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Cage model of polar fluids: Finite cage inertia generalization

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The itinerant oscillator model describing rotation of a dipole about a fixed axis inside a cage formed by its surrounding polar molecules is revisited in the context of modeling the dielectric relaxation of a polar fluid via the Langevin equation. The dynamical properties of the model are studied by averaging the Langevin equations describing the complex orientational dynamics of two bodies (molecule-cage) over their realizations in phase space so that the problem reduces to solving a system of three index linear differential-recurrence relations for the statistical moments. These are then solved in the frequency domain using matrix continued fractions. The linear dielectric response is then evaluated for extensive ranges of damping, dipole moment ratio, and cage-dipole inertia ratio and along with the usual inertia corrected microwave Debye absorption gives rise to significant far-infrared absorption with a comb-like structure of harmonic peaks. The model may be also regarded as an extension of Budó's [J. Chem. Phys. **17**, 686 (1949)] treatment of molecules containing rotating polar groups to include inertial effects. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4993791]

I. INTRODUCTION

The cage model or itinerant oscillator[1–6] introduced by Hill[7,8] and Sears[9] is a schematic representation of the dynamical behavior of a molecule in a fluid embodying the fact that a typical molecule of the fluid may vibrate about a temporary equilibrium position. Sears[9] used a translational version of the model to evaluate the velocity correlation function for liquid argon, while Hill[7,8] used a two-dimensional rotational version to explain relaxation (Debye) and far-infrared (FIR) absorption spectrum of dipolar fluids. Hill considered a specific mechanism whereby at any instant an individual polar molecule may be regarded as confined to a temporary equilibrium position in the potential well created by its cage of polar nearest neighbors, where the potential energy surface may in general have several minima. The molecule is considered to librate in this cage, i.e., execute torsional oscillations about temporary equilibrium positions. The Brownian motion of the cage gives rise to the Debye absorption,[10,11] while the librational motion of the molecule gives rise to the resonance absorption in the far infrared region. Using an approximate analysis of this model based on the Smoluchowski equation[10] for the rotational diffusion of an assembly of non-interacting dipolar molecules, Hill demonstrated that the frequency of the FIR absorption peak is inversely proportional to the square root of the moment of inertia of a molecule. Hill's treatment based on the small oscillation (harmonic potential) approximation was further expanded upon, using the Langevin equation of the theory of the Brownian motion, in a series of papers by Wyllie[12,13] and by Coffey *et al.*[14–17] The angular velocity and orientational correlation functions were explicitly evaluated in the small oscillation approximation.[5,6,10] These results are summarized in Refs. 1 and 2. All these analyses, however, invariably rely on a small oscillation approximation because no reliable method of treating the finite oscillations of a pendulum when the Brownian torques are included had existed. Thus, some of the most important nonlinear aspects of the relaxation processes were omitted, an example being the dependence of the frequency of oscillation of the dipole on the amplitude of the oscillation. A preliminary attempt to include nonlinear or anharmonic effects (cosine potential) has been made in Refs. 17 and 18. The equations of motion of the model when the restriction to fixed axis rotation is relaxed were given by Coffey.[18] Recently it became possible to treat the Brownian motion in a potential other than a parabolic one in a general fashion using matrix continued fractions.[19] The solution was illustrated[19] by considering the Brownian motion of a rotator in a cosine potential with a *fixed* equilibrium position.

The various applications to chemical physics are discussed extensively in Refs. 20–24. Yet another application of the model is relaxation of ferrofluids[25] (colloidal suspensions of single-domain ferromagnetic particles). A three-dimensional rotational version excluding inertial effects, termed an "egg model," has been used by Shliomis and Stepanov,[26] to simultaneously explain the Brownian and Néel relaxation in ferrofluids,[25] which are due to the rotational diffusion of the particles and random reorientations of the magnetization inside the particles, respectively. The analysis in the context of ferrofluids yields similar equations of motion to those given by Damle *et al.*[27] and by van Kampen[28] for the translational itinerant oscillator. This formulation has the advantage that, in the noninertial limit, the equations of motion automatically decouple into those of the molecule and its surroundings (cage). Such a decoupling of the exact equations of motion is also possible in the inertial case if we assume a massive cage. These results are summarized in Refs. 6 and 10. Moreover in Ref. 6, it was also shown how to extend the model to the fractional time random walk process where the characteristic waiting time between encounters of molecules is divergent.

The disadvantage of all these analyses, however, is that due to the inherent mathematical difficulties arising from the intrinsically nonlinear nature of the governing Langevin equations, they invariably rely on the assumption that the inertia of the molecule is much smaller than the inertia of the cage. The assumption allows one to decouple the equations of motion into the equation of motion of the cage itself which is just that of a free inertial rigid Brownian rotator and the motion of the encaged dipole or tagged molecule alone which is that of an inertial rigid Brownian rotator in a sinusoidal potential. Hence all the correlation functions of the model may be given in a closed form. However, in using this *ansatz*, some of the most important aspects of the relaxation processes are unavoidably omitted, for example, the perturbation of the cage rotation by the molecule. As a result, the relaxation modes of the system separate into those of the tagged molecule and those of its surroundings, irrespective of the form of the interaction potential between the cage and the tagged molecule, which in general is not physical.

It is the purpose of this paper to illustrate using linear response theory (which relates the ac response to the step-off response following the removal of a constant field **F**) how the itinerant oscillator model may be solved exactly for the first time for the case of *finite inertia of the cage* as compared to that of the molecule. In this case, the rotational motion of the cage is no longer independent and is undoubtedly influenced by the probe. The treatment of a cage with finite inertia may be justified as follows. In solid bodies (e.g., ferromagnetic particles), the internal potentials are due to the crystalline structure of the bodies and in consequence are rather stable.[10] This is not true of fluids and dense liquids where the angular displacement of the surroundings is comparable with the displacement of a probe. Hence it is reasonable to conceive of the cage as undergoing drift or diffusive motion as it is intrinsic to the model. If the number of molecules surrounding the probe is not very large, it also seems reasonable to use finite cage inertia. Then the rotation of the cage can no longer be simplified by treating it as merely rotational Brownian motion of a heavy object since it must now be described in a more complicated manner as rotation *perturbed by the probe molecule*.

We shall describe the cage model mainly in the context of the theory of dielectric relaxation. By averaging the Langevin equations describing the complex dynamics of two bodies (molecule-cage) over its realizations, the problem is first reduced to solving a system of linear differential-recurrence relations for the statistical moments. It is then shown how these three-term differential-recurrence relations may be formally solved for the Fourier transform of the after-effect function via matrix continued fractions, thereby allowing one to exactly analyze the susceptibility spectrum $\chi(\omega)$ of the model regardless of the inertia ratio and dipole-cage interaction strength. In this form, the model may be regarded as an extension of Budó's[29] treatment of molecules containing rotating polar groups to include inertial effects, thereby automatically leading to far infrared resonance (THz) absorption as well as the accompanying microwave Debye absorption so that both absorptions may be linked together in the same model.

