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Langevin equation method for the rotational Brownian motion and orientational relaxation in liquids

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Abstract

A theory of orientational relaxation for the inertial rotational Brownian motion of a linear molecule (rotator in space) is developed in the context of the Langevin equation method without recourse to the Fokker–Planck equation. The general term in the time-dependent infinite hierarchy of differential-recurrence relations for the orientational correlation functions describing the relaxation behaviour of the system is derived by averaging the corresponding Euler–Langevin equation. The solution of this hierarchy is obtained in terms of continued fractions. The correlation times and the spectra of the orientational correlation functions are calculated for typical values of the model parameters.

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1. Introduction

Models of the rotational Brownian motion are frequently used for the study of molecular dynamics in liquids in order to compare spectra obtained by various probe techniques such as dielectric relaxation, the dynamic Kerr effect, infrared absorption, Raman scattering, etc, with the corresponding theoretical spectra [1–3]. The theoretical treatment of rotational Brownian motion has hitherto been mainly based on the Fokker–Planck equation [4]. This equation is a partial differential equation for the time evolution of the orientational distribution function of a molecule in phase space. The Fokker–Planck equation in the context of a dynamical system, the motion of which (in the absence of heat) bath is governed by Hamilton's equations with a separable and additive Hamiltonian (comprising the sum of the kinetic and potential energies), is usually known as the Klein–Kramers equation. Integration of the phase space distribution function with respect to the angular velocities yields the orientational distribution function in configuration space. The Klein–Kramers equation can be derived by calculating the drift

and the diffusion coefficients from the underlying inertial Langevin equation governing the time behaviour of the set of random variables describing the rotational Brownian motion of a molecule in the fluid. The solution of the Fokker–Planck equation has been usually obtained by separating the variables which gives rise to an equation of Sturm–Liouville type which possesses solutions in the form of known functions only in a few specialized cases (just as in the analogous problem of the solution of the Schrödinger equation in wave mechanics) or by expanding the distribution function as an appropriate Fourier series in the phase space variables which yields an infinite hierarchy of linear differential-recurrence equations for the time-dependent moments (the expectation values of the Fourier coefficients). The infinite hierarchy can be solved numerically the approach being analogous to matrix mechanics in quantum theory. A comprehensive discussion of the Fokker–Planck equation method and its applications to the study of orientational relaxation in fluids is given, e.g., in [1, 3, 5–14].

An alternative approach to the problem has been given by Coffey [15] who derived the exact infinite hierarchy of differential-recurrence equations for the moments governing the dynamics by averaging directly [15, 16] the Langevin equation for the simple model of the inertial rotation of a planar rotator without recourse to the Fokker–Planck equation (this model has been reconsidered and applied recently to the calculation of the transient nonlinear response [17]). The key step in applying the method is first to convert by appropriate transformation the Langevin equation into an equation for the quantity the statistical average of which is desired, and then to average that equation over its realizations in phase space. The transformed Langevin equation contains not only the quantity, the average of which is desired, but also the next higher order average and so on. It is thus the generating equation of a hierarchy of averages. This eliminates the excessive step in the theory of constructing and solving the corresponding Fokker–Planck equation entirely. The Langevin equation method has been further developed by Coffey *et al* (see, e.g., [18–21]) for the *non-inertial* rotation in three dimensions where a number of exact solutions for the complex polarizability, correlation times, etc, were obtained. We also remark that Coffey [16] and Coffey *et al* [22] were also able to treat the *inertial* Brownian rotation of a linear (needle-like) molecule in space. However, the first few equations of the hierarchies only were obtained [16] and no straightforward method of the solution of the hierarchy of moment equations (arising from the transformation and averaging procedure) governing the relaxation of the system including inertial effects has been given in [16, 22]. It is the purpose of this paper to show how the general term in the hierarchy of differential-recurrence equations for inertial rotation in space arises naturally from the vector Langevin equations defined as Stratonovich stochastic equations [22]. Thus the problem of constructing and solving the Klein–Kramers equation is bypassed entirely as was accomplished in [15, 17] for the inertial rotation in a plane. The advantage in computational labour that the averaging method has over the solution by the Fokker–Planck method is considerable. Neither the derivation of that equation nor knowledge of the intricate transformations used to effect the separation of the variables in it, and to solve the resulting simultaneous recurrence relations is required.

It is apparent from the work described in [16, 18, 21, 22] that problems involving inertial effects can easily be treated for rotation about a space-fixed axis only. If the axis of rotation is no longer space-fixed then the separation of variables method of the solution of the Klein–Kramers equation is rather difficult to use when inertial effects are included [18]. Moreover, the rotation of a linear molecule in space presents new features mainly arising from the nonlinear nature of the Euler–Langevin equations, which do not occur in the corresponding space-fixed axis rotator response. Thus, the solution of the moving axes rotator problem is necessary for a comprehensive understanding of the role played by inertia in the relaxation process. The separation of variables method when applied to the needle model in the context

of the Klein–Kramers equation, first involves the expansion of the angular velocity part of the phase space distribution function in products of Hermite polynomials in the angular velocity components. This procedure leads to a set of partial differential-recurrence relations in the space coordinates and the time for the configuration space distribution function. These may be solved simultaneously and (after considerable algebra together with a further expansion in associated Legendre functions) may be converted into a set of simultaneous ordinary differential-recurrence relations (see, e.g., [6, 14]). Furthermore, considerable mathematical manipulation is required in order to solve the simultaneous algebraic recurrence relations, which result from Fourier transformation over time of the ordinary differential-recurrence relations.

Here the Langevin equation approach proposed in [15, 16, 18, 22] is generalized to treat comprehensively the inertial effects in the orientational relaxation of an assembly of linear molecules undergoing rotational Brownian motion in space as this is the simplest model for the purpose of demonstration of the influence of inertial effects in space rotation. Our approach is based on the solution of the recurrence relations for the statistical moments in terms of continued fractions [18, 24]. If the recurrence relation is a three-term one, it is possible to obtain exact analytical expressions for the Fourier–Laplace transform of the orientational correlation functions in terms of ordinary continued fractions and for the relaxation times in terms of known mathematical functions (in some cases). However, in the majority of problems this situation does not occur because the number of recurring terms in the underlying recurrence relations is generally greater than 3. Nevertheless, as demonstrated by Risken [23] and then extensively elaborated upon by Coffey *et al* [18], it is always possible to reduce a multi-term scalar recurrence relation to a three-term matrix one (tridiagonal form). Thus the solution can be given in terms of matrix continued fractions. Here, we shall use this powerful method for the calculation of the quantities of interest, namely, the orientational correlation functions and the corresponding relaxation times. Moreover, it is worth mentioning that the algorithms employed in such an approach are very effective which will allow progress well beyond the previous methods available for the solution of the problem.

