Rotational correlation functions for asymmetric-top molecules in extended-diffusion models

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A new method for calculating vectorial correlation functions of extended-diffusion models is presented. It permits one to treat rotations of asymmetric-top molecules in liquids much more efficiently than by applying the methods which have already been published.

I. INTRODUCTION

Vectorial correlation functions for asymmetric-top molecules in the liquid state have recently been analyzed in much detail.[1-3] They have been determined by calculating the free-rotor correlation functions and by building them into the J or M extended-diffusion models.[4] The results are only available in numerical form; in general, the computing time turns out to be relatively long.

The purpose of the present paper is to give a new and much more efficient method for calculating these functions. In the symmetric-top limit, the St. Pierre and Steele results[5] are immediately rederived.

II. FREE-ROTOR LIMIT

A. Symmetry considerations

The rotational correlation functions $G(t)$ considered here are of the form $\langle \vec{u}(0)\cdot\vec{u}(t)\rangle$ where $\vec{u}(t)$ is a unit vector fixed in a molecule and rotating with it. In what follows, the molecular frame OXYZ is always assumed to be oriented in such a way that the inertia tensor $\overleftrightarrow{I}$ of the molecule is diagonalized ($I_X \leq I_Y \leq I_Z$). Then, using symmetry arguments, $G(t)$ can be shown to take the following form[1]:

$$G(t)=u_X^2(0)\langle R_{XX}(t)\rangle + u_Y^2(0)\langle R_{YY}(t)\rangle + u_Z^2(0)\langle R_{ZZ}(t)\rangle\,, \tag{1}$$

where the matrix $\overleftrightarrow{R}(t)$ relates the vector $\vec{u}(0)$ to $\vec{u}(t)$.

In this molecular frame, four regions may be defined according to the orientation of the angular momentum $\vec{J}(t)$ of the rotor. In the first and second regions, $\vec{J}(t)$ rotates around the Z axis [$J_Z(t)>0$ for region I and $J_Z(t)<0$ for region II]. In the third and fourth regions, $\vec{J}(t)$ rotates around the X axis [$J_X(t)>0$ for region III and $J_X(t)<0$ for region IV]. Using a set of three variables denoted by J, θ, and φ, (Ref. 1) the averaging operation can be expressed in each region separately. In addition, the integration over the regions I and II can be replaced by the integration over the region I; similarly, the integration over the regions III and IV can be replaced by that over region III. If N designates the region I or the region III, respectively, one has:

$$\langle R_{ii}(t)\rangle_N = dnia_N \int_0^{\theta_{MN}} \sin\theta d\theta \int_0^{\infty} J^2 dJ \exp(-\Lambda_N J^2) \times \int_0^{4K} d\varphi\, R_{ii}(t)\,, \tag{2a}$$

$$\Lambda_{\rm I} = (2k_BT)^{-1}(\cos^2\theta/I_Z + \sin^2\theta/I_X)\,; \tag{2b}$$

$$\Lambda_{\rm III} = (2k_BT)^{-1}(\cos^2\theta/I_X + \sin^2\theta/I_Z)\,, \tag{2c}$$

where K is the complete elliptic integral of the first kind[6] with the modulus k. The values of k, $dnia$, and θ_M are given in Ref. 1 for each of these regions.

In the following, $R_{ii}^{(\rm I)}(t)$ denotes the expression of $R_{ii}(t)$ for the region I.[1] With this notation, $G(t)$ finally takes the form

$$\begin{aligned} G(t) = 2Q^{-1}\{ & u_X^2(0)[\langle R_{XX}^{(\rm I)}(t)\rangle_{\rm I} + \langle R_{ZZ}^{(\rm I)}(t)\rangle_{\rm III}] \\ & + u_Y^2(0)[\langle R_{YY}^{(\rm I)}(t)\rangle_{\rm I} + \langle R_{YY}^{(\rm I)}(t)\rangle_{\rm III}] \\ & + u_Z^2(0)[\langle R_{ZZ}^{(\rm I)}(t)\rangle_{\rm I} + \langle R_{XX}^{(\rm I)}(t)\rangle_{\rm III}]\}\,, \end{aligned} \tag{3a}$$