II. SOLUTION OF THE LANGEVIN EQUATIONS FOR A DIPOLE INTERACTING WITH ITS SURROUNDINGS

A typical member of a system of dipolar molecules (specified by an angle ϕ_1) and cage (specified by an angle ϕ_2) rotating about a fixed axis in an external uniform dc applied field **F** (which is needed in order to use linear response theory) is in general governed by a Hamiltonian H given by

$$H = \frac{1}{2}I_1\dot{\phi}_1^2 + \frac{1}{2}I_2\dot{\phi}_2^2 - \mu_1 F\cos\phi_1 - \mu_2 F\cos\phi_2 - \mu_1 R\cos(\phi_1 - \phi_2), \tag{1}$$

where $F = |\mathbf{F}|$, μ_1 and I_1 are the dipole moment and the moment of inertia of the molecule, respectively, and μ_2 and I_2 are the dipole moment and the moment of inertia of the surroundings (i.e., the cage), respectively. The final term in Eq. (1) represents the dipole-cage interaction, where R is the reaction field of the surroundings[10] which represents their influence on the probe molecule. Here we shall use the quasi-stationary approximation for the reaction field $R(t) = R$. The equation of motion of the encaged polar molecule in the external uniform dc field and the field of the rotating cage is in accordance with that of van Kampen,[30]

$$I_1\ddot{\phi}_1(t) = \zeta_1\left(\dot{\phi}_2(t) - \dot{\phi}_1(t)\right) - \mu_1 R\sin(\phi_1(t) - \phi_2(t)) - \mu_1 F\sin\phi_1(t) + \lambda_1(t). \tag{2}$$

The terms $\zeta_1\left(\dot{\phi}_2(t) - \dot{\phi}_1(t)\right)$ and $\lambda_1(t)$ represent the dissipative and fluctuating Brownian torques acting on the molecule due to the heat bath. The equation of motion of the cage in the presence of the dc field **F** and the field of the polar molecule is on applying Newton's third law[30]

$$I_2\ddot{\phi}_2(t) = \zeta_1\left(\dot{\phi}_1(t) - \dot{\phi}_2(t)\right) - \zeta_2\dot{\phi}_2(t) - \mu_1 R\sin(\phi_2(t) - \phi_1(t)) - \mu_2 F\sin\phi_2(t) - \lambda_1(t) + \lambda_2(t). \tag{3}$$

The terms $-\zeta_2\dot{\phi}_2(t)$ and $\lambda_2(t)$ are again the dissipative and the stochastic torques on the surroundings of the cage which are generated by the heat bath in which the cage is embedded. In Eqs. (2) and (3), the white noise torques $\lambda_i(t)$ are centered Gaussian random variables with correlation functions

$$\overline{\lambda_i(t)\,\lambda_i(t')} = 2kT\zeta_i\delta(t - t'), \tag{4}$$

where kT is the thermal energy (k is Boltzmann's constant).

In order to use linear response theory, we consider the special case where a small external dc field **F**, which has been applied to the system in the infinite past, is suddenly switched off at time $t = 0$. In our study, we are interested in the relaxation of the system consisting of the cage and embedded dipole, starting from an initial equilibrium state at $t = 0$ with the Maxwell-Boltzmann distribution function $W_F(\phi_1, \phi_2, \dot{\phi}_1, \dot{\phi}_2)$ given by

$$W_F(\phi_1, \phi_2, \dot{\phi}_1, \dot{\phi}_2) = Z_F^{-1} e^{-\eta_1^2\dot{\phi}_1^2 - \eta_2^2\dot{\phi}_2^2 + \xi_1 \cos\phi_1 + \xi_2 \cos\phi_2 + \xi_{\text{int}} \cos(\phi_1 - \phi_2)} \tag{5}$$

to another equilibrium state as $t \to \infty$ with the new Maxwell-Boltzmann distribution function

$$W_0(\phi_1, \phi_2, \dot{\phi}_1, \dot{\phi}_2) = W_{F=0}(\phi_1, \phi_2, \dot{\phi}_1, \dot{\phi}_2) = Z_0^{-1} e^{-\eta_1^2\dot{\phi}_1^2 - \eta_2^2\dot{\phi}_2^2 + \xi_{\text{int}} \cos(\phi_1 - \phi_2)}. \tag{6}$$

Here Z_F is the partition function defined as

$$Z_F = \int_0^{2\pi}\int_0^{2\pi}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\eta_1^2\dot{\phi}_1^2 - \eta_2^2\dot{\phi}_2^2 + \xi_1 \cos\phi_1 + \xi_2 \cos\phi_2 + \xi_{\text{int}} \cos(\phi_1 - \phi_2)} \times d\dot{\phi}_1 d\dot{\phi}_2 d\phi_1 d\phi_2,$$

where $\eta_1 = \sqrt{I_1/(2kT)}$ and $\eta_2 = \sqrt{I_2/(2kT)}$ are characteristic time constants, $\xi_1 = \mu_1 F/(kT)$ and $\xi_2 = \alpha\xi_1 = \mu_2 F/(kT)$ are the field-dipole and field-cage interaction parameters, $\alpha = \mu_2/\mu_1$ is the ratio of dipole moments, and $\xi_{\text{int}} = \mu_1 R/(kT)$ is the dipole-cage interaction parameter. The dynamics of the cage-dipole system immediately following the removal of the external dc field may be described using the normalized relaxation function

$$C(t) = \frac{\varphi(t) + \psi(t)}{\varphi(0) + \psi(0)}, \quad t > 0, \tag{7}$$

where we have defined the individual response functions

$$\varphi(t) = \mu_1 \left(\langle\cos\phi_1\rangle(t) - \langle\cos\phi_1\rangle_0\right), \tag{8}$$

$$\psi(t) = \mu_2 \left(\langle\cos\phi_2\rangle(t) - \langle\cos\phi_2\rangle_0\right). \tag{9}$$

Here the angular brackets $\langle A\rangle(t)$ are the time-dependent ensemble averages associated with an observable A and the brackets $\langle A\rangle_0$ designate the *equilibrium* ensemble averages, namely,

$$\langle A\rangle_0 = \int_0^{2\pi}\int_0^{2\pi}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} A(\phi_1, \phi_2, \dot{\phi}_1, \dot{\phi}_2) W_0(\phi_1, \phi_2, \dot{\phi}_1, \dot{\phi}_2) \times d\dot{\phi}_1 d\dot{\phi}_2 d\phi_1 d\phi_2. \tag{10}$$

In the linear approximation in the applied dc field, $\mu_i F/(kT) \ll 1$, the initial conditions for the functions $\varphi(t)$ and $\psi(t)$ are

$$\varphi(0) \approx \frac{F}{kT}\left[\mu_1^2\left(\left\langle\cos^2\phi_1\right\rangle_0 - \langle\cos\phi_1\rangle_0^2\right) + \mu_1\mu_2 \times \left(\langle\cos\phi_1\cos\phi_2\rangle_0 - \langle\cos\phi_1\rangle_0\langle\cos\phi_2\rangle_0\right)\right], \tag{11}$$

$$\psi(0) \approx \frac{F}{kT}\left[\mu_2^2\left(\left\langle\cos^2\phi_2\right\rangle_0 - \langle\cos\phi_2\rangle_0^2\right) + \mu_1\mu_2 \times \left(\langle\cos\phi_1\cos\phi_2\rangle_0 - \langle\cos\phi_1\rangle_0\langle\cos\phi_2\rangle_0\right)\right]. \tag{12}$$

Thus, the individual response function $\varphi(t)$ now refers to the embedded dipole while $\psi(t)$ refers to that of the surroundings. Since we have assumed in order to use linear response theory that the initial amplitude F of the external uniform dc field is small ($\mu_i F/(kT) \ll 1$), the complex susceptibility $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$ and so the ac response of such an assembly can then be determined from the linear response theory formula[31,32]

$$\frac{\chi(\omega)}{\chi} = 1 - i\omega\int_0^{\infty} C(t)e^{-i\omega t}dt, \tag{13}$$

where $\chi = \chi'(0) = [\varphi(0) + \psi(0)]\,F^{-1}$ is the static susceptibility and the normalized relaxation function $C(t)$ is given by Eqs. (7)–(9).