2. Rotational Brownian motion of a thin rod

Let us consider the rotational Brownian motion of a thin rod, or rotator, representing the linear polar molecule. In the molecular coordinate system $oxyz$ rigidly connected to the rotator, the angular velocity ω and the angular momentum M of the rotator are defined as [1]

$$\omega = (\omega_x, \omega_y, \omega_z) = (\dot{\vartheta}, \dot{\varphi} \sin \vartheta, \dot{\varphi} \cos \vartheta) \quad (1)$$

and

$$M = (I\omega_x, I\omega_y, 0) = (I\dot{\vartheta}, I\dot{\varphi} \sin \vartheta, 0) \quad (2)$$

where I is the moment of inertia, ϑ and φ are the polar and azimuthal angles, respectively. In the absence of external fields, the rotational Brownian motion of the rotator is governed by the vector Euler–Langevin equation [1, 18]

$$\frac{d}{dt} M(t) + \omega(t) \times M(t) + \zeta \omega(t) = \lambda(t) \quad (3)$$

where $\zeta \omega(t)$ and $\lambda(t)$ are the frictional and white noise torques due to the Brownian motion of the surroundings, respectively. The white noise torque has the following properties:

$$\overline{\lambda_j(t)} = 0 \quad \overline{\lambda_j(t) \lambda_m(t')} = 2kT \zeta \delta_{j,m} \delta(t - t') \quad (j, m = x, y, z) \quad (4)$$

where k is the Boltzmann constant, T is the temperature, ζ is the friction (drag) coefficient, $\delta(t)$ is the Dirac-delta function, $\delta_{j,m}$ is Kronecker's delta and the overbar means the statistical

average over an ensemble of rotators that all start at the instant t with the same sharp values of the angular velocity and the orientation [5, 15]. The $\lambda_j(t)$ must also satisfy Isserlis's theorem [17] for centred Gaussian random variables, namely, for $2n$ λ :

$$\overline{\lambda_1 \lambda_2 \dots \lambda_{2n}} = \overline{\lambda_1(t_1) \lambda_2(t_2) \dots \lambda_{2n}(t_{2n})} = \sum \prod_{k_i < k_j} \overline{\lambda_{k_i}(t_{k_i}) \lambda_{k_j}(t_{k_j})} \quad (5)$$

where the sum is taken over all distinct products of expectation value pairs, each of which is formed by selecting n pairs of time intervals from $2n$ time points and for $2n+1$ λ :

$$\overline{\lambda_1 \lambda_2 \dots \lambda_{2n+1}} = \overline{\lambda_1(t_1) \lambda_2(t_2) \dots \lambda_{2n}(t_{2n+1})} = 0. \quad (6)$$

We proceed by noting equation (3), rewritten for the vector components in the molecular frame as [4]

$$I \dot{\omega}_x(t) + \zeta \omega_x(t) - I \omega_y^2(t) \cot \vartheta(t) = \lambda_x(t) \quad (7)$$

$$I \dot{\omega}_y(t) + \zeta \omega_y(t) + I \omega_x(t) \omega_y(t) \cot \vartheta(t) = \lambda_y(t). \quad (8)$$

Equations (7) and (8) combined with the definition of the angular velocity components in equation (1), namely, $\dot{\vartheta} = \omega_x$, $\dot{\varphi} = \omega_y / \sin \vartheta$, constitute a system of nonlinear stochastic differential equations. In order to proceed we shall use the Stratonovich definition [23] of the average of these equations because that is the mathematical idealization of the orientational relaxation process. Thus, it is unnecessary to transform the Langevin equations (7) and (8) to Itô equations (e.g. [3]). Moreover, one can apply the usual rules of calculus [5, 15, 24].

We now introduce the functions

$$f_n^{l,m}(t) = P_l^m[\cos \vartheta(t)] s_n^m[\omega_x(t), \omega_y(t)] \quad (0 \leq m \leq l; l, n = 0, 1, 2, \dots) \quad (9)$$

where $P_l^m(z)$ are the associated Legendre functions [25] and the functions $s_n^m(\omega_x, \omega_y)$ are given in terms of finite series of products of Hermite polynomials $H_n(z)$ [25] in the components ω_x, ω_y of the angular velocity as

$$s_n^{2m+M}(\omega_x, \omega_y) = \sum_{q=0}^n \frac{r_{2m+M}(n, q)}{q!(n-q)!} H_{2n-2q+M}(\eta \omega_x) H_{2q}(\eta \omega_y). \quad (10)$$

Here $M = 0$ or 1 , $\eta = \sqrt{I/(2kT)}$, and the coefficients of the series $r_{2m+M}(n, q)$ are determined from the orthogonal properties of $s_n^m(\omega_x, \omega_y)$ by the recurrence relations

$$r_{2m}(n, q) = \left(n - q + \frac{1}{2}\right) \left(1 - \frac{2q+1}{2m-1}\right) r_{2m-1}(n, q) + (n-q) \frac{2q+1}{2m-1} r_{2m-1}(n, q+1) \quad (11)$$

$$r_{2m+1}(n, q) = \left(1 + \frac{q}{m}\right) r_{2m}(n, q) - \frac{q}{m} r_{2m}(n, q-1) \quad (12)$$

with $r_0(n, q) = r_1(n, q) = 1$. One has, for example, $r_2(n, q) = n - 2q$, $r_3(n, q) = n - 4q$, $r_4(n, q) = n(n-1) - 8q(n-q)$, etc. The orthogonality properties of $s_n^m(\omega_x, \omega_y)$, namely,

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} s_n^m(\omega_x, \omega_y) s_{n'}^{m'}(\omega_x, \omega_y) e^{-\eta^2(\omega_x^2 + \omega_y^2)} d\omega_x d\omega_y \sim \delta_{n,n'} \delta_{m,m'}$$

result from the orthogonality of the Hermite polynomials and equations (11) and (12).

