may only be applied to angular frequencies such that $\omega < 1/\tau$ ($\tau$ is the Debye relaxation time). Beyond this limit, one attains the microwave and far-infrared (FIR) regions where it is necessary to include molecular inertial effects, which means that the orientational probability density function $W$ allowing one to describe the dielectric relaxation process must depend not only on the angular coordinates but also on the velocity variables. This can be accomplished by solving either the Fokker-Planck-Kramers (FPK) equation [3] or the stochastic Langevin equation [4], both methods giving completely equivalent results for the desired relaxation functions. If, for the sake of mathematical simplicity, we consider rotation in plane that assumes that the molecules acted on by the electric field $\mathbf{E}(t)$ are compelled to rotate in two dimensions (disk model), the FPK equation is

$$\frac{\partial W}{\partial t} + \omega \frac{\partial W}{\partial \theta} - \frac{1}{I}\frac{\partial V}{\partial \theta}\frac{\partial W}{\partial \omega} = \frac{\xi}{I}\left(\frac{\partial}{\partial \omega}\omega + \frac{kT}{I}\frac{\partial^2}{\partial \omega^2}\right)W, \quad (1)$$

subject to the initial condition (Green's function)

$$W(\theta,\dot{\theta};0) = \delta(\theta-\theta_0)\,\delta(\dot{\theta}-\dot{\theta}_0),$$

where $W = W(\theta,\dot{\theta};t)$, $\theta$ is the polar angle that specifies the direction of the dipole axis with that of the applied electric field, $\omega = \dot{\theta}$, $I$ the moment of inertia of the dipole about its rotation axis, $\xi$ the rotational friction coefficient, $k$ the Boltzmann constant, $T$ the absolute temperature, and $\delta$ is the Dirac-delta function. If $\mu$ denotes the amplitude of the permanent moment, the orientational potential energy acting on the molecule impressed by $\mathbf{E}(t)$ is

$$V = -\boldsymbol{\mu}\cdot\mathbf{E} = -\mu E \cos\theta. \quad (2)$$

In Eq. (1), the angular position $\theta$ is a slow variable and the angular velocity $\omega$ a fast variable. We note the coupling between these two quantities given by the second and third terms in the left-hand side of this equation. Correlatively, the Langevin equation (from which the FPK equation can be extracted) governing the motion of a Brownian particle (molecule in this instance) is

$$\begin{aligned} \dot{\theta} &= \omega, \\ \dot{\omega} &= -\frac{\xi}{I}\omega - \frac{1}{I}\frac{\partial V}{\partial \theta} + \frac{\lambda(t)}{I}, \end{aligned} \quad (3)$$

where $\theta$ is now a stochastic variable, and $\lambda(t)$ is a white noise driving torque (centered Gaussian variable) due to the Brownian motion (many collisions in the surroundings) defined by

$$\begin{aligned} \overline{\lambda(t)} &= 0, \\ \overline{\lambda(t_1)\lambda(t_2)} &= 2\xi kT\,\delta(t_1-t_2). \end{aligned} \quad (4)$$

In Eq. (4), the overbar represents a statistical average over an assembly of particles all starting with the same initial conditions at time $t$. By using Eq. (3) as well as Eq. (1), we work in the Markovian limit [5], i.e., in the situation where the stochastic damping torque $M$ has the following form:

$$M = -\xi\int_0^t \omega(t')\,\delta(t-t')\,dt' = -\xi\omega(t). \quad (5)$$

From the second relation of Eq. (4), we readily have

$$\xi kT = \int_0^\infty \overline{\lambda(t)\lambda(0)}\,dt,$$

which clearly shows the interaction of the Brownian particle with its thermal environment. The friction coefficient has a constant (static) value so that the noise correlation time represented by the area under the curve of the normalized noise torque autocorrelation function is vanishingly small corresponding to a memory-free process.

In what follows, we shall consider the Brownian motion of a particle embedded in a viscoelastic dielectric fluid so constituting a non-Markovian system. This approach seems to be more realistic for describing relaxation phenomena of condensed matter in general and liquids in particular [6]. Recently, considerable efforts have been devoted to the study of the dynamics of activated rate processes [7–10] based on a non-Markovian theory with memory friction. All the results so obtained refer to the remarkable and pioneering paper of Kramers [11] and are related to the calculation of the escape rate of a particle over a potential barrier. The interested reader may find many references on the subject in review articles [12,13]. More recently, Volkov and Leonov [14] have developed a theory of non-Markovian translational Brownian motion in a viscoelastic fluid and established the time evolution of the probability distribution function of a Brownian particle in terms of its position, velocity, and acceleration. Raĭkher and Rusakov [15], on the other hand, have studied the dynamic susceptibility of a magnetic suspension in a viscoelastic liquid carrier by deriving a stochastic Langevin equation in which appear two terms containing the third and the second derivatives with respect to time of the angular variable $\theta$, namely, $\dddot{\theta}$ and $(1/\tau_M)\ddot{\theta}$, where $\tau_M$ denotes a typical stress relaxation time.

In previous papers [16–18], we have already studied the nonlinear dielectric relaxation as well as the dynamic Kerr effect by including molecular inertia only. The main purpose of this work is to construct a FPK equation in two dimensions taking into account both inertial and elastic effects with a view to calculating the dielectric absorption of an assembly of noninteracting dipolar molecules in a viscous and elastic fluid. To accomplish this, we shall start from the generalized Langevin equation [19] containing a colored noise term and show that the orientational probability distribution function of the underlying FPK equation will depend now on three variables in phase space rather than two, namely, $W = W(\theta,\dot{\theta},Z;t)$. Therefore, we shall be led to define three time scales, the Debye relaxation time $\tau = \xi/(kT)$, the friction time $\tau_F = I/\xi$, and the elastic time $\tau_{\rm el}$. Hence, after having established an exact expression for $\langle \cos\theta \rangle(t)$ the expectation value of the first Legendre polynomial characteristic of dielectric relaxation, we shall see how the relaxation spectra in the FIR are modified according to the relative value of each of these times in comparison with the two others.

## II. DERIVATION OF THE VISCOELASTIC FOKKER-PLANCK EQUATION

If viscoelastic effects take place in a dielectric liquid acted on by an alternating electric field of the form $E(t) = E_0 \cos \omega t$, the motion of a molecule may be described by replacing Eq. (3) with the generalized Langevin equation

$$\begin{aligned} &\dot{\theta} = \omega, \\ &\dot{\omega} = -\frac{1}{I}\frac{\partial V}{\partial \theta} - \int_0^t X(t_1 - t_2)\,\omega(t_2)\,dt_2 + \frac{\Lambda(t)}{I}, \end{aligned} \tag{6}$$

where $X(t)$ is the memory friction kernel and $\Lambda(t)$ a colored noise torque [20] arising from the thermal bath such that

$$\begin{aligned} &\overline{\Lambda(t)} = 0 \quad \text{(zero mean value)}, \\ &\overline{\Lambda(t_1)\Lambda(t_2)} = IkTX(t_1 - t_2). \end{aligned} \tag{7}$$

The second relation in Eq. (7) obtained from the fluctuation-dissipation theorem indicates that $\Lambda(t_1)$ and $\Lambda(t_2)$ are correlated with a correlation time different from zero.