III. MATRIX CONTINUED FRACTION SOLUTION FOR THE RESPONSE FUNCTION

The one-sided Fourier transform of the normalized relaxation function $C(t)$ is calculated as follows. As shown in Appendix A, the Langevin equations, Eqs. (2) and (3), can be transformed into differential-recurrence equations for the statistical moments $f_{m_2\, q_2}^{m_1\, q_1}(t)$ pertaining to the observables, which are given by

$$f_{m_2\, q_2}^{m_1\, q_1}(t) = \left\langle H_{m_1}(\eta_1\dot{\phi}_1) H_{m_2}(\eta_2\dot{\phi}_2) e^{-iq_1\phi_1} e^{-iq_2\phi_2}\right\rangle(t), \quad m_i = 0, 1, 2\ldots,\ q_i = 0, \pm 1, \pm 2\ldots, \tag{14}$$

where $H_m(z)$ are the Hermite polynomials. The ensuing calculation advantage is that (in this step-off case) the indices q_1 and q_2 are no longer independent of each other; thus, we may introduce the simplified moments $c_{m_1\, m_2}^{q}(t) = f_{m_2\, -q+1}^{m_1\, q}(t)$ associated with the expectation values of observables. Finally taking account of the general form of the differential-recurrence equations for the functions $f_{m_2\, q_2}^{m_1\, q_1}(t)$ from Appendix A, Eq. (A6), we have the corresponding differential-recurrence equations for the moments $c_{m_1\, m_2}^{q}(t)$ (where the external field parameters ξ_1 and ξ_2 are now zero), viz.,

$$\begin{aligned}\eta\frac{d}{dt}c_{m_1\, m_2}^{q} = &-\left(\gamma_1\beta_1 m_1 + \frac{\gamma_2^2}{\gamma_1}\beta_1 m_2 + \gamma_2\beta_2 m_2\right)c_{m_1 m_2}^{q} + \gamma_2\beta_1 m_2 c_{m_1+1\, m_2-1}^{q} + \gamma_2\beta_1 m_1 c_{m_1-1\, m_2+1}^{q} + 2\gamma_2\beta_1 m_1 m_2 c_{m_1-1 m_2-1}^{q} \\ &- 2\frac{\gamma_2^2}{\gamma_1}\beta_1 m_2\,(m_2 - 1)\,c_{m_1\, m_2-2}^{q} + \frac{i\xi_{\text{int}}}{2}\left[\gamma_1 m_1\left(c_{m_1-1\, m_2}^{q-1} - c_{m_1-1\, m_2}^{q+1}\right) + \gamma_2 m_2\left(c_{m_1\, m_2-1}^{q+1} - c_{m_1\, m_2-1}^{q-1}\right)\right] \\ &- \frac{i}{2}\gamma_1 q\left(c_{m_1+1 m_2}^{q} + 2m_1 c_{m_1-1 m_2}^{q}\right) + \frac{i}{2}\gamma_2(q-1)\left(c_{m_1 m_2+1}^{q} + 2m_2 c_{m_1 m_2-1}^{q}\right).\end{aligned} \tag{15}$$

Here $\eta^{-1} = \eta_1^{-1} + \eta_2^{-1}$, $\gamma_i = \eta/\eta_i$ is an inertia ratio, and all other notations are given in Appendix A. The set of Eq. (15) represents three index linear differential-recurrence equations. The solution of this system of equations for $c^{q}_{m_1\,m_2}(t) = f^{m_1\,q}_{m_2\,-q+1}(t)$ is far simpler than those for $f^{m_1\,q_1}_{m_2\,q_2}(t)$ which comprise four index differential-recurrence equations and which are obtained when $\mathbf{F} \neq 0$.

Proceeding, we first introduce the supercolumn vector $\mathbf{C}_n(t)$, which is defined as follows:

$$\mathbf{C}_n(t) = \begin{pmatrix} \mathbf{c}_{0\,n}(t) \\ \mathbf{c}_{1\,n-1}(t) \\ \vdots \\ \mathbf{c}_{n\,0}(t) \end{pmatrix}, \quad \mathbf{c}_{m_1\,m_2}(t) = \begin{pmatrix} \vdots \\ c^{-1}_{m_1\,m_2}(t) \\ c^{0}_{m_1\,m_2}(t) \\ c^{1}_{m_1\,m_2}(t) \\ \vdots \end{pmatrix}, \quad n \geq 0. \tag{16}$$

Thus the multi-term differential-recurrence equation recurrence Eq. (15) for the expectation values of the observables can be transformed into a supermatrix four-term differential-recurrence equation of the form

$$\eta \frac{d}{dt}\mathbf{C}_n(t) = \mathbf{Q}_n^{--}\mathbf{C}_{n-2}(t) + \mathbf{Q}_n^{-}\mathbf{C}_{n-1}(t) + \mathbf{Q}_n\mathbf{C}_n(t) + \mathbf{Q}_n^{+}\mathbf{C}_{n+1}(t), \tag{17}$$

where the supermatrices $\mathbf{Q}_n^{-}$, $\mathbf{Q}_n$, and $\mathbf{Q}_n^{+}$ are given in Appendix B. By taking the Laplace transform of Eq. (17), we have the algebraic four-term recurrence equation in the frequency domain

$$\eta s\tilde{\mathbf{C}}_n(s) - \delta_{n\,0}\eta\mathbf{C}_0(0) = \mathbf{Q}_n^{--}\tilde{\mathbf{C}}_{n-2}(s) + \mathbf{Q}_n^{-}\tilde{\mathbf{C}}_{n-1}(s) + \mathbf{Q}_n\tilde{\mathbf{C}}_n(s) + \mathbf{Q}_n^{+}\tilde{\mathbf{C}}_{n+1}(s), \tag{18}$$

where

$$\tilde{\mathbf{C}}_n(s) = \int_0^\infty \mathbf{C}_n(t)e^{-st}dt. \tag{19}$$

Here we have used the initial condition $\mathbf{C}_n(0) = 0$ for $n > 0$ because $\left\langle H_n e^{-iq\phi_i} \right\rangle = 0$ for $n > 0$ as demanded by the initial Maxwell-Boltzmann distribution. The initial value vector $\mathbf{C}_0(0)$ is given in Appendix B. Next by invoking the general continued-fraction method for solving matrix recurrence relations,[10,33] we have the formal solution for the spectrum $\tilde{\mathbf{C}}_0(s)$ which contains the elements of interest to us as defined in Eq. (22), viz.,

$$\tilde{\mathbf{C}}_0(s) = \eta\mathbf{\Delta}_0(s)\mathbf{C}_0(0), \tag{20}$$

where the matrix $\mathbf{\Delta}_n(s)$ is to be calculated from its matrix continued-fraction definition, viz.,

$$\mathbf{\Delta}_n(s) = \left[\eta s\mathbf{I} - \mathbf{Q}_n - \mathbf{Q}_n^{+}\mathbf{\Delta}_{n+1}(s)\left(\mathbf{Q}_{n+1}^{-} + \mathbf{Q}_{n+1}^{+}\mathbf{\Delta}_{n+2}(s)\mathbf{Q}_{n+2}^{--}\right)\right]^{-1}. \tag{21}$$