We desire an infinite hierarchy of differential-recurrence equations for the averaged values of $f_n^{l,m}(t)$ over its realizations in phase space (here configuration, which is angular velocity space), which are analogues of the observables in quantum mechanics. By appropriate transformation of the variables in equations (7) and (8) and subsequent use of Isserlis's

theorem as applied in appendices B and C of chapter 10 of [18], this is accomplished by evaluating

$$\frac{d}{dt} \overline{f_n^{l,m}(t)} = \lim_{\tau \rightarrow 0} \frac{P_l^m[\cos \vartheta(t+\tau)] s_n^m[\omega_x(t+\tau), \omega_y(t+\tau)] - P_l^m(\cos \vartheta) s_n^m(\omega_x, \omega_y)}{\tau} \quad (13)$$

where

$$\omega_x(t+\tau) = \omega_x - \frac{\zeta}{I} \int_t^{t+\tau} \omega_x(t') dt' + \int_t^{t+\tau} \omega_y^2(t') \cot \vartheta(t') dt' + \frac{1}{I} \int_t^{t+\tau} \lambda_x(t') dt' \quad (14)$$

$$\omega_y(t+\tau) = \omega_y - \frac{\zeta}{I} \int_t^{t+\tau} \omega_y(t') dt' - \int_t^{t+\tau} \omega_x(t') \omega_y(t') \cot \vartheta(t') dt' + \frac{1}{I} \int_t^{t+\tau} \lambda_y(t') dt' \quad (15)$$

are integral forms of equations (7) and (8). We remark here that the time τ is of such short duration that the angular velocities do not significantly alter during τ and neither does any external conservative torque. Nevertheless τ is supposed to be sufficiently long so that the chance that the rapidly fluctuating stochastic torque $\lambda(t)$ takes on a given value at time $t+\tau$ is independent of the value, which the torque possessed at time t . We further remark that ϑ , ω_x and ω_y and $\vartheta(t)$, $\omega_x(t)$ and $\omega_y(t)$ in equation (13) have different meanings, namely, $\vartheta(t)$, $\omega_x(t)$ and $\omega_y(t)$ are stochastic variables (processes) while ϑ , ω_x and ω_y are the sharp values at time t (recall that the time τ is infinitesimally small). Instead of using different symbols for the two quantities, we have distinguished the sharp values at time t from the stochastic variables by deleting the time argument as in [4, 18].

Thus, evaluating the right-hand side of equation (13) explicitly, one can derive the differential-recurrence relations for the moments $\overline{f_n^{l,m}}$ (the derivation is given in appendix A):

$$\eta \frac{d}{dt} \overline{f_n^{l,0}} = -2n\beta' \overline{f_n^{l,0}} + \frac{1}{2} \overline{f_n^{l,1}} + 2 \overline{f_{n-1}^{l,1}} \quad (16)$$

$$\begin{aligned} \eta \frac{d}{dt} \overline{f_n^{l,2m-M}} = & -(2n+M)\beta' \overline{f_n^{l,2m-M}} + \overline{f_{n-1+M}^{l,2m+1-M}} + \frac{1}{4} \overline{f_{n+M}^{l,2m+1-M}} - (l+2m-M)(l-2m \\ & + 1+M) \left[\frac{1}{4} (n-m+1+M) \overline{f_{n+M}^{l,2m-1-M}} + (n+m) \overline{f_{n-1+M}^{l,2m-1-M}} \right] \end{aligned} \quad (17)$$

where $m \geq 1$ and $M = 0$ or 1 , and $\beta' = \zeta \eta / I$. All the quantities $\overline{f_n^{l,m}}$ in equations (16) and (17) are functions of the sharp values ϑ , ω_x and ω_y which are themselves random variables with the probability density function $W(\vartheta, \omega_x, \omega_y, t)$. Therefore, in order to obtain equations for the moments, which govern the relaxation dynamics of the system, we must also average equation (16) over W [18]. However, if the system under consideration is in equilibrium (as in the present problem), all such averages are either constant or zero indicating that one must first construct from equations (16) and (17) a set of differential-recurrence equations for the appropriate equilibrium correlation functions (CFs) [18, 20].

As far as the majority of applications is concerned, the quantities of interest are the orientational equilibrium CFs $C_l(t)$ for the Legendre polynomials P_l defined as (in a physical system these are the observables rather than the sharp averages)

$$C_l(t) = \langle P_l[\cos \vartheta(0)] P_l[\cos \vartheta(t)] \rangle. \quad (18)$$

These characterize the orientational relaxation in liquids (the angular brackets denote the equilibrium ensemble averages). Having determined the correlation function $C_l(t)$, one can

also evaluate the corresponding orientational correlation time τ_l defined as the area under the normalized correlation function $C_l(t)/C_l(0)$ [3], namely,

$$\tau_l = \frac{1}{C_l(0)} \int_0^\infty C_l(t) dt. \quad (19)$$

By way of illustration, we shall obtain below exact analytical solutions in terms of ordinary continued fractions for the spectra of the first, $C_1(t) = \langle P_1[\cos \vartheta(0)]P_1[\cos \vartheta(t)] \rangle$, and the second, $C_2(t) = \langle P_2[\cos \vartheta(0)]P_2[\cos \vartheta(t)] \rangle$, order equilibrium orientational correlation functions (these CFs are used for the interpretation of dielectric and infrared absorption and Raman and Rayleigh scattering measurements) [2]. We also propose a general method for the evaluation of the spectra of higher order CFs in terms of matrix continued fractions.

3. Evaluation of the CF spectrum $\tilde{C}_1(\omega)$

One can readily derive differential-recurrence equations for the equilibrium CF for the first Legendre polynomial ($l = 1$), namely, $c_n^{1,m}(t) = \langle \cos \vartheta(0) \overline{f_n^{1,m}(t)} \rangle$ (so that $c_0^{1,0}(t) \equiv C_1(t)$) by multiplying equations (16) and (17) by $\cos \vartheta(0)$ and by averaging the equations so obtained over the equilibrium distribution function W_0 at the instant $t = 0$. Using the Laplace transformation, these equations can be written as a system of algebraic recurrence relations, namely,

$$(\eta s + 2n\beta')\tilde{c}_n^{1,0}(s) - 2\tilde{c}_{n-1}^{1,1}(s) - \tilde{c}_n^{1,1}(s)/2 = \delta_{n,0}\eta c_0^{1,0}(0) \quad (20)$$

$$[\eta s + (2n+1)\beta']\tilde{c}_n^{1,1}(s) + 2(n+1)\tilde{c}_n^{1,0}(s) + (n+1)\tilde{c}_{n+1}^{1,0}(s)/2 = 0 \quad (21)$$

where $\tilde{f}(s) = L\{f(t)\} = \int_0^\infty e^{-st} f(t) dt$. Here, we have taken into account that all the $c_n^{1,0}(0)$ vanish with the exception of $n = 0$, namely, $c_0^{1,0}(0) = 1/3$ (this follows from the orthogonality property of the associated Legendre functions [25]).