If we choose for the friction kernel an exponentially decaying function with time constant $\tau_{\rm el}$ such that

$$X(t) = \frac{\zeta}{I\tau_{\rm el}} \exp(-t/\tau_{\rm el}), \tag{8}$$

Eq. (6) becomes

$$\begin{aligned} &\dot{\theta} = \omega, \\ &\dot{\omega} = -\frac{1}{I}\frac{\partial V}{\partial \theta} + Z, \\ &\dot{Z} = -\frac{1}{\tau_{\rm el}} Z - \frac{\xi}{I\tau_{\rm el}}\,\omega + \frac{\eta(t)}{I}, \end{aligned} \tag{9}$$

where $Z$ is a new variable having the dimensions of an acceleration and standing for the elastic nature of the medium, the time evolution of which governs the dynamics of the particle interacting with the thermal bath, and $\eta(t)$ is a white Gaussian noise satisfying the classical relations

$$\begin{aligned} &\overline{\eta(t)} = 0, \\ &\overline{\eta(t_1)\,\eta(t_2)} = 2(\xi kT/\tau_{\rm el}^2)\,\delta(t_1 - t_2). \end{aligned} \tag{10}$$

Note that the prefactor $\xi/(I\tau_{\rm el})$ in Eq. (8) has this form in order to ensure the correct dimensions of units. From the set of relations in Eq. (9), it is shown that the non-Markovian process described by Eq. (6) can be reduced to a Markov process [21–23] containing an extra variable ($Z$ in this instance). This is completely equivalent to the Mori [24] representation of the Laplace transform of $X(t)$ in the form of a continued-fraction expansion

$$\begin{aligned} \tilde{X}(s) = \cfrac{\Delta_1^2}{s + \lambda_1 + \cfrac{\Delta_2^2}{s + \lambda_2 + \Delta_3^2}} \\ \ddots \qquad\qquad \\ + \cfrac{\Delta_n^2}{s + \tilde{X}_n(s)}\,, \end{aligned} \tag{11}$$

by truncating it at the first convergent ($\Delta_n^2 = 0$ for $n \geqslant 2$), namely,

$$\widetilde{X}(s)=\frac{\Delta_1^2}{s+\lambda_1}, \tag{12}$$

with $\Delta_1^2=\xi/(I\tau_{\mathrm{el}})$ and $\lambda_1=1/\tau_{\mathrm{el}}$.

At this stage, it is easy to derive the viscoelastic FP equation associated with the Langevin equation [Eq. (9)]. Denoting by $W(\theta,\dot{\theta},Z;t)$ the new orientational probability density function, we have $(x_1=\theta, x_2=\dot{\theta}, x_3=Z)$

$$\begin{aligned}\frac{\partial W}{\partial t}=&-\sum_i\left[\frac{\partial}{\partial x_i}D_i^{(1)}(x_1,x_2,x_3)\right]W\\&+\sum_{i,j}\left[\frac{\partial^2}{\partial x_i\partial x_j}D_{ij}^{(2)}(x_1,x_2,x_3)\right]W,\end{aligned} \tag{13}$$

where $D_i^{(1)}$ and $D_{ij}^{(2)}$ are the drift and diffusion coefficients [3], respectively, such that

$$D_1^{(1)}=\omega,\quad D_2^{(1)}=-\frac{1}{I}\frac{\partial V}{\partial\theta}+Z,\quad D_3^{(1)}=-\frac{1}{\tau_{\mathrm{el}}}Z-\frac{\xi}{I\tau_{\mathrm{el}}}\omega,$$

$$D_{11}^{(2)}=D_{22}^{(2)}=D_{12}^{(2)}=D_{21}^{(2)}=D_{13}^{(2)}=D_{31}^{(2)}=D_{23}^{(2)}=D_{32}^{(2)}=0,$$

$$D_{33}^{(2)}=\frac{\xi kT}{I^2\tau_{\mathrm{el}}^2}. \tag{14}$$

and hence

$$\frac{\partial}{\partial t}W(\theta,\dot{\theta},Z;t)=\mathcal{L}W(\theta,\dot{\theta},Z;t), \tag{15}$$

where

$$\begin{aligned}\mathcal{L}=&-\frac{\partial}{\partial\theta}\dot{\theta}+\frac{\partial}{\partial\dot{\theta}}\left(\frac{1}{I}\frac{\partial V}{\partial\theta}-Z\right)+\frac{\partial}{\partial Z}\left(\frac{\xi}{I\tau_{\mathrm{el}}}\dot{\theta}+\frac{1}{\tau_{\mathrm{el}}}Z\right)\\&+\frac{\xi kT}{I^2\tau_{\mathrm{el}}^2}\frac{\partial^2}{\partial Z^2}\end{aligned}$$

is the appropriate Liouville operator.

Note that we have a new coupling effect between $\dot{\theta}$ and $Z$ in addition to that between $\theta$ and $\dot{\theta}$, which is only present in the Markov limit. Defining the generalized potential $U$ associated with the three variables $\theta$, $\dot{\theta}$, and $Z$ by

$$U(\theta,\dot{\theta},Z)=V(\theta)+\frac{1}{2}I\dot{\theta}^2+\frac{1}{2}\frac{\tau_{\mathrm{el}}I^2}{\xi}Z^2, \tag{16}$$

the stationary value of $W$ at equilibrium obeying a Maxwell-Boltzmann distribution is simply

$$W(\theta,\dot{\theta},Z)=C\exp\left[-\frac{U(\theta,\dot{\theta},Z)}{kT}\right], \tag{17}$$

where $C$ is a normalization constant

$$C=1\bigg/\int\int\int W(\theta,\dot{\theta},Z)d\theta\, d\dot{\theta}\, dZ.$$

## III. MATRIX FORMULATION

Equation (15) gives the time evolution of $W$ in phase space enlarged to a third variable $Z$, which allows us to consider the Brownian motion of the molecule moving in the viscoelastic fluid as a Markov process in this space. Moreover, this equation is subject to the following initial condition:

$$W(\theta,\dot{\theta},Z;0)=\delta(\theta-\theta_0)\delta(\dot{\theta}-\dot{\theta}_0)\delta(Z-Z_0). \tag{18}$$

Our method for solving Eq. (15) rests on the same procedure as that we have developed in our previous works [16,18] on dielectric relaxation including inertial effects only. Following Sack [25], we take the Fourier transform of $W$ in velocity-elasticity space, which yields

$$\begin{aligned}\Phi(\theta,u,v,t)&=\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}W(\theta,\dot{\theta},Z;t)\\&\quad\times\exp[-i(u\dot{\theta}+vZ)]d\dot{\theta}\, dZ\\&=\langle\exp[-i(u\dot{\theta}+vZ)]\rangle,\end{aligned} \tag{19}$$

where the angular brackets represent an ensemble average, and setting

$$\Psi(\theta,u,v,t)=\exp\left(\frac{kT}{2I}u^2+\frac{\xi kT}{2I^2\tau_{\mathrm{el}}}v^2\right)\Phi(\theta,u,v,t), \tag{20}$$