Having determined the column vector $\tilde{\mathbf{C}}_0(s)$, we then have the spectrum of the relaxation function $C(t)$ given by Eq. (7),

$$\tilde{C}(i\omega) = \frac{\tilde{\varphi}(i\omega) + \tilde{\psi}(i\omega)}{\varphi(0) + \psi(0)} = \frac{\tilde{c}^{1}_{00}(i\omega) + \tilde{c}^{1\,*}_{00}(-i\omega) + \alpha\left[\tilde{c}^{0}_{00}(i\omega) + \tilde{c}^{0\,*}_{00}(-i\omega)\right]}{c^{1}_{00}(0) + c^{1\,*}_{00}(0) + \alpha\left[c^{0}_{00}(0) + c^{0\,*}_{00}(0)\right]}, \tag{22}$$

where the asterisks denote the complex conjugate and we have noted that the response functions of the dipole $\varphi(t)$ and cage $\psi(t)$ are given in terms of the elements of the column vector $\mathbf{C}_0(t)$, Eq. (16), as

$$\varphi(t) = \frac{\mu_1}{2}\left(c^{1}_{00}(t) + c^{1\,*}_{00}(t)\right), \quad \psi(t) = \frac{\mu_2}{2}\left(c^{0}_{00}(t) + c^{0\,*}_{00}(t)\right), \tag{23}$$

while the corresponding spectra in the frequency domain are

$$\tilde{\varphi}(i\omega) = \frac{\mu_1}{2}\left[\tilde{c}^{1}_{00}(i\omega) + \tilde{c}^{1\,*}_{00}(-i\omega)\right], \quad \tilde{\psi}(i\omega) = \frac{\mu_2}{2}\left[\tilde{c}^{0}_{00}(i\omega) + \tilde{c}^{0\,*}_{00}(-i\omega)\right]. \tag{24}$$

These equations, on calculating the matrix continued-fraction Eq. (21), will yield an exact numerical solution of our problem.

IV. APPROXIMATE EXPRESSIONS FOR THE COMPLEX SUSCEPTIBILITY

For purposes of calculation, it is also useful to have analytical solutions for particular limiting cases, thereby yielding some insight into the underlying physics as well as serving as a benchmark for the matrix continued fraction solution given above. First by adding Eqs. (2) and (3), we have for $F = 0$,

$$I_2\ddot{\phi}_2(t) + I_1\ddot{\phi}_1(t) = -\zeta_2\dot{\phi}_2(t) + \lambda_2(t). \tag{25}$$

Next on dividing Eq. (2) by I_1 and Eq. (3) by I_2 and subtracting the second equation from the first, we have

$$\ddot{\theta}(t) + \frac{\zeta_1}{I_1}\left(1 + \frac{I_1}{I_2}\right)\dot{\theta}(t) - \frac{I_1\zeta_2}{I_2}\dot{\phi}_2(t) + \frac{\mu_1 R}{I_1}\left(1 + \frac{I_1}{I_2}\right)\sin\theta(t) = \lambda_1(t) + \frac{I_1}{I_2}\left[\lambda_1(t) - \lambda_2(t)\right], \tag{26}$$

where $\theta(t) = \phi_1(t) - \phi_2(t)$. Clearly, Eqs. (25) and (26) decouple in the limit $I_1/I_2 \ll 1$ and so lead to the itinerant oscillator equations[34]

$$I_2\ddot{\phi}_2(t) = -\zeta_2\dot{\phi}_2(t) + \lambda_2(t), \tag{27}$$

$$I_1\ddot{\theta}(t) = -\zeta_1\dot{\theta}(t) - \mu_1 R\sin\theta(t) + \lambda_1(t). \tag{28}$$

The equations of motion have now been reduced to the Langevin equation of a free Brownian rotator and that of a dipole in a cosine potential. Furthermore, for infinite cage inertia $I_1 \ll I_2$, the cage (surroundings) autocorrelation function is[6,10,34] available in the closed form,

$$C_s(t) = \frac{\psi(t)}{\psi(0)} = \frac{\langle\cos\phi_2\rangle(t) - \langle\cos\phi_2\rangle_0}{\langle\cos\phi_2\rangle(0) - \langle\cos\phi_2\rangle_0} \approx \frac{\langle\cos\phi_2(0)\cos\phi_2(t)\rangle}{\langle\cos\phi_2(0)\cos\phi_2(0)\rangle} = \exp\left\{-\frac{1}{2\beta_2}\left[\frac{t}{\eta_2} + \frac{1}{\beta_2}\left(e^{-\frac{\beta_2 t}{\eta_2}} - 1\right)\right]\right\}. \tag{29}$$

On expanding the double exponential, we have

$$C_s(t) = e^{\gamma_2} \sum_{n=0}^{\infty} \frac{1}{(-2\beta_2^2)^n n!} e^{-(1+2\beta_2^2 n)\frac{t}{2\eta_2\beta_2}}. \tag{30}$$

The Laplace transform of Eq. (30) is ($s = i\omega$)

$$\tilde{C}_s(i\omega) = \frac{2\eta\beta_2}{\gamma_2} e^{(2\beta_2^2)^{-1}} \times \sum_{n=0}^{\infty} \frac{1}{(-2\beta_2^2)^n n! \left(1 + 2\beta_2^2 n + 2i\omega\eta\beta_2/\gamma_2\right)}. \tag{31}$$

Equation (31) is useful for calculating the susceptibility of the surroundings via the linear response formula, Eq. (13), which in this case is

$$\frac{\chi_s(\omega)}{\chi_s'(0)} = 1 - i\omega\tilde{C}_s(i\omega). \tag{32}$$

Now the dipole autocorrelation function $\varphi(t)$ has been examined in detail[10,15,35] in the small oscillation (itinerant oscillator) approximation. Invariably $\varphi(t)$ gives rise to a pronounced FIR absorption peak in the frequency domain. The characteristic frequency ω_0 of this FIR peak is given by

$$\omega_0 = \frac{\gamma_1}{\eta}\sqrt{\frac{\xi_{\text{int}}}{2}}, \tag{33}$$

and the complete expression for the overall correlation function $C(t)$ as defined by Eq. (7) is given in the *small oscillation* and *large cage approximation* by the product

$$C(t) = C_s(t)C_{\mu_1}(t) = C_s(t)\exp\left\{-\frac{1}{\xi_{\text{int}}}\left[1 - \exp\left(-\frac{\beta_1\gamma_1 t}{2\eta}\right) \times \left(\cos(\omega_1 t) + \frac{\beta_1}{2\omega_1}\sin(\omega_1 t)\right)\right]\right\}, \tag{34}$$

where the damped natural frequency of dipole librations ω_1 is given by the equation

$$\omega_1 = \frac{\gamma_1}{2\eta}\sqrt{2\xi_{\text{int}} - \beta_1^2}. \tag{35}$$

The term in curly braces in Eq. (34) obviously represents an infinite set of decaying harmonic oscillations giving rise in the frequency domain to a comb-like harmonic peak structure at FIR frequencies.