The solution of equations (20) and (21) can be obtained as a scalar continued fraction as follows. First of all, equations (20) and (21) can be rearranged as a three-term recurrence equation, namely,

$$[\eta s - q_n(s)]\tilde{c}_n^{1,0}(s) - q_n^+(s)\tilde{c}_{n+1}^{1,0}(s) - q_n^-(s)\tilde{c}_{n-1}^{1,0}(s) = \delta_{n,0}\eta c_0^{1,0}(0) \quad (22)$$

where

$$q_n(s) = -\frac{n}{(2n-1)\beta' + \eta s} - 2n\beta' - \frac{(n+1)}{(2n+1)\beta' + \eta s} \quad (23)$$

$$q_n^+(s) = -\frac{(n+1)/4}{(2n+1)\beta' + \eta s} \quad (24)$$

$$q_n^-(s) = -\frac{4n}{(2n-1)\beta' + \eta s}. \quad (25)$$

Equation (22) may be solved using the continued fraction

$$\frac{\tilde{c}_0^{1,0}(s)}{c_0^{1,0}(0)} = \eta \left/ \left(\eta s - q_0(s) - \frac{q_0^+(s)q_1^-(s)}{\eta s - q_1(s) - \frac{q_1^+(s)q_2^-(s)}{\eta s - \dots}} \right) \right.$$

or

$$\frac{\tilde{c}_n^{1,0}(i\omega)}{c_0^{1,0}(0)} = \eta \left/ \left(i\omega\eta + \frac{1}{\beta' + i\omega\eta} - \frac{1}{(\beta' + i\omega\eta)^2} \right. \right. \\ \left. \left. \times \frac{1}{\frac{1}{\beta' + i\omega\eta} + 2\beta' + i\omega\eta + \frac{2}{3\beta' + i\omega\eta} - \left(\frac{2}{3\beta' + i\omega\eta} \right)^2 \times \dots} \right) \right. \quad (26)$$

On using the equality

$$\frac{n}{A} - \frac{n^2}{A^2} \frac{1}{\frac{n}{A} + B} = \frac{n}{A + \frac{n}{B}}.$$

Equation (26) can be further rearranged to yield

$$\frac{\tilde{c}_n^{1,0}(i\omega)}{c_0^{1,0}(0)} = \frac{\eta}{i\omega\eta + \frac{1}{\beta' + i\omega\eta + \frac{1}{2\beta' + i\omega\eta + \frac{2}{3\beta' + i\omega\eta + \frac{2}{4\beta' + i\omega\eta + \frac{3}{5\beta' + i\omega\eta + \dots}}}}}}. \quad (27)$$

Having determined the CF spectrum $\tilde{C}_1(\omega) = \tilde{c}_0^{1,0}(i\omega)$, one can evaluate the orientational correlation time τ_1 defined by equation (19) for $n = 1$, namely,

$$\tau_1 = \frac{1}{C_1(0)} \int_0^\infty C_1(t) dt = \frac{\tilde{c}_0^{1,0}(0)}{c_0^{1,0}(0)} \quad (28)$$

and the normalized complex susceptibility $\hat{\chi}(\omega) = \hat{\chi}'(\omega) - i\hat{\chi}''(\omega)$. This is given by linear response theory as [21]

$$\hat{\chi}(\omega) = \frac{\chi(\omega)}{\chi'(0)} = 1 - i\omega \frac{\tilde{c}_0^{1,0}(i\omega)}{c_0^{1,0}(0)} \quad (29)$$

where $\chi'(0) = N\mu^2/3kT$ is the static susceptibility, N is the number of dipoles per unit volume and μ is the dipole moment of a molecule. Equations (27) and (29) coincide with the result of Sack [6] for the complex dielectric susceptibility.

In the high damping limit ($\beta' \gg 1$), the inertia-corrected Debye equation for the complex susceptibility [18] is recovered from equations (27)–(29), namely,

$$\hat{\chi}(\omega) = \frac{1}{1 + i\omega\tau_D - \eta^2\omega^2} \quad (30)$$

along with the following Taylor series expansion for τ_1 :

$$\tau_1 = \tau_D \left[1 + \gamma - \frac{2}{3}\gamma^2 + \frac{2}{3}\gamma^3 - \frac{11}{15}\gamma^4 + \frac{5}{6}\gamma^5 + O(\gamma^6) \right]. \quad (31)$$

Here $\tau_D = \eta\beta' = \zeta/2kT$ is the Debye relaxation time and $\gamma = 1/(2\beta'^2)$ is the inertial (Sack's [6]) parameter. Equation (30) will be a good approximation to the continued fraction solution for $\gamma \leq 0.05$ [6]. The small value of γ (or, equivalently, the large value of β') indicates that equilibrium of the angular velocities is almost attained before a dipole has time to change its direction appreciably. For larger values of γ the higher order terms in the continued

fractions became progressively more important, but the classical model is then no longer a good approximation in view of discrete spacing of rotational levels and a quantum-mechanical treatment must be used [5]. Equation (31) is in complete agreement with the results of [1, 9]. The high damping limit is the case of greatest interest in the explanation of dielectric relaxation data of molecular liquids. For example, for liquid chloroform at 25 °C [18]

$$I = 2.7 \times 10^{-38} \text{ g cm}^{-2} \quad \tau_D = 6.4 \times 10^{-12} \text{ s} \quad \zeta/I = 1.9 \times 10^{13} \text{ s}^{-1}$$

leading to $\gamma \sim 4 \times 10^{-3}$.

4. Evaluation of the CF spectrum $\tilde{C}_2(\omega)$

In like manner, one may obtain the system of recurrence equations for the Laplace transforms of the corresponding CFs for the second Legendre polynomial ($l = 2$), namely, $c_n^{2,m}(t) = \langle P_2[\cos \vartheta(0)] f_n^{2,m}(t) \rangle$ so that $c_0^{2,0}(t) \equiv C_2(t)$. By multiplying equations (16) and (17) by $P_2[\cos \vartheta(0)]$ and by averaging the equations so obtained over the equilibrium distribution function W_0 at the instant $t = 0$, we have from equations (16) and (17) for $l = 2$

$$(\eta s + 2n\beta')\tilde{c}_n^{2,0}(s) - \frac{1}{2}\tilde{c}_n^{2,1}(s) - 2\tilde{c}_{n-1}^{2,1}(s) = \eta c_0^{2,0}(0)\delta_{n,0} \quad (32)$$

$$[s\eta + (2n+1)\beta']\tilde{c}_n^{2,1}(s) + \frac{3}{2}(n+1)\tilde{c}_{n+1}^{2,0}(s) + 6(n+1)\tilde{c}_n^{2,0}(s) - \tilde{c}_n^{2,2}(s) - \frac{1}{4}\tilde{c}_{n+1}^{2,2}(s) = 0 \quad (33)$$

$$(s\eta + 2n\beta')\tilde{c}_n^{2,2}(s) + n\tilde{c}_n^{2,1}(s) + 4(n+1)\tilde{c}_{n-1}^{2,1}(s) = 0. \quad (34)$$

Here, we note that all the $c_n^{2,m}(0)$ vanish save $n = 0$ and $m = 0$, namely, $c_0^{2,0}(0) = 1/5$.