Eq. (15) becomes

$$\begin{aligned}&\frac{\partial\Psi}{\partial t}-iu\frac{kT}{I}\frac{\partial\Psi}{\partial\theta}+i\frac{\partial^2\Psi}{\partial u\partial\theta}-\frac{1}{I}\frac{\partial V}{\partial\theta}iu\Psi-u\frac{\partial\Psi}{\partial v}\\&\quad+\frac{\xi}{I\tau_{\mathrm{el}}}v\frac{\partial\Psi}{\partial u}+\frac{1}{\tau_{\mathrm{el}}}v\frac{\partial\Psi}{\partial v}=0.\end{aligned} \tag{21}$$

We remark the presence in this equation of cross terms in the reciprocal variables $u$ and $v$ illustrating the strong dependence of elastic effects on inertial ones. As shown in Eq. (2), the potential energy $V(\theta,t)$ is an even periodic function of $\theta$ so that we can expand $\Psi(\theta,u,v;t)$ in Fourier series

$$\Psi(\theta,u,v,t)=\sum_{p=-\infty}^{+\infty}a_p(u,v,t)e^{-ip\theta}. \tag{22}$$

By substitution of Eq. (22) into Eq. (21), we have

$$\begin{aligned}&\frac{\partial a_p}{\partial t}+p\left(\frac{\partial a_p}{\partial u}-\frac{kT}{I}ua_p\right)-\frac{u}{2I}[\mu E(a_{p+1}-a_{p-1})]-u\frac{\partial a_p}{\partial v}\\&\quad+\frac{\xi}{I\tau_{\mathrm{el}}}v\frac{\partial a_p}{\partial u}+\frac{1}{\tau_{\mathrm{el}}}v\frac{\partial a_p}{\partial v}=0.\end{aligned} \tag{23}$$

Expanding again $a_p(u,v,t)$ in power series of $u$ and $v$ as

$$a_p(u,v,t)=\sum_{m=0}^{\infty}\sum_{n=0}^{\infty}u^m v^n b_p^{m,n}(t), \tag{24}$$

where the $b_p^{m,n}(t)$ are the relaxation functions, we finally arrive at

$$\dot{b}_p^{m,n}(t)+p\left[(m+1)b_p^{m+1,n}(t)-\frac{kT}{I}\,b_p^{m-1,n}(t)\right]-\frac{1}{2I}\,\mu E b_{p+1}^{m-1,n}(t)-b_{p-1}^{m-1,n}(t)-(n+1)b_p^{m-1,n+1}(t)+\frac{\xi}{I\tau_{\mathrm{el}}}\,(m+1)b_p^{m+1,n-1}(t)+\frac{1}{\tau_{\mathrm{el}}}\,nb_p^{m,n}(t)=0. \tag{25}$$

This set of differential-recurrence equations of Brinkman type [26] involves three indices $p$, $m$, and $n$. Given a fixed value of $p$, the influence of inertial and elastic effects on the relaxation spectra is described by varying $m$ and $n$, respectively. According to the successive expansions we have used for obtaining the relaxation functions $b_p^{m,n}(t)$, it is clear that the appropriate values for electric polarization are $p=\pm 1$, $m=n=0$. Starting from Eqs. (18), (22), and (24), we have indeed

$$\langle\cos\,\theta\rangle(t)=\frac{1}{2}\,\frac{b_1^{0,0}(t)+b_{-1}^{0,0}(t)}{b_0^{0,0}}, \tag{26}$$

which is the quantity we require. Furthermore, we shall restrict ourselves to dynamic electro-optical responses up to the first order of the electric field $E(t)$, which allows us to seek $b_p^{m,n}(t)$ in the form

$$b_p^{m,n}(t)={}^{(0)}b_p^{m,n}(t)+{}^{(1)}b_p^{m,n}(t), \tag{27}$$

where the left superscript stands for the order of the perturbation field. If in Eq. (25) we put $p=0$ and consider the zero order perturbation corresponding to statistical equilibrium, we have

$$\frac{\xi}{I\tau_{\mathrm{el}}}\,(m+1){}^{(0)}b_0^{m+1,n-1}+\frac{1}{\tau_{\mathrm{el}}}\,n{}^{(0)}b_0^{m,n}=(n+1){}^{(0)}b_0^{m-1,n+1}. \tag{28}$$

For $n=0$, we immediately find

$${}^{(0)}b_0^{m-1,1}=0 \quad \text{for any } m \text{ value.}$$

Then, varying $m$ and $n$ in Eq. (28) and proceeding to successive iterations, it is easy to prove that

$${}^{(0)}b_0^{m,0}=0 \quad \text{(Maxwell-Boltzmann distribution of velocity)} \tag{29}$$

$${}^{(0)}b_0^{0,n}=0 \quad \text{(Maxwell-Boltzmann distribution of elasticity)},$$

and hence ${}^{(0)}b_0^{m,n}(t)$ is time independent, so that

$${}^{(0)}b_0^{m,n}(t)={}^{(0)}b_0^{m,n}\,\delta_{m,0}\delta_{n,0}, \tag{30}$$

where $\delta_{ij}$ is the usual Kronecker delta symbol.

Remarking again that to the first order in the electric field strength all the ${}^{(1)}b_0^{m,n}$ must vanish, in particular ${}^{(1)}b_0^{0,0}=0$, and that the ${}^{(1)}b_p^{m,n}(t)$ are real functions of time, Eq. (26) reduces to

$$\langle\cos\,\theta\rangle(t)=\frac{{}^{(1)}b_1^{0,0}(t)}{b_0^{0,0}}, \tag{31}$$

so that the infinite set of differential-recurrence equations we have to solve is

$${}^{(1)}\dot{b}_1^{m,n}(t)+\left[(m+1)\;{}^{(1)}b_1^{m+1,n}(t)-\frac{kT}{I}\;{}^{(1)}b_1^{m-1,n}(t)\right]+\frac{\mu E}{2I}\;{}^{(0)}b_0^{m-1,n}(t)-(n+1)\;{}^{(1)}b_1^{m-1,n+1}(t)+\frac{\xi}{I\tau_{\mathrm{el}}}\,(m+1)\;{}^{(1)}b_1^{m+1,n-1}(t)+\frac{1}{\tau_{\mathrm{el}}}\,n\;{}^{(1)}b_1^{m,n}(t)=0. \tag{32}$$