Furthermore, if the cage inertial parameter as defined in Ref. 4 is sufficiently small $\left(\beta_2^{-2} = I_2 kT/\zeta_2^2 \leq 0.1\right)$ and the dipole kinetic energy satisfies the condition $I_1\omega_0^2 \ll kT$, the exact complex susceptibility for small oscillations, using Eqs. (13) and (34), may be closely approximated by the simple closed expression[10,34,35]

$$\frac{\chi(\omega)}{\chi} = \frac{1}{1 + i\eta\omega\tau_D}\left[\frac{2\beta_2^2}{2\beta_2^2 + i\eta\omega\tau_D} + \frac{i\eta\omega\tau_D}{\xi_{\text{int}} - 2(\eta\omega/\gamma_1)^2 + 2i\beta_1\eta\omega/\gamma_1}\right], \tag{36}$$

where $\tau_D = 2\beta_2/\gamma_2$ is the Debye relaxation time of the cage. The form of Eq. (36) was originally given in Ref. 14 for the single friction itinerant oscillator model (see also Ref. 1). The first (or non-resonant) term in Eq. (36) stemming from $C_s(t)$ is essentially the well-known Rocard equation[36] of the inertia corrected Debye theory of dielectric relaxation of noninteracting dipoles, and so due to the heavily damped cage motion, the second lightly damped harmonic oscillator term $C_{\mu_1}(t)$ represents in our simplified picture the high frequency FIR effects due to the cage-embedded dipole interaction. If the series expansion of the exact small oscillation solution Eq. (34) leading directly to the approximate Eq. (36) is continued, one can clearly see the emergence of the FIR peak structure at harmonics of the fundamental frequency given by Eq. (35).

V. RESULTS AND DISCUSSION

We exhibit the results of numerical analysis of the susceptibility $\chi(\omega)$ of the model in Figs. 1–8. In Figs. 1 and 2, we show $\chi(\omega)$ versus ω for various values of the dipole-cage interaction parameter ξ_{int} for a relatively lightly damped cage and dipole. Clearly the real part of the susceptibility $\chi'(\omega)$ does not differ appreciably from that of the cage alone even for strong dipole-cage interaction. However, this is not so for the imaginary part of the susceptibility $\chi''(\omega)$ where even for moderate dipole-cage coupling (curve 1), we see a pronounced FIR shoulder. The shoulder gradually evolves into a distinct peak structure as the interaction increases with a steady progress of

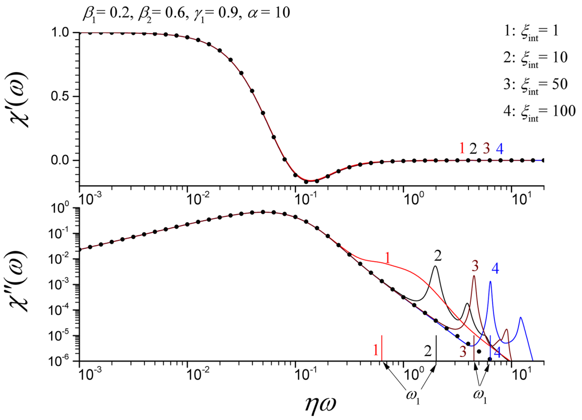

FIG. 1. Real and imaginary parts of susceptibility: numerically exact solution from Eq. (13) vs ω for various values of the dipole-cage interaction parameter ξ_{int}. Circles: pure cage susceptibility Eq. (32).

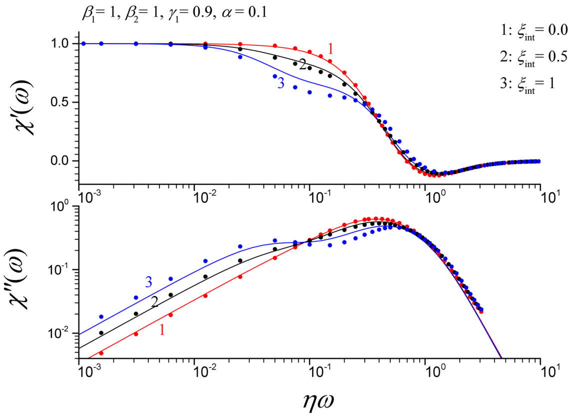

FIG. 2. Real and imaginary parts of susceptibility: numerically exact solution from Eq. (13) vs ω for various values of the dipole-cage interaction parameter ξ_{int}. Circles: result yielded by the closed form small oscillation solution for the correlation function Eq. (34).

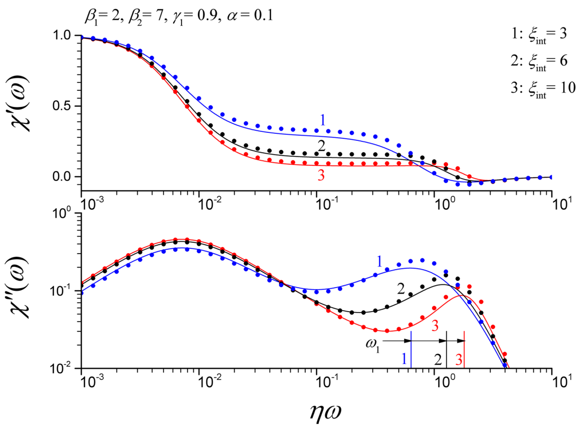

FIG. 3. Real and imaginary parts of susceptibility: numerically exact solution from Eq. (13) vs ω for various values of the dipole-cage interaction parameter ξ_{int}. Circles: approximate small oscillation solution Eq. (36).

the fundamental frequency of the peak structure to higher and higher frequencies as ξ_{int} increases which is to be expected in view of the damped natural frequency Eq. (35). Figure 2 which pertains to relatively strong damping of both dipole and cage shows that the closed form small oscillation solution, Eq. (34), provides a reasonable approximation to the exact solution in this case, the accuracy of which decreases as the dipole-cage coupling strength increases. Here the damping on both entities is so strong that the distinct peak structure does not appear at all, the only manifestation of the high frequency behavior being the more rapid high frequency fall-off of $\chi''(\omega)$ in comparison to that of the cage alone as depicted in Fig. 1. Figure 3 for a lightly damped dipole shows how the approximate small oscillation solution Eq. (36) provides a good approximation to the exact matrix continued fraction solution. Furthermore for the parameter values chosen, Eq. (36) provides a better and better approximation to the exact continued fraction solution as the interaction strength is increased together with a progressive shift of the fundamental frequency to higher and higher values as the interaction strength is increased again in accordance with Eqs. (33) and (35). Figure 4 shows that the effect of the dipole moment ratio as compared to the pure cage susceptibility is profound with the FIR response effects becoming more and more pronounced as the cage dipole moment increases.

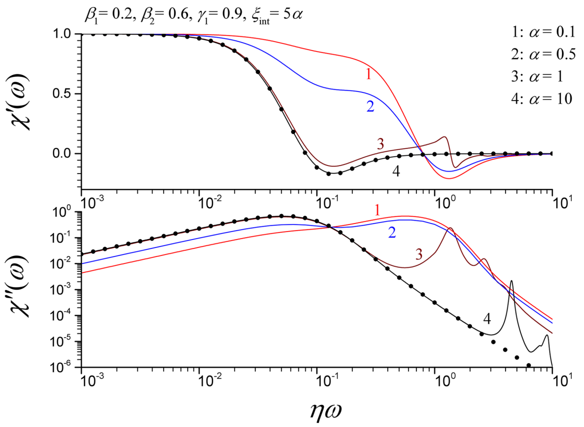

FIG. 4. Real and imaginary parts of susceptibility: numerically exact solution from Eq. (13) vs ω for various values of the dipole moment ratio parameter α. Circles: cage susceptibility Eq. (32).