Just as the first-order response, equations (32)–(34) can be rearranged as a three-term recurrence equation for $\tilde{c}_n^{2,1}(s)$. Thus, the exact solution for $\tilde{c}_0^{2,1}(s)$ in terms of an infinite continued fraction combined with the relation

$$s\tilde{c}_0^{2,0}(s) = c_0^{2,0}(0) + \frac{1}{2\eta}\tilde{c}_0^{2,1}(s)$$

(that is, equation (32) at $n = 0$) yields

$$\frac{\tilde{c}_0^{2,0}(s)}{c_0^{2,0}(0)} = \frac{\eta}{\eta s + \frac{\eta}{3}} \quad (35)$$

$$\frac{\eta}{\eta s + \beta' + \frac{5}{\eta s + 2\beta'} - \frac{b_0}{\eta s + a_1 - \frac{b_1}{\eta s + a_2 - \frac{b_2}{\eta s + a_3 - \dots}}}}$$

where

$$a_n = (2n+1)\beta' + \frac{4n+3}{2n\beta' + \eta s} + \frac{4n+5}{2(n+1)\beta' + \eta s}$$

and

$$b_n = \frac{16(n+1)(n+2)}{[2(n+1)\beta' + \eta s]^2}.$$

Here the function

$$\tilde{c}_0^{2,0}(i\omega) = \tilde{C}_2(\omega) \quad (36)$$

is the spectrum of the autocorrelation function of the second-order Legendre polynomial which pertains to the Raman and Rayleigh scattering as well as to the dynamic Kerr-effect [2, 3].

Having determined the spectrum of the correlation function $\tilde{C}_2(\omega)$, one may evaluate the orientational correlation time τ_2 , namely,

$$\tau_2 = \frac{\tilde{c}_0^{2,0}(0)}{c_0^{2,0}(0)}. \tag{37}$$

In the high damping limit ($\beta' \gg 1$), equations (35) and (37) yield the Taylor series expansion for τ_2 :

$$\tau_2 = \frac{\tau_D}{3} \left[1 + 5\gamma - \frac{32}{3}\gamma^2 + \frac{368}{9}\gamma^3 - \frac{23\,464}{135}\gamma^4 + \frac{1\,549\,628}{2025}\gamma^5 + O(\gamma^6) \right]. \tag{38}$$

Equation (38) is in complete agreement with the results of [1, 9].

5. Evaluation of the CF spectrum $\tilde{C}_l(\omega)$ for an arbitrary l

In order to proceed, we must derive differential-recurrence equations for the equilibrium CF $c_n^{l,m}(t) = \langle P_l[\cos \vartheta(0)] f_n^{2,m}(t) \rangle$ so that $c_0^{l,0}(t) \equiv C_l(t)$. This is accomplished by multiplying equations (16) and (17) by $P_l[\cos \vartheta(0)]$ and averaging the equations so obtained over the equilibrium distribution function W_0 at the instant $t = 0$. In order to evaluate the l th order equilibrium orientation correlation function $C_l(t)$, the $l + 1$ independent equations (16) and (17) must be considered. Hence, it is simpler to represent the solution in terms of matrix continued fractions. In order to solve the hierarchy of moment equations so obtained, we introduce a column vector $C_n(t)$ comprising $l + 1$ elements:

$$C_n(t) = \begin{pmatrix} c_{n-1}^{l,0}(t) \\ c_{n-1}^{l,1}(t) \\ \vdots \\ c_{n-1}^{l,l}(t) \end{pmatrix}.$$

Then the hierarchy of equations for $c_n^{l,m}(t)$ can be transformed into the matrix three-term differential-recurrence equation

$$\eta \frac{d}{dt} C_n(t) = Q_n^- C_{n-1}(t) + Q_n C_n(t) + Q_n^+ C_{n+1}(t) \quad (n = 1, 2, 3, \dots) \tag{39}$$

where $C_0(t) = \mathbf{0}$ and Q_n, Q_n^+ and Q_n^- are $(l + 1) \times (l + 1)$ square matrices with elements to be determined from equations (16) and (17). The initial conditions are given by

$$C_1(0) = \begin{pmatrix} C_l(0) \\ 0 \\ \vdots \\ 0 \end{pmatrix} \quad \text{and} \quad C_n(0) = \mathbf{0} \quad \text{for all } n \geq 2$$

where $C_l(0) = (2l + 1)^{-1}$. On taking the Laplace transform of equation (39), we have the matrix three-term recurrence relation

$$(\eta s \mathbf{I} - Q_n) \tilde{C}_n(s) - Q_n^+ \tilde{C}_{n+1}(s) - Q_n^- \tilde{C}_{n-1}(s) = \delta_{n,1} \eta C_1(0) \quad (n \geq 1). \tag{40}$$

The exact solution for the Laplace transform $\tilde{C}_1(s)$ is then given by the matrix continued fraction [17, 23]

$$\tilde{C}_1(s) = \eta \frac{\mathbf{I}}{\eta s \mathbf{I} - Q_1 - Q_1^+ \frac{\mathbf{I}}{\eta s \mathbf{I} - Q_2 - Q_2^+ \frac{\mathbf{I}}{\eta s \mathbf{I} - Q_3 - Q_3^+ \dots}} Q_2^-} C_1(0). \tag{41}$$

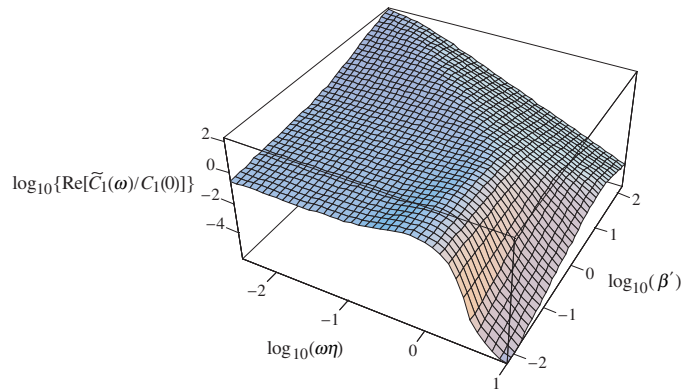


Figure 1. 3D plot of $\log_{10}\{\text{Re}[\tilde{C}_1(\omega)/C_1(0)]\}$ as a function of $\log_{10}(\omega\eta)$ and $\log_{10}(\beta')$.