These equations can be written in matrix form by first fixing $n$ and varying $m$ from 0 to $M$, which yields

$$[\dot{B}_{1,n}^{(1)}]+\frac{\xi}{I\tau_{\mathrm{el}}}\,[F][B_{1,n-1}^{(1)}]-(n+1)[J][B_{1,n+1}^{(1)}]+[G_{1,n}][B_{1,n}^{(1)}]=\frac{\mu E}{2I}\,[C_{0,n}^{(0)}], \tag{33}$$

where $[B_{1,n}^{(1)}]$, $[B_{0,n}^{(1)}]$, and $[C_{0,n}^{(0)}]$ are column matrices of $(M+1)$ elements, and $[F]$, $[J]$, and $[G_{1,n}](M+1)\times(M+1)$ square matrices

$$[B_{1,n}^{(1)}]=\begin{pmatrix} {}^{(1)}b_1^{0,n} \\ {}^{(1)}b_1^{1,n} \\ {}^{(1)}b_1^{2,n} \\ \vdots \\ {}^{(1)}b_1^{M,n} \end{pmatrix}, \quad [F]=\begin{pmatrix} 0 & 1 & 0 & \cdots & 0 \\ 0 & 0 & 2 & \ddots & \vdots \\ \vdots & & \ddots & \ddots & 0 \\ \vdots & & & \ddots & M \\ 0 & 0 & \cdots & \cdots & 0 \end{pmatrix},$$

$$[J]=\begin{pmatrix} 0 & 0 & 0 & \cdots & 0 \\ 1 & 0 & 0 & \ddots & \vdots \\ 0 & 1 & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & \ddots & 0 \\ 0 & \cdots & 0 & 1 & 0 \end{pmatrix},$$

$$[G_{1,n}]=\begin{pmatrix} \frac{n}{\tau_{\mathrm{el}}} & 1 & 0 & \cdots & \cdots & \cdots & 0 \\ -\frac{kT}{I} & \frac{n}{\tau_{\mathrm{el}}} & 2 & \ddots & & & \vdots \\ 0 & -\frac{kT}{I} & \ddots & \ddots & \ddots & & \vdots \\ \vdots & \ddots & \ddots & \ddots & \ddots & \ddots & \vdots \\ \vdots & & \ddots & \ddots & \ddots & \ddots & 0 \\ \vdots & & & \ddots & \ddots & \ddots & M \\ 0 & \cdots & \cdots & \cdots & 0 & -\frac{kT}{I} & \frac{n}{\tau_{\mathrm{el}}} \end{pmatrix},$$

$$[C^{(0)}_{0,n}]=[J][B^{(0)}_{0,n}], \quad [B^{(0)}_{0,n}]=\begin{pmatrix} {}^{(0)}b_0^{0,n}\\ {}^{(0)}b_0^{1,n}\\ {}^{(0)}b_0^{2,n}\\ \vdots \\ {}^{(0)}b_0^{M,n}\end{pmatrix} = {}^{(0)}b_0^{0,0}\begin{pmatrix}\delta_{n,0}\\ 0\\ 0\\ \vdots\\ 0\end{pmatrix}. \tag{34}$$

By varying $n$ now from 0 to $N$ we can put

$$[\mathcal{B}_1]=\begin{pmatrix}[B^{(1)}_{1,0}]\\ [B^{(1)}_{1,1}]\\ [B^{(1)}_{1,2}]\\ \vdots\\ [B^{(1)}_{1,N}]\end{pmatrix}, \tag{35}$$

and Eq. (33) becomes

$$[\dot{\mathcal{B}}_1]+[A_1][\mathcal{B}_1]=-\frac{\mu E}{2I}[\mathcal{C}_0], \tag{36}$$

where $[A_1]$ is the viscoelastic dielectric matrix characteristic of the system under consideration, the dimension of which is $(M+1)(N+1)\times(M+1)(N+1)$, viz.,

$$[A_1] = \begin{pmatrix} [G_{1,0}] & -[J] & 0 & \cdots & 0\\ \dfrac{\xi}{I\tau_{\mathrm{el}}}[F] & [G_{1,1}] & -2[J] & \ddots & \vdots\\ 0 & \dfrac{\xi}{I\tau_{\mathrm{el}}}[F] & \ddots & \ddots & 0\\ \vdots & \ddots & \ddots & \ddots & -N[J]\\ 0 & \cdots & 0 & \dfrac{\xi}{I\tau_{\mathrm{el}}}[F] & [G_{1,N}] \end{pmatrix},$$

and

$$[\mathcal{C}_0]=[J][\mathcal{B}_0], \quad [\mathcal{B}_0]=\begin{pmatrix}[B^{(0)}_{0,0}]\\ [B^{(0)}_{0,1}]\\ \vdots\\ [B^{(0)}_{0,N}]\end{pmatrix}=\begin{pmatrix}[B^{(0)}_{0,0}]\\ [0]\\ \vdots\\ [0]\end{pmatrix}. \tag{37}$$

As appears in Eq. (32) as well in matrices $[G_{1,n}]$ and $[A_1]$, we see that three time scales may be distinguished, namely, $\tau_{\mathrm{el}}$, $\sqrt{\tau_F\tau_{\mathrm{el}}}$, and $\sqrt{\tau\tau_F}$, since $kT/I=(kT/\xi)(\xi/I)=1/(\tau\tau_F)$, and $\xi/(I\tau_{\mathrm{el}})=1/\tau_F\tau_{\mathrm{el}}$. When viscoelasticity is taken into account together with inertia, this demonstrates both resulting effects are coupled and cannot be separated.

## IV. EXPRESSION FOR THE DYNAMIC SUSCEPTIBILITY

We shall solve Eq. (36) when $E(t)$ is an alternating electric field applied at time $t=0$. Taking the Fourier transform of both sides of Eq. (36), one finds

$$\begin{aligned}[][\tilde{\mathcal{B}}(\Omega)]=&-\{i\Omega[\mathbf{I}]+[A_1]\}^{-1}\pi\lambda_0[J][\mathcal{B}_0]\\ &\times[\delta(\omega-\Omega)+\delta(\omega+\Omega)],\end{aligned} \tag{38}$$

where

$$[\tilde{\mathcal{B}}(\Omega)]=\int_{-\infty}^{+\infty}[\mathcal{B}_1(t)]e^{-i\Omega t}dt,$$

$$\lambda_0=\frac{\mu E_0}{2I},$$

and $[\mathbf{I}]$ is the identity matrix.

So, the time evolution of $[\mathcal{B}_1(t)]$, which is suitable for the viscoelastic dielectric relaxation, may be easily performed by inverting the terms of Eq. (38) in the time domain

$$[\mathcal{B}_1(t)]=\mathrm{Re}\ \lambda_0\{i\omega[\mathbf{I}]+[A_1]\}^{-1}[J][\mathcal{B}_0]e^{i\omega t}, \tag{39}$$

where Re means ‘‘real part of.’’