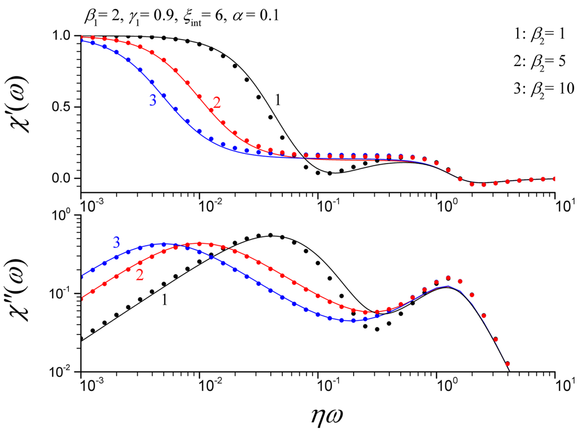

FIG. 5. Real and imaginary parts of susceptibility: numerically exact solution from Eq. (13) vs ω for various values of the cage friction parameter β_2. Circles: approximate small oscillation solution Eq. (36).

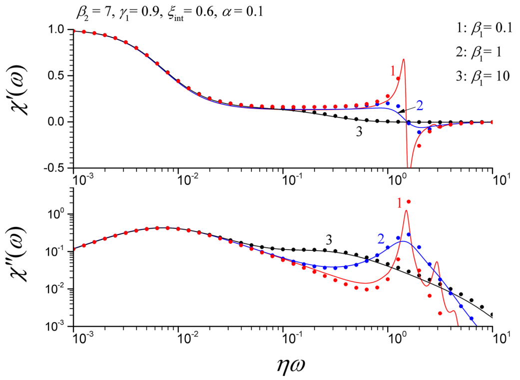

FIG. 6. Real and imaginary parts of susceptibility: numerically exact solution from Eq. (13) vs ω for various values of the dipole friction parameter β_1. Circles: approximate small oscillation solution Eq. (36). Exact solution displays the characteristic comb-like structure.

Figure 5 shows the complex susceptibility for various values of the cage friction parameter β_2 for given dipole-cage interaction. It is clear that in this case of a relatively highly damped dipole that the simple single resonance formula given by Eq. (36) provides a reasonable description of the high frequency behavior. In contrast, Fig. 6 shows that for small damping of the dipole, Eq. (36) fails as the high frequency peak structure

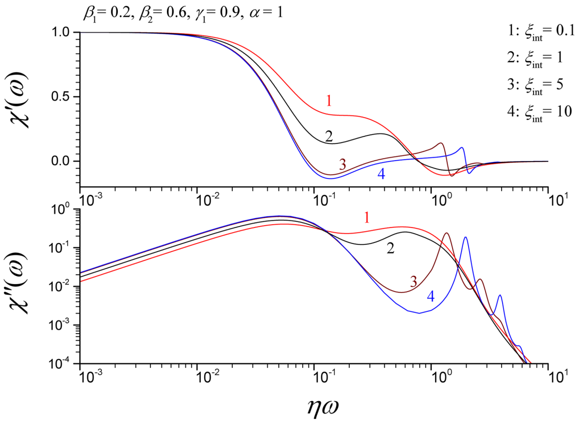

FIG. 7. Real and imaginary parts of susceptibility: numerically exact solution from Eq. (13) vs ω for various values of the dipole-cage interaction parameter ξ_{int}.

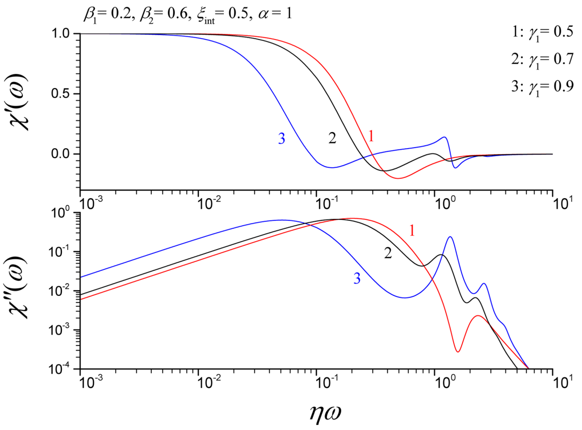

FIG. 8. Real and imaginary parts of susceptibility: numerically exact solution from Eq. (13) vs ω for various values of the dipole inertia parameter γ_1.

predicted by the exact solution cannot be reproduced at all. Figure 7 shows that as the dipole-cage interaction parameter ξ_{int} is increased, the FIR resonance absorption is greatly increased at the expense of the mid-frequency absorption (curve 1). Figure 8 shows that the FIR absorption becomes more and more pronounced as the dipole inertia parameter increases again as one would intuitively expect.

VI. CONCLUSION

The caging phenomenon is a common hallmark of diffusion in both dense liquids[37] and granular systems.[38] As far as applications to dielectric relaxation are concerned, the cage model or itinerant oscillator is a simple mechanical system which seamlessly links the microwave and FIR absorption and can explain their role, namely, a caged-dipole effect (i.e., the FIR absorption peaks) and a rotational diffusion effect at low frequencies (i.e., Debye-like peak). In essence, the model represents the diffusion of a dipole molecule in a periodic cosine potential under the influence of a thermal bath. The periodic potential, representing the dipole-cage interaction, is not fixed but moves since the cage itself undergoes rotational Brownian motion. The model, which was originally used in translational guise to describe diffusion in cold liquids,[10,39] has also recently found applications in the description of microrheology in living matter[40] and mesorheological granular experiments.[38] Also in a much modified form, it has been used to examine the stability of large synchronous generators connected to low inertia systems where predominantly renewable energy sources like wind turbine generators or photovoltaic installations are connected.[41]

Here we have restricted ourselves to linear response theory which nevertheless is able to reproduce some noticeable phenomena observed in a liquid. Previously for the purpose of mathematical simplification, the cage was considered as being much heavier in comparison to the embedded dipolar molecule, which allowed one to separate the equations of motion of the cage and molecule. Here, in contrast we have given a rigorous solution of the problem in terms of matrix continued fractions by taking into account the finite inertia of the cage as well as large oscillations of the dipole in the cosine potential. For the purposes of physical interpretation, some limiting cases have been recovered, namely, the case of a massive cage and small oscillations of the dipole allowing one to assess the accuracy of these solutions.

The assumption of a cage with finite inertia and the exact matrix continued fraction solution is the main advance on the previous treatments.[10] The exact solution which we have presented here permits one to analyse the situation when the cage diffusion is no longer independent and is simultaneously influenced by the probe allowing one to reproduce previous results which have been obtained for heavy cages. Thus, it also allows one to examine the range of validity of the existing approximations. This influence is reflected in the susceptibility spectrum $\chi(\omega)$ of the model. The calculations may with suitable adaptation be used to describe ferrofluids. Here relaxation over the internal magnetocrystalline anisotropy barriers inside a ferrofluid particle occurs along with Debye relaxation of the fluid particle itself.