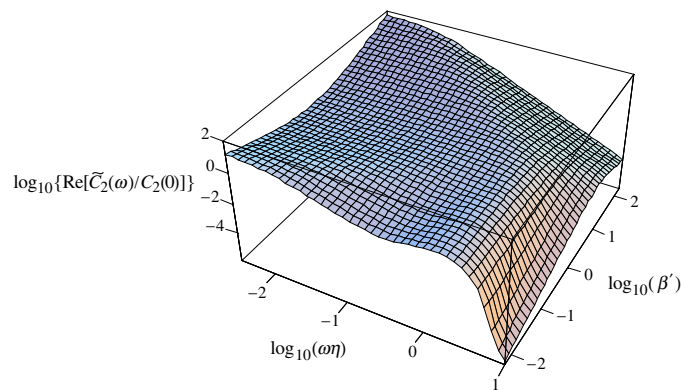


Figure 2. 3D plot of $\log_{10}\{\text{Re}[\tilde{C}_2(\omega)/C_2(0)]\}$ as a function of $\log_{10}(\omega\eta)$ and $\log_{10}(\beta')$.

where \mathbf{I} is the unit matrix and the fraction lines denote matrix inversion. Explicit solutions for $l = 1$ and $l = 2$ are given in appendix B (both (ordinary and matrix) continued fraction solutions give the same results and can be used for an independent check of calculations).

The 3D plots of $\log_{10}\{\text{Re}[\tilde{C}_1(\omega)/C_1(0)]\}$ and $\log_{10}\{\text{Re}[\tilde{C}_2(\omega)/C_2(0)]\}$ versus $\log_{10}(\omega\eta)$ and $\log_{10}(\beta')$ are shown in figures 1 and 2. Two limiting cases may be used to check the numerical calculations. In the low damping limit ($\beta' \rightarrow 0$), the spectra $\tilde{C}_l(\omega)$ reduce to those of the free rotation model ($\beta' \equiv 0$) [26], namely,

$$\frac{\tilde{C}_l^{FR}(\omega)}{C_l(0)} = \frac{1}{i\omega} \left\{ \left[d_{0,0}^l \left(\frac{\pi}{2} \right) \right]^2 - 2 \sum_{m=1}^l \left[d_{0,m}^l \left(\frac{\pi}{2} \right) \right]^2 (\omega\eta/m)^2 e^{-(\eta\omega/m)^2} E_1[(-\eta\omega/m)^2] \right\} \quad (42)$$

where

$$E_1(z) = \int_z^\infty \frac{\exp(-t)}{t} dt$$

is the first-order exponential integral function [25] and the $d_{M,M'}^l(\vartheta)$ are functions familiar in the theory of angular momentum; explicit equations for $d_{M,M'}^l(\vartheta)$ are given, e.g., in [27, p 78]. For $l = 1$ and $l = 2$, equation (42) yields

$$\tilde{C}_1^{FR}(\omega) = i\omega\eta^2 e^{-\eta^2\omega^2} E_1(-\eta^2\omega^2) \quad (43)$$

and

$$\tilde{C}_2^{FR}(\omega) = -\frac{i}{4\omega} + i\frac{3}{16}\omega\eta^2 e^{-\eta^2\omega^2/4} E_1(-\eta^2\omega^2/4). \quad (44)$$

In the opposite (high damping) limit, $\beta' \rightarrow \infty$, the form of the spectrum $\tilde{C}_l(\omega)$ becomes Lorentzian (see figures 1 and 2) and coincides with that predicted by the Debye model of noninertial rotational diffusion [3], namely,

$$\frac{\tilde{C}_l^D(\omega)}{C_l(0)} = \frac{\tau_l^D}{1 + i\omega\tau_l^D} \quad (45)$$

where $\tau_l^D = \frac{2\tau_D}{l(l+1)}$ is the orientational correlation time for the Debye model [3].

6. Discussion

On using the Langevin equation method, we have obtained exact analytical solutions (in terms of ordinary continued fractions) for the one-sided Fourier transforms of the first, $C_1(t)$, and the second, $C_2(t)$, order equilibrium orientational correlation functions for the inertial Brownian motion of linear molecule freely rotating in space. Moreover, we have proposed a general method for the calculation of higher order correlation functions $C_l(t)$ for any l in terms of matrix continued fractions. The same method may also be applied to the rotating sphere and symmetric top models, the only difference being that it is more tedious to evaluate the Hermite polynomial averages as they now contain ω_z .

The method of solution of orientational problems, which we have proposed, is quite general because it is based on the concept of the equation of motion of an observable which in turn is based on the dynamical (Langevin) theory [28] of the Brownian motion. The attractive feature of the dynamical method is that it allows one to compute directly from the dynamical equations of motion the spectra of the equilibrium CFs $\tilde{C}_l(\omega)$ for any values of γ and ω , taking account of the effect of molecular inertia on orientational relaxation in liquids. The distinct advantage that the dynamical (Langevin) method has over the Fokker–Planck equation approach is that it avoids both the derivation of that equation for the distribution function $W(\vartheta, \omega_x, \omega_y, t)$ of linear molecules in phase space, which for the problem in question is [1, 6]

$$\begin{aligned} \frac{\partial W}{\partial t} + \omega_x \frac{\partial W}{\partial \vartheta} + \omega_y \cot \vartheta \left(\omega_y \frac{\partial W}{\partial \omega_x} - \omega_x \frac{\partial W}{\partial \omega_y} \right) &= \frac{\zeta}{I} \left[\frac{\partial}{\partial \omega_x} \left(\omega_x W + \frac{k_B T}{I} \frac{\partial W}{\partial \omega_x} \right) \right. \\ &\left. + \frac{\partial}{\partial \omega_y} \left(2\omega_y W + \frac{k_B T}{I \cos^2 \vartheta} \frac{\partial W}{\partial \omega_y} \right) \right] \end{aligned} \quad (46)$$

and also the complex mathematical manipulations associated with the separation of variables methods of solution of that equation, which combine to obscure the physics underlying the problem.