In view of the calculation of $\langle\cos\theta\rangle(t)$ in Eq. (31), which is essentially given by ${}^{(1)}b_1^{0,0}(t)$, it suffices to take the first component of $[\mathcal{B}_1(t)]$ corresponding to $n=0$ and then to consider the first element of the vector $[B^{(1)}_{1,0}]$ where $m=0$. Hence, the only useful quantity we need to evaluate in the right-hand side of Eq. (39) is the element $a_{12}$ in the first row and second column of the adjoint matrix of $(i\omega[\mathbf{I}]+[A_1])$ since $[J][\mathcal{B}_0]$ reduces to

$$[J][\mathcal{B}_0]={}^{(0)}b_0^{0,0}\begin{pmatrix}0\\ 1\\ 0\\ 0\\ \cdot\\ \cdot\\ \cdot\end{pmatrix}. \tag{40}$$

By putting

$$[\mathcal{A}_1]=i\omega[\mathbf{I}]+[A_1],$$

$$\det[\mathcal{A}_1]=A(\omega)+iB(\omega)$$

$$a_{12}(\omega)=a(\omega)+ib(\omega),$$

(where det denotes ‘‘determinant of’’) we have

$$\begin{aligned}\langle\cos\theta\rangle(t)&=\mathrm{Re}\left[\lambda_0\frac{a_{12}(\omega)}{\det[\mathcal{A}_1]}(\cos\omega t+\sin\omega t)\right],\\ &=\frac{\lambda_0}{A^2+B^2}[(Aa+Bb)\cos\omega t\\ &\quad+(Ba-bA)\sin\omega t].\end{aligned} \tag{41}$$

The electric polarization $P(t)$ is therefore given by

$$P(t)=\mathcal{N}\mu\langle\cos\theta\rangle(t)=\mathrm{Re}[\varepsilon_0\chi(\omega)E_0e^{i\omega t}], \tag{42}$$

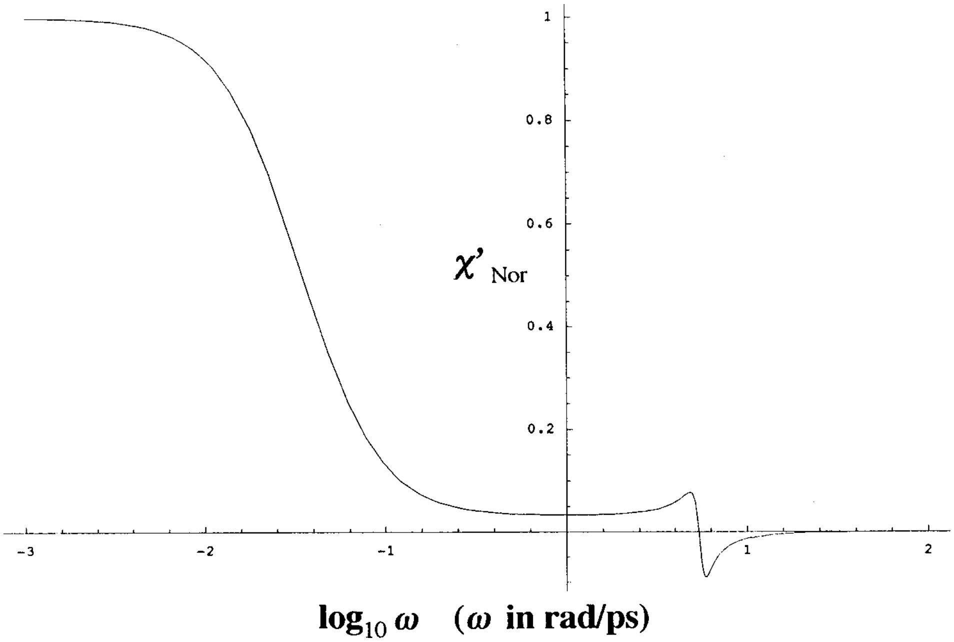

FIG. 1. Plot of the real part of the normalized electric susceptibility $\chi'_{\mathrm{Nor}}$ as a function of the angular frequency $\omega$ for $\alpha^2=1$, $\beta=30$, and $\gamma=1$ (case of small viscoelasticity $\tau_{\mathrm{el}}/\tau \ll 1$).

where $\mathcal{N}$ is the number of dipoles per unit volume, $\chi(\omega)=\chi'(\omega)-i\chi''(\omega)$ the complex electric susceptibility, and $\varepsilon_0$ the absolute dielectric permittivity of the liquid. The real and imaginary parts of $\chi(\omega)$ are

$$\chi'(\omega)=\frac{\mathcal{N}\mu^2}{2\varepsilon_0 I}\frac{Aa+Bb}{A^2+B^2},$$
$$\chi''(\omega)=\frac{\mathcal{N}\mu^2}{2\varepsilon_0 I}\frac{Ba-bA}{A^2+B^2}. \tag{43}$$

For numerical convenience, we shall rather consider the normalized expressions $\chi'_{\mathrm{Nor}}(\omega)$ and $\chi''_{\mathrm{Nor}}(\omega)$, the subscript ''Nor'' standing for normalized

$$\chi'_{\mathrm{Nor}}(\omega)=\frac{\chi'(\omega)}{\chi'(0)},\quad \chi''_{\mathrm{Nor}}(\omega)=\frac{\chi''(\omega)}{\chi'(0)}, \tag{44}$$

where $\chi'(0)$ is the value of $\chi'(\omega)$ at zero frequency.

The dynamic step-on response that we have derived in Eq. (41) deviates considerably from the simple Debye model, in the sense that such a response is strictly nonlinear insofar as both inertial and viscoelastic effects are taken into account.

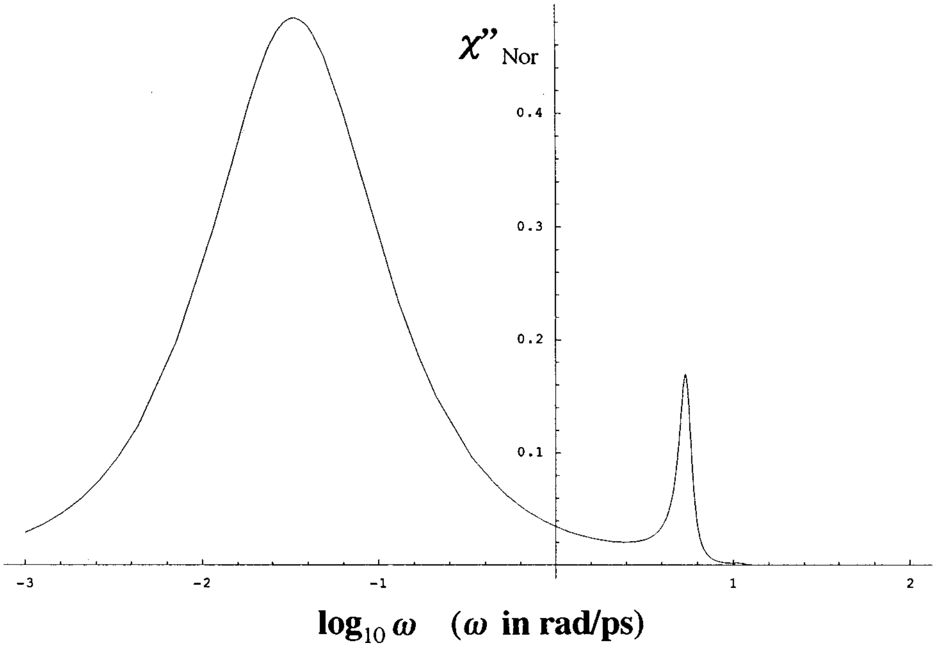

FIG. 2. Plot of the imaginary part of the normalized electric susceptibility $\chi''_{\mathrm{Nor}}$ as a function of the angular frequency $\omega$ for $\alpha^2=1$, $\beta=30$, and $\gamma=1$.