$$Q = (2\pi k_BT)^{3/2}(I_XI_YI_Z)^{1/2}. \tag{3b}$$

B. Integration over the variables φ, θ, J

According to Eq. (2), the determination of $\langle R_{ii}^{(\rm I)}(t)\rangle_N$ requires integrations over φ, θ, and J. Only the average over φ was analytical in Refs. 1 and 2 and the integrals over J and θ were calculated numerically. The novelty here is that the integration over J is also analytical. The average over φ is determined by[1]

$$\int_0^{4K} d\varphi\, R_{ii}^{(\rm I)}(t,\varphi) = 4KA_{ii}^{(\rm I)}(t)\,, \tag{4}$$

where the dependence of $R_{ii}(t)$ on φ is explicitly stated by putting $R_{ii}(t)\equiv R_{ii}(t,\varphi)$. The elements $A_{ii}^{(\rm I)}(t)$ satisfy the relation,

$$A_{ii}^{(\mathrm{I})}(t)=[R_{ii}^{(\mathrm{I})}(t,0)Z(K-mt)+R_{ii}^{(\mathrm{I})}(t,K)Z(mt)]/[Z(mt)+Z(K-mt)]\,, \quad (5)$$

where $Z(u)$ is the Jacobi Zeta function.[7] The value of m entering into $\langle A_{ii}^{(\mathrm{I})}(t)\rangle_{\mathrm{I}}$ and $\langle A_{ii}^{(\mathrm{I})}(t)\rangle_{\mathrm{III}}$ is given by Eqs. (2d) and (A1d) of Ref. 1, respectively.

The next problem is to integrate over J. Equation (5) can be expanded in series[8] of $q=\exp(-\pi K'/K)$ where K' is the complete elliptic integral with the complementary modulus $k'=(1-k^2)^{1/2}$. One obtains

$$A_{XX}^{(\mathrm{I})}(t)=\sum_{n=0}^{\infty}[\eta_{X1}C_{2n+1}^{(-)}((-1)^n a)g(2n+1,(-1)^n\lambda,t)+\eta_{X2}C_{2n+1}^{(-)}((-1)^{n+1}a)g(2n+1,(-1)^{n+1}\lambda,t)+\eta_{X3}C_{2n+1}^{(+)}(0)g(2n+1,0,t)]\,, \quad (6a)$$

$$A_{YY}^{(\mathrm{I})}(t)=\sum_{n=0}^{\infty}\{\eta_{Y1}C_{2n+1}^{(+)}((-1)^n a)g(2n+1,(-1)^n\lambda,t)+\eta_{Y2}C_{2n+1}^{(+)}((-1)^{n+1}a)g(2n+1,(-1)^{n+1}\lambda,t)+\eta_{Y3}C_{2n+1}^{(-)}(0)g(2n+1,0,t)\}\,, \quad (6b)$$

$$A_{ZZ}^{(\mathrm{I})}(t)=\eta_{Z1}C_0^{(-)}(a)g(0,\lambda,t)+\eta_{Z4}C_0^{(+)}(0)+\sum_{n=1}^{\infty}\{\eta_{Z1}[C_{4n}^{(-)}(a)g(4n,\lambda,t)+C_{4n}^{(-)}(-a)g(4n,-\lambda,t)]+\eta_{Z2}[C_{4n-2}^{(-)}(a)g(4n-2,\lambda,t)+C_{4n-2}^{(-)}(-a)g(4n-2,-\lambda,t)]+\eta_{Z3}C_{4n}^{(+)}(0)g(4n,\lambda,t)+\eta_{Z4}C_{4n}^{(+)}(0)g(4n,0,t)\}\,. \quad (6c)$$