APPENDIX A: RECURRENCE RELATIONS FOR THE FUNCTIONS $f_{m_2\,q_2}^{m_1\,q_1}(t)$

The time derivative of the function $f_{m_2\,q_2}^{m_1\,q_1}(t)$ associated with the observables is

$$\frac{d}{dt} f_{m_2\,q_2}^{m_1\,q_1}(t) = \left\langle \left[\dot{H}_{m_1} - \frac{iq_1}{2\eta_1}\left(H_{m_1+1} + 2m_1 H_{m_1-1}\right)\right] H_{m_2} e^{-iq_1\phi_1} e^{-iq_2\phi_2} + \left[\dot{H}_{m_2} - \frac{iq_2}{2\eta_2}\left(H_{m_2+1} + 2m_2 H_{m_2-1}\right)\right] H_{m_1} e^{-iq_1\phi_1} e^{-iq_2\phi_2} \right\rangle. \tag{A1}$$

The terms involving derivatives like $\dot{H}_{m_1} H_{m_2} e^{-iq_1\phi_1} e^{-iq_2\phi_2}$ and $H_{m_1} \dot{H}_{m_2} e^{-iq_1\phi_1} e^{-iq_2\phi_2}$ occurring on the right hand side of Eq. (A1) can be written as

$$\dot{H}_{m_1} H_{m_2} e^{-iq_1\phi_1} e^{-iq_2\phi_2} = 2\eta_1 \ddot{\phi}_1 m_1 H_{m_1-1} H_{m_2} e^{-iq_1\phi_1} e^{-iq_2\phi_2} = -m_1 H_{m_1-1} H_{m_2} e^{-iq_1\phi_1} e^{-iq_2\phi_2} \Bigg(2\beta_1 \left(\dot{\phi}_1 - \dot{\phi}_2\right) + \frac{\xi_{int}}{\eta_1} \sin\left(\phi_1 - \phi_2\right) + \frac{\xi_1}{\eta_1} \sin\phi_1 - \frac{\lambda_1}{\eta_1 kT} \Bigg), \tag{A2}$$

where

$$\beta_i = \frac{\zeta_i \eta_i}{I_i} = \frac{\zeta_i}{2\eta_i kT}. \tag{A3}$$

Thus averaging[10] of the term $\dot{H}_{m_1} H_{m_2} e^{-iq_1\phi_1} e^{-iq_2\phi_2}$ leads to

$$\begin{aligned}\left\langle \dot{H}_{m_1} H_{m_2} e^{-iq_1\phi_1} e^{-iq_2\phi_2} \right\rangle = &-\frac{\beta_1}{\eta_1} m_1 \left\langle H_{m_1} H_{m_2} e^{-iq_1\phi_1} e^{-iq_2\phi_2} \right\rangle + \frac{\beta_1}{\eta_2} m_1 \left\langle H_{m_1-1} \left(H_{m_2+1} + 2m_2 H_{m_2-1}\right) e^{-iq_1\phi_1} e^{-iq_2\phi_2} \right\rangle \\ &+ \frac{i\xi_{\text{int}}}{2\eta_1} m_1 \left\langle H_{m_1-1} H_{m_2} \left(e^{-i(q_1-1)\phi_1} e^{-i(q_2+1)\phi_2} - e^{-i(q_1+1)\phi_1} e^{-i(q_2-1)\phi_2} \right) \right\rangle \\ &+ \frac{i\xi_1}{2\eta_1} m_1 \left\langle H_{m_1-1} H_{m_2} (e^{-i(q_1-1)\phi_1} - e^{-i(q_1+1)\phi_1}) e^{-iq_2\phi_2} \right\rangle . \end{aligned} \tag{A4}$$

In a similar manner, averaging[10] of the term $H_{m_1} \dot{H}_{m_2} e^{-iq_1\phi_1} e^{-iq_2\phi_2}$ yields

$$\begin{aligned}\left\langle H_{m_1} \dot{H}_{m_2} e^{-iq_1\phi_1} e^{-iq_2\phi_2} \right\rangle = &\frac{\beta_1}{\eta_2} m_2 \left\langle H_{m_1+1} H_{m_2-1} e^{-iq_1\phi_1} e^{-iq_2\phi_2} \right\rangle - \frac{\beta_2}{\eta_2} m_2 \left\langle H_{m_1} H_{m_2} e^{-iq_1\phi_1} e^{-iq_2\phi_2} \right\rangle - \frac{\eta_1\beta_1}{\eta_2^2} m_2 \langle H_{m_1} \left(H_{m_2}\right. \\ &\left. + \; 2\left(m_2 - 1\right) H_{m_2-2}\right) e^{-iq_1\phi_1} e^{-iq_2\phi_2} \Big\rangle + \frac{i\xi_{\text{int}}}{2\eta_2} m_2 \left\langle H_{m_1} H_{m_2-1} \left(e^{-i(q_1+1)\phi_1} e^{-i(q_2-1)\phi_2} \right.\right. \\ &\left.\left. - \; e^{-i(q_1-1)\phi_1} e^{-i(q_2+1)\phi_2} \right) \right\rangle + \frac{i\xi_2}{2\eta_2} m_2 \left\langle H_{m_1} H_{m_2-1} e^{-iq_1\phi_1} \left(e^{-i(q_2-1)\phi_2} - e^{-i(q_2+1)\phi_2} \right) \right\rangle . \end{aligned} \tag{A5}$$

Finally, by utilizing Eqs. (A4) and (A5), we have the differential-recurrence equations for the statistical moments $f_{m_2\,q_2}^{m_1\,q_1}(t)$, Eq. (14), viz.,

$$\begin{aligned}\eta \frac{d}{dt} f_{m_2\,q_2}^{m_1\,q_1} = &-\left(\gamma_1\beta_1 m_1 + \frac{\gamma_2^2}{\gamma_1}\beta_1 m_2 + \gamma_2\beta_2 m_2 \right) f_{m_2\,q_2}^{m_1\,q_1} + \gamma_2\beta_1 m_2 f_{m_2-1\,q_2}^{m_1+1\,q_1} + \gamma_2\beta_1 m_1 f_{m_2+1\,q_2}^{m_1-1\,q_1} + 2\gamma_2\beta_1 m_1 m_2 f_{m_2-1\,q_2}^{m_1-1\,q_1} \\ &- 2\frac{\gamma_2^2}{\gamma_1}\beta_1 m_2 \left(m_2 - 1\right) f_{m_2-2\,q_2}^{m_1\,q_1} + \frac{i\xi_{\text{int}}}{2} \left[\gamma_1 m_1 \left(f_{m_2\,q_2+1}^{m_1-1\,q_1-1} - f_{m_2\,q_2-1}^{m_1-1\,q_1+1} \right) + \gamma_2 m_2 \left(f_{m_2-1\,q_2-1}^{m_1\,q_1+1} - f_{m_2-1\,q_2+1}^{m_1\,q_1-1} \right) \right] \\ &- \frac{i}{2} \left[\gamma_1 q_1 \left(f_{m_2\,q_2}^{m_1+1\,q_1} + 2m_1 f_{m_2\,q_2}^{m_1-1\,q_1} \right) + \gamma_2 q_2 \left(f_{m_2+1\,q_2}^{m_1\,q_1} + 2m_2 f_{m_2-1\,q_2}^{m_1\,q_1} \right) \right] + \frac{i}{2} \left[\gamma_1\xi_1 m_1 (f_{m_2\,q_2}^{m_1-1\,q_1-1} - f_{m_2\,q_2}^{m_1-1\,q_1+1}) \right. \\ &\left. + \; \gamma_2\xi_2 m_2 \left(f_{m_2-1\,q_2-1}^{m_1\,q_1} - f_{m_2-1\,q_2+1}^{m_1\,q_1} \right) \right] . \end{aligned} \tag{A6}$$