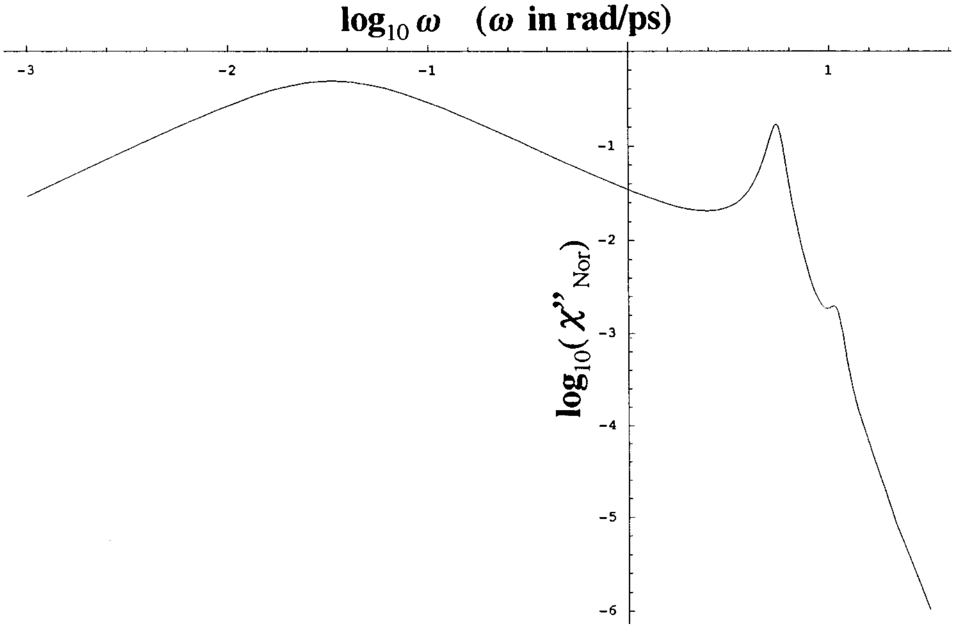

FIG. 3. Plot of the logarithm of $\chi''_{\rm Nor}$ (dielectric loss) as a function of the angular frequency $\omega$. Note the presence of a small resonant peak practically invisible in Fig. 2. The parameters $\alpha^2$, $\beta$, and $\gamma$ have the same values as in Figs. 1 and 2.

However, we recall that our calculation is confined to the linear approximation in the electric field strength (first order perturbation).

### V. DISPERSION AND ABSORPTION SPECTRA

Two series of dispersion $\chi'_{\rm Nor}(\omega)$ and absorption $\chi''_{\rm Nor}(\omega)$ spectra have been plotted by varying the $S1$ set of three parameters, $\alpha=\sqrt{kT/I}=1/\sqrt{\tau\tau_F}$, $\beta=1/\tau_F$, $\gamma=1/\tau_{\rm el}$, one pertaining to small viscoelasticity, the other to moderate viscoelasticity. All these curves present resonant behavior at high frequencies, clearly identified by at least one resonant peak for $\chi''_{\rm Nor}(\omega)$ that never becomes negative, and by the negative values attained by $\chi'_{\rm Nor}(\omega)$ in these regions. As long as elasticity and inertia remain small, the Debye-like profiles lying in the low-frequency band are practically unaffected, the maximum of $\chi''_{\rm Nor}(\omega)$ being slightly less than 0.5 and shifted to the right as expected when inertia is considered. The beginning of inertial and elastic effects can be detected by the broadening of these profiles in their terminal part (low frequency, inertia-corrected Debye theory). This is shown in Figs. 1 and 2 where our choice of the $S1$ set corresponds to $\tau_F/\tau=1.1\times10^{-3}$ and $\tau_{\rm el}/\tau=0.0333$ $(\tau_{\rm el}<\tau)$. In Fig. 2, we note the occurrence of a relatively damped FIR peak accompanied by an almost imperceptible second peak (strongly damped) best viewed in Fig. 3 where a log-log scale (dielec-

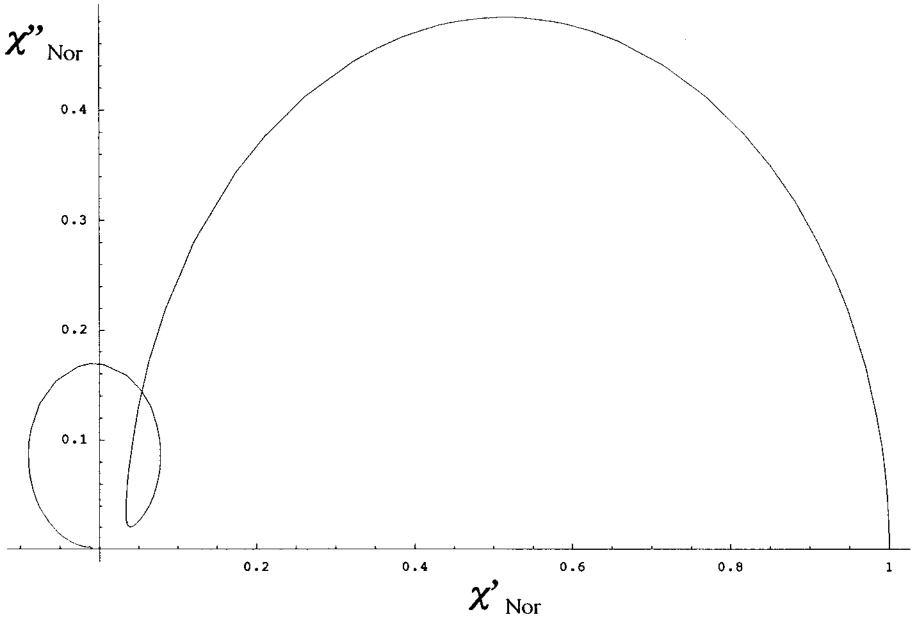

FIG. 4. Cole-Cole diagram. Note the occurrence of a loop in the high-frequency region. The parameters $\alpha^2$, $\beta$, and $\gamma$ have the same values as in Figs. 1 and 2.