The coefficients η_{in} and $C_n^{(\pm)}$ depend only on the variable θ. Their expressions are detailed in Appendix A. In particular, it appears that the leading powers of the expansions of $C_{2n+1}^{(\pm)}$, $C_{4n}^{(\pm)}$, and $C_{4n-2}^{(\pm)}$ are respectively q^{2n}, q^{4n-4}, and q^{4n-3}. Thus, the expansion of $A_{ii}^{(\mathrm{I})}(t)$ in Eqs. [(6a)–(6c)] is rapidly converging. On the other hand,

$$g(n,\lambda,t)=2\cos(\mu_n Jt)\,, \quad (7a)$$

$$\mu_n=(n\pi m/2K+\lambda)/J\,, \quad (7b)$$

where λ is given by Eqs. (3d) and (A2d) of Ref. 1. Notice that μ_n is independent of J. The integration over J of $A_{ii}^{(\mathrm{I})}(t)$ is obtained by using Eqs. [(6a)–(6c)] and the analytical expression of $\langle g(n,\lambda,t)\rangle_{JN}$ given in Appendix B, with

$$\langle g(n,\lambda,t)\rangle_{JN}\equiv\int_0^{\infty}J^2dJ\exp(-\Lambda_N J^2)g(n,\lambda,t)\,. \quad (8)$$

Finally, the average on θ over the first and third regions still remains numerical.

C. Discussion

The following comments can be made on the series expansion of $A_{ii}^{(\mathrm{I})}(t)$: (i) The series [(6a)–(6c)] have the advantage of converging very rapidly.[9] Thus the desired accuracy is most often obtained by truncating the series after the terms in q^7; the errors in $G(t)$ are then of the order 10^{-6}. (ii) It is often useful to have $\mathrm{I}(\omega)$, the Fourier transform of $G(t)$. $\mathrm{I}(\omega)$ is obtained, as $G(t)$, from Eqs. [(1), (4), and (6a)–(6c)] with the value of $\langle g(n,\lambda,\omega)\rangle_{JN}$ given in Appendix B. The calculation of $\mathrm{I}(\omega)$ then involves only one numerical integration, that over θ. (iii) The term $\eta_{Z4}C_0^{(+)}(0)$ of Eq. (6c) gives the asymptotic behavior of $G(t)$ and the Q branch of $\mathrm{I}(\omega)$. (iv) The symmetric top limit ($\mathrm{I}_X=\mathrm{I}_Y$ or $\mathrm{I}_Y=\mathrm{I}_Z$) of $G(t)$ can be examined as a check. In this limit q tends to zero and $\exp(\pm a)$ to $(1\pm\cos\theta)/\sin\theta$. The St. Pierre and Steele expressions[10] of $G(t)$ are then directly deducible from Eqs. [(6a)–(6c)] and from the symmetric-top limit of $\langle g(n,\lambda,t)\rangle_{JN}$.

III. *J* AND *M* MODELS

The J and M models are often used to describe rotational motions in liquids.[4] These models have been recently generalized to the study of the asymmetric-top molecules.[2] Here $\tilde{\mathrm{R}}_J(t)$ and $\tilde{\mathrm{R}}_M(t)$ designate the $\tilde{\mathrm{R}}$ matrix calculated, respectively, in the J and M models. It can be easily seen that the correlation function is similar to that given in Eq. (1); it is sufficient to replace $\tilde{\mathrm{R}}(t)$ by $\tilde{\mathrm{R}}_J(t)$ or $\tilde{\mathrm{R}}_M(t)$. The matrix elements $\langle R_{Jii}(t)\rangle$ or $\langle R_{Mii}(t)\rangle$ are obtainable from their Laplace transforms denoted by $\langle\tilde{R}_{Jii}(s)\rangle$ or $\langle\tilde{R}_{Mii}(s)\rangle$. One has[2]