APPENDIX B: MATRICES $\mathbf{Q}_n^-$, $\mathbf{Q}_n$, AND $\mathbf{Q}_n^+$ AND INITIAL VALUE VECTOR $C_n(0)$

The supermatrices $\mathbf{Q}_n^-$, $\mathbf{Q}_n$, and $\mathbf{Q}_n^+$ in Eq. (17) are

$$\mathbf{Q}_n = \begin{pmatrix} \mathbf{q}_{0\,n} & \mathbf{p}_n & 0 & \cdots & 0 \\ \mathbf{p}_1 & \mathbf{q}_{1\,n-1} & \mathbf{p}_{n-1} & \ddots & \vdots \\ 0 & \mathbf{p}_2 & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & \mathbf{q}_{n-1\,1} & \mathbf{p}_1 \\ 0 & \cdots & 0 & \mathbf{p}_n & \mathbf{q}_{n\,0} \end{pmatrix}, \tag{B1}$$

$$\mathbf{Q}_n^+ = \frac{i}{2} \begin{pmatrix} \gamma_2(\mathbf{r} - \mathbf{I}) & -\gamma_1\mathbf{r} & 0 & \cdots & 0 \\ 0 & \gamma_2(\mathbf{r} - \mathbf{I}) & -\gamma_1\mathbf{r} & \ddots & \vdots \\ \vdots & \ddots & \ddots & \ddots & 0 \\ 0 & \cdots & 0 & \gamma_2(\mathbf{r} - \mathbf{I}) & -\gamma_1\mathbf{r} \end{pmatrix}, \tag{B2}$$

$$\mathbf{Q}_n^- = \frac{i}{2} \begin{pmatrix} \gamma_2\mathbf{w}_n & 0 & \cdots & 0 \\ -\gamma_1\mathbf{s}_1 & \gamma_2\mathbf{w}_{n-1} & \ddots & \vdots \\ 0 & -\gamma_1\mathbf{s}_2 & \ddots & 0 \\ \vdots & \ddots & \ddots & \gamma_2\mathbf{w}_1 \\ 0 & \cdots & 0 & -\gamma_1\mathbf{s}_n \end{pmatrix}, \tag{B3}$$

$$\mathbf{Q}_n^{--} = \begin{pmatrix} \mathbf{u}_n & 0 & \cdots \\ \mathbf{v}_{1\,n-1} & \ddots & \ddots \\ 0 & \ddots & \mathbf{u}_2 \\ \vdots & \ddots & \mathbf{v}_{n-1\,1} \\ 0 & \cdots & 0 \end{pmatrix}, \tag{B4}$$

while the submatrices have the form

$$\mathbf{q}_{n_1\,n_2} = -\left(\gamma_1\beta_1 n_1 + \frac{\gamma_2^2}{\gamma_1}\beta_1 n_2 + \gamma_2\beta_2 n_2 \right) \mathbf{I}, \tag{B5}$$

$$\mathbf{p}_n = \gamma_2\beta_1 n \mathbf{I}, \tag{B6}$$

$$\mathbf{u}_n = -2\frac{\gamma_2^2}{\gamma_1}\beta_1 n \left(n - 1\right) \mathbf{I}, \tag{B7}$$

$$\mathbf{v}_{n_1\,n_2} = 2\gamma_2\beta_1 n_1 n_2 \mathbf{I}, \tag{B8}$$

$$\mathbf{r} = \begin{pmatrix} \ddots & \ddots & \ddots & & \\ \ddots & -1 & 0 & 0 & \\ \ddots & 0 & 0 & 0 & \ddots \\ \ddots & 0 & 0 & 1 & \ddots \\ \ddots & \ddots & \ddots & \ddots & \ddots \end{pmatrix}, \tag{B9}$$

$$\mathbf{s}_n = n\begin{pmatrix} \ddots & \ddots & \ddots & \ddots & & & \\ \ddots & -4 & \xi_{\text{int}} & 0 & \ddots & & \\ \ddots & -\xi_{\text{int}} & -2 & \xi_{\text{int}} & 0 & \ddots & \\ \ddots & 0 & -\xi_{\text{int}} & 0 & \xi_{\text{int}} & 0 & \ddots \\ & \ddots & 0 & -\xi_{\text{int}} & 2 & \xi_{\text{int}} & \ddots \\ & & \ddots & 0 & -\xi_{\text{int}} & 4 & \ddots \\ & & & \ddots & \ddots & \ddots & \ddots \end{pmatrix}, \tag{B10}$$

$$\mathbf{w}_n = n\begin{pmatrix} \ddots & \ddots & \ddots & \ddots & & & \\ \ddots & -6 & \xi_{\text{int}} & 0 & \ddots & & \\ \ddots & -\xi_{\text{int}} & -4 & \xi_{\text{int}} & 0 & \ddots & \\ \ddots & 0 & -\xi_{\text{int}} & -2 & \xi_{\text{int}} & 0 & \ddots \\ & \ddots & 0 & -\xi_{\text{int}} & 0 & \xi_{\text{int}} & \ddots \\ & & \ddots & 0 & -\xi_{\text{int}} & 2 & \ddots \\ & & & \ddots & \ddots & \ddots & \ddots \end{pmatrix}. \tag{B11}$$

The initial value vector in Eq. (18) is calculated in the following manner:

$$\mathbf{C}_0(0) = \begin{pmatrix} \vdots \\ c_{00}^{-1}(0) \\ c_{00}^{0}(0) \\ c_{00}^{1}(0) \\ \vdots \end{pmatrix}, \tag{B12}$$

where the elements are given by

$$\begin{aligned} c_{00}^{q}(0) &= \left\langle e^{-iq\phi_1+i(q-1)\phi_2}\right\rangle(0) - \left\langle e^{-iq\phi_1+i(q-1)\phi_2}\right\rangle_0 \\ &= Z^{-1}\int_0^{2\pi}\int_0^{2\pi} e^{\xi_1\cos\phi_1+\xi_2\cos\phi_2+\xi_{\text{int}}\cos(\phi_1-\phi_2)}d\phi_1 d\phi_2 \\ &\quad - Z_0^{-1}\int_0^{2\pi}\int_0^{2\pi} e^{\xi_{\text{int}}\cos(\phi_1-\phi_2)}d\phi_1 d\phi_2. \end{aligned} \tag{B13}$$

Next using the series expansion of Eq. (B13) with respect to ξ, we have $c_{00}^{q}(0)$ in terms of the modified Bessel functions,

$$\begin{aligned} c_{00}^{q}(0) &\approx \xi_1\left\langle(\cos\phi_1 + \alpha\cos\phi_2)\left(e^{-iq\phi_1+i(q-1)\phi_2}\right)\right\rangle_0 \\ &= \frac{I_{q-1}(\xi_{\text{int}}) + \alpha I_q(\xi_{\text{int}})}{2I_0(\xi_{\text{int}})}, \end{aligned} \tag{B14}$$

where $I_q(z)$ are the modified Bessel functions of the first kind and we have also used the fact that $\langle\cos\phi_1 + \alpha\cos\phi_2\rangle_0 = 0$.

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