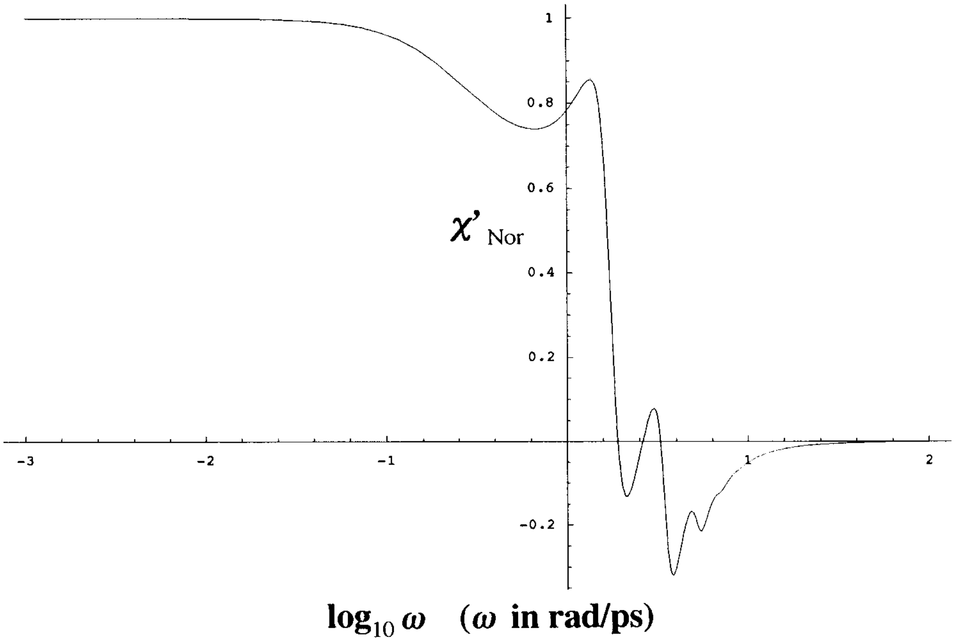

FIG. 5. Plot of the real part of the normalized electric susceptibility $\chi'_{\mathrm{Nor}}$ as a function of the angular frequency $\omega$ for $\alpha^2=4$, $\beta=15$, and $\gamma=0.2$ (case of moderate viscoelasticity $\tau_{\mathrm{el}}/\tau \geqslant 1$).

tric loss) has been used. We have thought interesting to plot a Cole-Cole diagram as well, as illustrated in Fig. 4 in order to show how it deviates from the usual Debye semicircle. At low to mid frequencies, the familiar and skewed semicircle is recovered, terminated by a loop at high frequencies. These results have been obtained by truncating the $[A_1]$ matrix at $M=N=3$, which was sufficient for ensuring correct convergence (six significant digits) with our choice of the $S1$ parameter set. In Figs. 5–7, analogous curves are presented, but this time with $\tau_F/\tau=1.77\times10^{-2}$ and $\tau_{\mathrm{el}}/\tau=1.333$ $(\tau_{\mathrm{el}}>\tau)$. These values correspond to a new set of parameters $\alpha$, $\beta$, $\gamma$ $(S2)$ such that viscoelastic effects are much more pronounced than with $S1$ and manifest themselves by higher resonant peaks causing a large damping of the Debye absorption. This is in accordance with the results presented by Raĭkher and Rusakov [15] for a magnetic suspension in a viscoelastic fluid [see their Fig. 1(b)] and obtained from a quite different theoretical approach. Moreover, we can verify the equidistance between these peaks, the maximum of the first one being far more than 0.5, about 1.12. The Cole-Cole diagram presented in Fig. 8 shows how the shape of this plot is affected in its early part (flattening) by the viscoelastic strength. As angular frequency increases, the maximum height of the arc reaches approximately 1.12, which is much

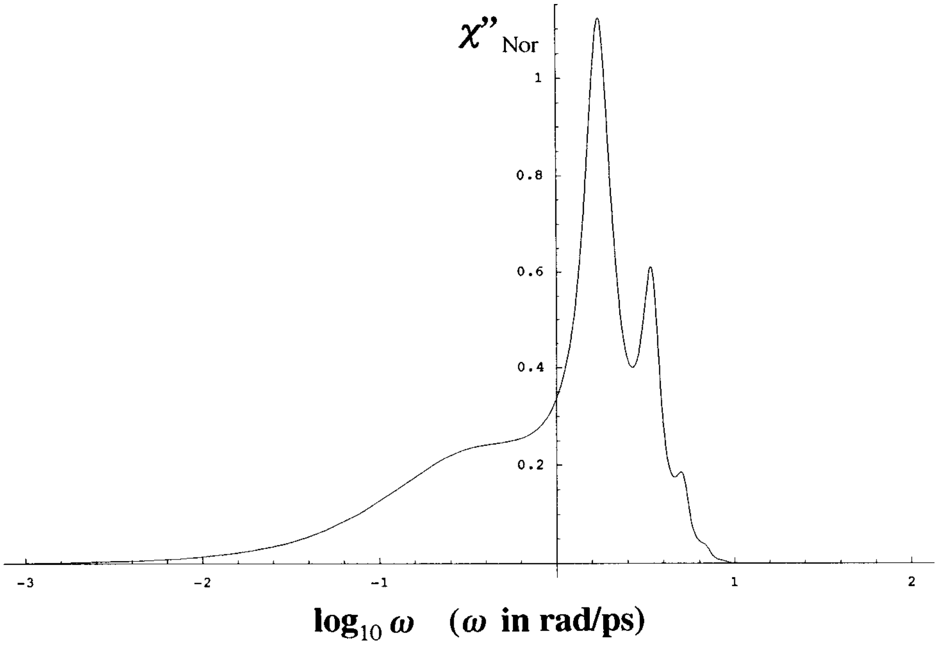

FIG. 6. Plot of the imaginary part of the normalized electric susceptibility $\chi''_{\mathrm{Nor}}$ as a function of the angular frequency $\omega$ for $\alpha^2=4$, $\beta=15$, and $\gamma=0.2$.