$$\langle\tilde{R}_{Jii}(s)\rangle=\frac{\langle\tilde{R}_{ii}(s+\tau^{-1})\rangle}{[1-\tau^{-1}\langle\tilde{R}_{ii}(s+\tau^{-1})\rangle]}\,, \quad (9a)$$

$$\langle\tilde{R}_{Mii}(s)\rangle=\left\langle\frac{\langle\tilde{R}_{ii}(s+\tau^{-1})\rangle_{\theta\varphi}}{[1-\tau^{-1}\langle\tilde{R}_{ii}(s+\tau^{-1})\rangle_{\theta\varphi}]}\right\rangle_J\,, \quad (9b)$$

where $\tilde{R}(s+\tau^{-1})$ is the Laplace transform of $\tilde{\mathrm{R}}(t)$ calculated in the precedent section, τ is the mean collision time, and

$$\langle R\rangle_{\theta\varphi} = N_{\theta\varphi}^{-1}\left(dnia_{\mathrm{I}}\int_0^{\theta_{M\mathrm{I}}}\sin\theta d\theta K\exp(-\Lambda_{\mathrm{I}}J^2)R + dnia_{\mathrm{III}}\int_0^{\theta_{M\mathrm{III}}}\sin\theta d\theta K\exp(-\Lambda_{\mathrm{III}}J^2)R\right), \quad (10a)$$

$$N_{\theta\varphi} = dnia_{\mathrm{I}}\int_0^{\theta_{M\mathrm{I}}}\sin\theta\, d\theta K\exp(-\Lambda_{\mathrm{I}}J^2) + dnia_{\mathrm{III}}\int_0^{\theta_{M\mathrm{III}}}\sin\theta d\theta K\exp(-\Lambda_{\mathrm{III}}J^2), \quad (10b)$$

$$\langle R\rangle_J = 8Q^{-1}\int_0^{\infty} J^2 dJ N_{\theta\varphi}R. \quad (10c)$$

In the J model, $\langle R_{J\,ii}(s)\rangle$ is calculated in the following way.

(i) The average over φ of $\tilde{R}_{ii}(s+\tau^{-1})$ is determined analytically by means of Eq. (4),

(ii) The analytical integration over J of $\tilde{A}_{ii}(s+\tau^{-1})$ is obtained by using Eqs. [(6a)–(6c)] and the expression of $\langle\tilde{g}(n,\lambda,s)\rangle_{J,N}$ given in Appendix B,

(iii) The average over θ in the first and third regions is calculated numerically. For the M model, (i) $\langle\tilde{R}_{ii}(s+\tau^{-1})\rangle_\varphi$ is obtained as before, (ii) $\tilde{A}_{ii}(s+\tau^{-1})$ is expressed on the basis of the $\tilde{g}(n,\lambda,s)$ given in Appendix B, (iii) the integral over θ is calculated numerically and (iv) the average over J in the Eq. (9b) is also determined by applying numerical methods. Finally, the rotation matrix $\langle\vec{\mathrm{R}}(t)\rangle$ is the Fourier transform of $\mathrm{Re}\langle\vec{\mathrm{R}}(s)\rangle/\pi$.

IV. CONCLUSION

Before averaging over J or determining the Laplace or Fourier transforms, the expressions described by Eqs. [(6a)–(6c)] appear as rapidly varying oscillatory functions. Thus numerical integration on these expressions takes much computer time if good accuracy is required. The analytical solutions given in this paper furnish a much more efficient method; the computation time is divided by a factor of order 10^3 for the same accuracy. The result is a Fortran program giving (i) the correlation function in the free-rotor limit, (ii) the Fourier transform in the same limit, (iii) correlation functions and (iv) their Fourier transform in the J or M extended-diffusion models.