As far as comparison with experimental data is concerned, the Langevin–Fokker–Planck model is suitable only for the explanation of the rotational motion of small molecules (such as CO, N₂O, CF₄, and so on) in liquids [3, 11]. Here, the model reasonably describes experimental data on infrared absorption, Raman scattering, nuclear magnetic relaxation, etc (see, e.g., [3, 9, 11], where a detailed comparison with experiments is given); however, it is not applicable [2] to liquids composed of larger molecules, where the rotational motion is more hindered and has a librational character. The failure of the Langevin–Fokker–Planck model as well as all other inertia-corrected Debye type models [3] to account for the high-frequency molecular librations in neat liquids, even though they explain the return to transparency at high frequencies, is to

be expected [2] in view of the assumption made in the theory that all electrical interactions between dipoles may be neglected. The Langevin equation approach is also of interest when extended to other models of orientational relaxation such as the itinerant oscillator [29], which are concerned with the rotational Brownian motion in external potentials [18, 24], which simulate intermolecular interactions. These models simultaneously exhibit both resonance and relaxation behaviour, which heuristically explains both the low-frequency (relaxational) and high-frequency (librational) behaviour of dipole systems. We remark that such models (e.g., the itinerant oscillator) have been previously treated for rotation about a space-fixed axis only. It is evident that the Langevin equation treatment, as described, in principle affords a simple way of writing down the recurrence equations for any of the three-dimensional models.

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Appendix A. Derivation of differential-recurrence equations for $f_n^{l,k}$

In order to derive the hierarchy of equations for average values of $f_n^{l,k}(t)$ we first note that

$$\overline{\frac{d}{dt} f_n^{l,m}(t)} = P_l^m \overline{\frac{d}{dt} s_n^m} + s_n^m \overline{\frac{d}{dt} P_l^m}.$$

For $m = 0$, we can evaluate the two terms on the right-hand side of the above equation as follows:

$$\begin{aligned} \overline{s_n^0[\omega_x(t), \omega_y(t)] \frac{d}{dt} P_l^1[\cos \vartheta(t)]} &= \overline{\omega_x(t) s_n^0[\omega_x(t), \omega_y(t)] P_l^1[\cos \vartheta(t)]} \\ &= \frac{1}{2\eta} P_l^1[\cos \vartheta(t)] \sum_{q=0}^n \frac{1}{q!(n-q)!} \left[H_{2n-2q+1}^x(t) + 4(n-q) H_{2n-2q-1}^x(t) \right] H_{2q}^y(t) \\ &= \frac{1}{2\eta} \left[s_n^1(\omega_x, \omega_y) + 4s_{n-1}^1(\omega_x, \omega_y) \right] P_l^1(\cos \vartheta) \end{aligned} \quad (\text{A1})$$

and

$$\begin{aligned} \overline{P_l[\cos \vartheta(t)] \frac{d}{dt} s_n^0[\omega_x(t), \omega_y(t)]} &= \overline{4\eta P_l[\cos \vartheta(t)] \sum_{q=0}^n \frac{1}{q!(n-q)!} \left[(n-q) H_{2n-2q-1}^x(t) H_{2q}^y(t) \dot{\omega}_x(t) + q H_{2n-2q}^x(t) H_{2q-1}^y(t) \dot{\omega}_y(t) \right]} \\ &= -2n \frac{\beta'}{\eta} P_l[\cos \vartheta(t)] \sum_{q=0}^n \frac{1}{q!(n-q)!} H_{2n-2q}^x(t) H_{2q}^y(t) \\ &= -2n \frac{\beta'}{\eta} s_n^0(\omega_x, \omega_y) P_l(\cos \vartheta) \end{aligned} \quad (\text{A2})$$

where $H_n^j(t) \equiv H_n[\eta\omega_j(t)]$ ($j = x, y$) and $\dot{\omega}_x(t)$ and $\dot{\omega}_y(t)$ are given by equations (7) and (8). In order to simplify equations (A1) and (A2), we have used the identities [25, 27]

$$\frac{\partial}{\partial \vartheta} P_l(\cos \vartheta) = P_l^1(\cos \vartheta) \quad (\text{A3})$$

$$\frac{d}{dx} H_n(x) = 2n H_{n-1}(x) \quad (\text{A4})$$

$$H_{n+1}(x) = 2x H_n(x) - 2n H_{n-1}(x) \quad (\text{A5})$$

and the relations from Stratonovich calculus

$$\overline{\lambda_x(t) F[\vartheta(t), \varphi(t), \omega_y(t)] H_n[\eta \omega_x(t)]} = \frac{\zeta n}{\eta} F(\vartheta, \varphi, \omega_y) H_{n-1}(\eta \omega_x) \quad (\text{A6})$$

$$\overline{\lambda_y(t) G[\vartheta(t), \varphi(t), \omega_x(t)] H_n[\eta \omega_y(t)]} = \frac{\zeta n}{\eta} G(\vartheta, \varphi, \omega_x) H_{n-1}(\eta \omega_y) \quad (\text{A7})$$

where F and G are arbitrary functions. Equations (A6) and (A7) follow from Isserlis's theorem and are given in appendices A–C of [18] (see also [16], where particular simple cases of these equations have been obtained, namely, equations (25), (26), (A14), (A16) and (A19) of that paper). Combining equations (A1) and (A2), one can obtain equation (16)

In like manner, we have for $m \geq 1$ and $M = 0, 1$

$$\begin{aligned} s_n^{2m+M}[\omega_x(t), \omega_y(t)] \frac{d}{dt} P_l^{2m+M}[\cos \vartheta(t)] &= \omega_x(t) s_n^{2m+M}[\omega_x(t), \omega_y(t)] \frac{\partial}{\partial \vartheta} P_l^{2m+M}[\cos \vartheta(t)] \\ &= \frac{1}{4\eta} \left[P_l^{2m+M+1}(\cos \vartheta) - (l+2m+M)(l-2m+M-1) P_l^{2m+M-1}(\cos \vartheta) \right] \\ &\quad \times \sum_{q=0}^n \frac{r_{2m+M}(n, q)}{q!(n-q)!} \left[H_{2n-2q+M+1}^x + 2(2n-2q+M) H_{2n-2q+M-1}^x \right] H_{2q}^y \end{aligned} \quad (\text{A8})$$

and

$$\begin{aligned} P_l^{2m+M}[\cos \vartheta(t)] \frac{d}{dt} s_n^{2m+M}[\omega_x(t), \omega_y(t)] &= -\frac{\beta'}{\eta} (2n+M) P_l^{2m+M}(\cos \vartheta) s_n^{2m+M}[\omega_x, \omega_y] - \frac{1}{4(2m+M)\eta} \\ &\quad \times \left[P_l^{2m+M+1}(\cos \vartheta) + (l+2m+M)(l-2m+M-1) P_l^{2m+M-1}(\cos \vartheta) \right] \\ &\quad \times \sum_{q=0}^n \frac{(2n-2q+M)r_{2m+M}(n, q) - 2(n-q)r_{2m+M}(n, q+1)}{q!(n-q)!} \\ &\quad \times H_{2n-2q+M-1}^x \left[H_{2q+2}^y + 2(2q+1) H_{2q}^y \right]. \end{aligned} \quad (\text{A9})$$