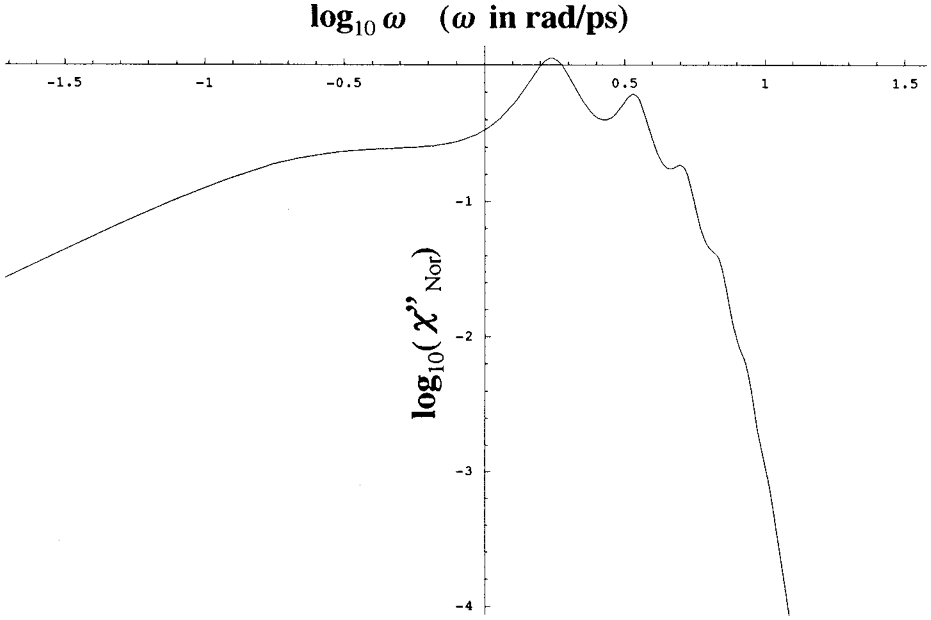

FIG. 7. Plot of the logarithm of $\chi''_{\mathrm{Nor}}$ (dielectric loss) as a function of the angular frequency $\omega$. Four equidistant and resonant peaks can be distinguished. The parameters $\alpha^2$, $\beta$, and $\gamma$ have the same values as in Figs. 5 and 6.

more than 0.5, the well-known value obtained in a pure Debye relaxation process. The last portion is characterized by loops reflecting the competition between the fast variables $\dot{\theta}$ (angular velocity) and $Z$ (angular acceleration). In other words, at very high frequencies, there is duality between inertia and elasticity, two strongly coupled physical entities. The resonant nature of our viscoelastic system produces harmonics arising from the coupling effect of the electric field with the molecules in the liquid, the frequency of which is a multiple of the natural frequency of the medium in the absence of any external perturbation. Starting from the Langevin equation [Eq. (9)] written in zero electric field and averaging over the whole assembly of particles, we have indeed

$$\langle \ddot{\omega}(t) \rangle + \frac{1}{\tau_{\mathrm{el}}} \langle \dot{\omega}(t) \rangle + \frac{1}{\tau_F \tau_{\mathrm{el}}} \langle \omega(t) \rangle = 0$$

or

$$\langle \ddot{\omega}(t) \rangle + \gamma \langle \dot{\omega}(t) \rangle + \beta\gamma \langle \omega(t) \rangle = 0, \tag{45}$$

where $\beta\gamma$ is the natural angular frequency. This second-order differential equation has oscillatory behavior only if the condition $\beta > \gamma/4$ is filled. This is precisely the case for the values chosen in $S1$ and $S2$ parameter sets. So, in the presence of an alternating field varying at the fundamental frequency $\omega$, resonance occurs every time that $\omega$ equals or is a multiple

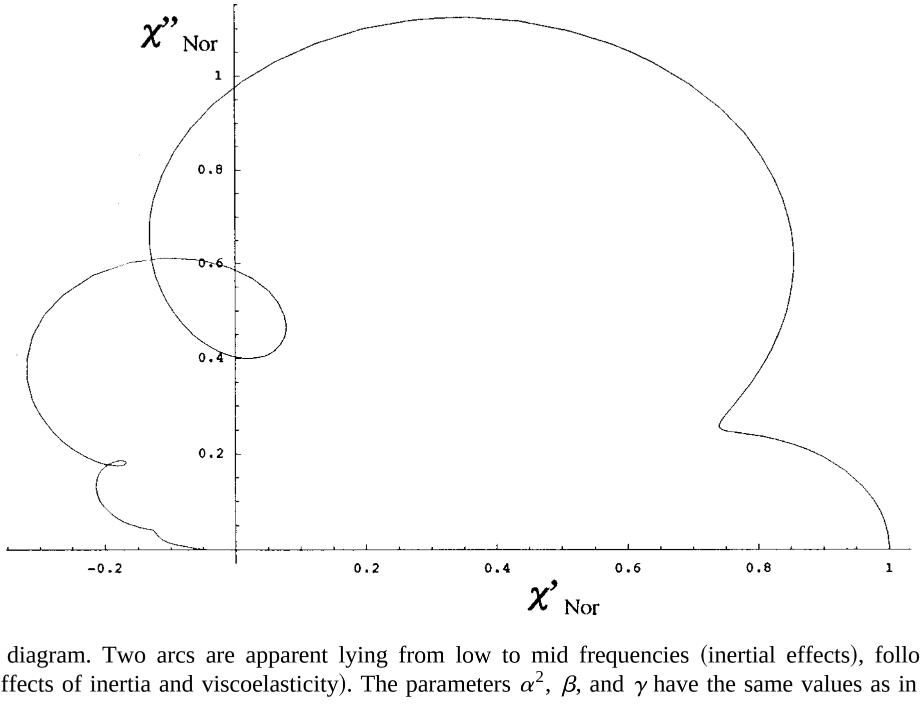

FIG. 8. Cole-Cole diagram. Two arcs are apparent lying from low to mid frequencies (inertial effects), followed by loops at high frequencies (coupled effects of inertia and viscoelasticity). The parameters $\alpha^2$, $\beta$, and $\gamma$ have the same values as in Figs. 5 and 6.

of $\beta\gamma$. The values of $M$ and $N$ needed for $S2$ until convergence is achieved are $M=16$, $N=12$, i.e., a $221\times221$ $[A_1]$ matrix.

## VI. CONCLUSIONS

We have derived a complete solution for the dielectric response arising from the sudden application of an alternating electric field to an assembly of dipole molecules moving in a viscoelastic liquid. Starting from the generalized Langevin equation with memory kernel, which is in essence non-Markovian, we have defined a three-dimensional Markov process in the variables $\theta$, $\dot{\theta}$, and $Z$ and established the underlying viscoelastic FPK equation. In order to solve this equation, we have used a matrix formulation in the same manner as that previously employed for Kerr effect relaxation including inertia only [16,18]. This procedure leads to a set of differential-recurrence equations of Brinkman type with three indices, $p$, $m$, and $n$, whence an expression for the complex dynamic susceptibility is established to first order in the electric field strength. By varying the size of the viscoelastic dielectric matrix $[A_1]$, we can calculate the nonlinear step-on dielectric response for any values of $\alpha$, $\beta$, and $\gamma$ accounting for the effect of coupling of molecular inertia and viscoelasticity on the orientational relaxation in liquids.

This model, although simplified, gives nevertheless interesting results on the resonant structure of the peaks in the FIR range. As recently pointed out [27], a better description of molecular interactions with their thermal environment would consist in considering dielectric absorption not only due to dipole permanent moments but also to induced dipole moments. This is possible with our approach by calculating $\langle\cos\theta\rangle(t)$ up to the third order in $E_0^3$ at least, but the mathematical task becomes more complicated and the numerical analysis longer (treatment of huge matrices). Moreover, our theoretical procedure cannot be compared effectively with the itinerant oscillator model [28–31] where a truncation of the Mori continued fraction at its second convergent is needed. The corresponding orientational probability density function $W$ would depend therefore on four variables, which would lead to a Brinkman equation with four indices.

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