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APPENDIX A

This appendix contains the factors η_{Ni} and the functions $C_n^{(\pm)}$ appearing in Eqs. [(6a)–(6c)]. In the following, β designates the value of $1-3q^4-q^8+8q^{12}+\cdots$ and u the value of $\cos\theta$:

$$\eta_{X1} = (1-u)q^{1/4}\Theta_1/2\beta H_1(ia),$$
$$\eta_{X2} = (1+u)q^{1/4}\Theta_1/2\beta H_1(ia),$$
$$\eta_{X3} = (1-u^2)q^{1/4}(k'/k)^{1/2}/\beta,$$
$$\eta_{Y1} = (1-k'u)q^{1/4}\Theta/2\beta H_1(ia),$$
$$\eta_{Y2} = (1+k'u)q^{1/4}\Theta/2\beta H_1(ia),$$
$$\eta_{Y3} = (1-u^2)q^{1/4}dn^2 ia/k^{1/2}\beta,$$
$$\eta_{Z1} = (1-u^2)^{1/2}(dnia+1)H_1/2\beta H_1(ia),$$
$$\eta_{Z2} = (1-u^2)^{1/2}(dnia-1)H_1/2\beta H_1(ia),$$
$$\eta_{Z3} = u^2(1-k')k'^{1/2}\beta,$$
$$\eta_{Z4} = u^2(1+k')k'^{1/2}/\beta.$$

Below, $C_n^{(\pm)}$ functions are given in q series up to the terms in q^7

$$C_0^{(\pm)}(2Kv/\pi) = 1+q^4[1\pm 4\cosh(2v)],$$
$$C_1^{(\pm)}(2Kv/\pi) = e^{-v}+q^4(e^{-v}+q^2e^{3v}) \pm 2q^3[(1+2q^4)e^{v}+q^2e^{-3v}],$$
$$C_2^{(\pm)}(2Kv/\pi) = qe^{-2v}+2q^5\cosh(2v) \pm 2q^3[1+q^4(2+e^{-4v})],$$
$$C_3^{(\pm)}(2Kv/\pi) = q^2e^{-3v}+q^4(e^{v}+q^2e^{-3v}) \pm 2q^3(1+2q^4)e^{-v},$$
$$C_4^{(\pm)}(2Kv/\pi) = q^4(1+e^{-4v})\pm 2q^4e^{-2v},$$
$$C_5^{(\pm)}(2Kv/\pi) = q^4(e^{-v}+q^2e^{-5v}) \pm 2q^5(e^{-3v}+q^2e^{v}),$$
$$C_6^{(\pm)}(2Kv/\pi) = q^5e^{-2v}\pm 2q^7(1+e^{-4v}),$$
$$C_7^{(\pm)}(2Kv/\pi) = q^6e^{-3v}\pm 2q^7e^{-v}.$$

APPENDIX B

This Appendix contains miscellaneous integrals including the functions $g(n,\lambda,t)$. For notation, see the text.

$$\langle g(n,\lambda,t)\rangle_{J,N} = 2^{-1}\pi^{1/2}\Lambda_N^{-3/2}(1-\mu_n^2t^2/2\Lambda_N) \times\exp(-\mu_n^2t^2/4\Lambda_N),$$
$$\langle g(n,\lambda,\omega)\rangle_{J,N} = |\mu_n|^{-3}\omega^2\exp(-\Lambda_N\omega^2/\mu_n^2),$$
$$\tilde{g}(n,\lambda,s) = (s+i\mu_nJ)^{-1}+(s-i\mu_nJ)^{-1},$$
$$\langle\tilde{g}(n,\lambda,s)\rangle_{J,N} = \pi^{1/2}\Lambda_N^{-1/2}s/\mu_n^2-\pi|\mu_n|^{-3}s^2 \times\exp(\Lambda_Ns^2/\mu_n^2) \times[1-\mathrm{erf}(\Lambda_N^{1/2}s/|\mu_n|)],$$

where $\mathrm{erf}(z)$ is the error function: $\mathrm{erf}(z) = 2\pi^{-1/2}\int_0^z \times\exp(-t^2)dt$. Padé approximants are very useful in calculating this function.[11]

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