Here equations (A4)–(A7) and the following relations of the associated Legendre functions have been used [27]:

$$2 \frac{\partial}{\partial \vartheta} P_l^m = P_l^{m+1} - (l+m)(l-m+1) P_l^{m-1} \quad (m \geq 1)$$

$$2m \cot \vartheta P_l^m = -P_l^{m+1} - (l+m)(l-m+1) P_l^{m-1} \quad (m \geq 1)$$

$$\begin{aligned} (2l+1) \sin \vartheta P_l^m &= P_{l-1}^{m+1} - P_{l+1}^{m+1} \\ &= (l-m+1)(l-m+2) P_{l+1}^{m-1} - (l+m-1)(l+m) P_{l-1}^{m-1} \end{aligned}$$

Noting equations (A8) and (A9), we have

$$\begin{aligned} \eta \frac{d}{dt} \overline{f_n^{l, 2m-1}} &= -(2n+1) \beta' \overline{f_n^{l, 2m-1}} + \overline{f_n^{l, 2m}} + d_{n,+1}^{2m-1,+1} \overline{f_{n+1}^{l, 2m}} - (l+2m-1)(l-2m+2) \\ &\quad \times \left[d_{n,+1}^{2m-1,-1} \overline{f_{n+1}^{l, 2m-2}} + d_{n,0}^{2m-1,-1} \overline{f_n^{l, 2m-2}} \right] \end{aligned} \quad (\text{A10})$$

and

$$\eta \frac{d}{dt} \overline{f_n^{l,2m}} = -2n\beta' \overline{f_n^{l,2m}} + \frac{1}{4} \overline{f_n^{l,2m+1}} + d_{n,-1}^{2m,+1} \overline{f_{n-1}^{l,2m+1}} \\ - (l+2m)(l-2m+1) \left[d_{n,0}^{2m,-1} \overline{f_n^{l,2m-1}} + d_{n,-1}^{2m,-1} \overline{f_{n-1}^{l,2m-1}} \right] \quad (\text{A11})$$

where

$$d_{n,0}^{2m,-1} = \frac{1}{4} \left[\left(1 - \frac{q}{m}\right) \frac{r_{2m}(n, q)}{r_{2m-1}(n, q)} + \frac{q}{m} \frac{r_{2m}(n, q-1)}{r_{2m-1}(n, q)} \right] = \frac{n-m+1}{4} \\ d_{n,-1}^{2m,\{\pm 1\}} = \left(1 \mp \frac{2q+1}{2m}\right) \frac{r_{2m}(n, q)}{r_{2m\pm 1}(n-1, q)} \pm \frac{2q+1}{2m} \frac{r_{2m}(n, q+1)}{r_{2m\pm 1}(n-1, q)} = \left\{ \begin{array}{c} 1 \\ n+m \end{array} \right\} \\ d_{n,0}^{2m-1,-1} = \left(n-q + \frac{1}{2}\right) \left(1 + \frac{2q+1}{2m-1}\right) \frac{r_{2m-1}(n, q)}{r_{2m-2}(n, q)} - \frac{(n-q)(2q+1)}{2m-1} \frac{r_{2m-1}(n, q+1)}{r_{2m-2}(n, q)} \\ = n+m \\ d_{n,+1}^{2m-1,\{\pm 1\}} = \frac{(n-q+1)}{4} \left(1 \pm \frac{2q}{2m-1}\right) \frac{r_{2m-1}(n, q)}{r_{2m-1\pm 1}(n+1, q)} \\ \mp \frac{(2n-2q+3)q}{4(2m-1)} \frac{r_{2m-1}(n, q-1)}{r_{2m-1\pm 1}(n+1, q)} = \frac{1}{4} \left\{ \begin{array}{c} 1 \\ n-m+2 \end{array} \right\}.$$

Thus equations (A10) and (A11) reduce to equation (17).

Appendix B. Matrix continued fraction solutions of equations (20)–(21) and (32)–(34)

For $l = 1$, the scalar recurrence relations (20) and (21) may be recast in the form of the matrix recurrence relations (40), where

$$\tilde{C}_n(s) = \begin{pmatrix} \tilde{c}_{n-1}^{1,0}(s) \\ \tilde{c}_{n-1}^{1,1}(s) \end{pmatrix} \quad \mathbf{Q}_n^- = \begin{pmatrix} 0 & 2 \\ 0 & 0 \end{pmatrix} \\ \mathbf{Q}_n = \begin{pmatrix} -2(n-1)\beta' & 1/2 \\ -2n & -(2n-1)\beta' \end{pmatrix} \quad \mathbf{Q}_n^+ = \begin{pmatrix} 0 & 0 \\ -n/2 & 0 \end{pmatrix}$$

and

$$C_1(0) = \begin{pmatrix} C_1(0) \\ 0 \end{pmatrix}.$$

For $l = 2$, the scalar recurrence equations (32)–(34) can also be recast in the form of the matrix three-term recurrence (40), where this time

$$\tilde{C}_n(s) = \begin{pmatrix} \tilde{c}_{n-1}^{2,0}(s) \\ \tilde{c}_{n-1}^{2,1}(s) \\ \tilde{c}_{n-1}^{2,2}(s) \end{pmatrix} \quad C_1(0) = \begin{pmatrix} C_2(0) \\ 0 \\ 0 \end{pmatrix} \quad \mathbf{Q}_n^- = \begin{pmatrix} 0 & 2 & 0 \\ 0 & 0 & 0 \\ 0 & -4n & 0 \end{pmatrix} \\ \mathbf{Q}_n^+ = \begin{pmatrix} 0 & 0 & 0 \\ -3n/2 & 0 & 1/4 \\ 0 & 0 & 0 \end{pmatrix} \quad \mathbf{Q}_n = \begin{pmatrix} -2\beta'(n-1) & 1/2 & 0 \\ -6n & -\beta'(2n-1) & 1 \\ 0 & -(n-1) & -2\beta'(n-1) \end{pmatrix}.$$

In both cases ($l = 1$ and $l = 2$), the matrix continued fraction solutions are rendered by equations (41). The calculation shows that the matrix continued fraction solutions rendered by equations (41) and the ordinary continued fraction solutions (27) and (35) coincide.

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