

The modified collective-mode approach: dielectric relaxation in water

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2000 J. Phys.: Condens. Matter 12 L505

(<http://iopscience.iop.org/0953-8984/12/30/104>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.221

The article was downloaded on 16/05/2010 at 05:25

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

The modified collective-mode approach: dielectric relaxation in waterI P Omelyan[†] and M V TokarchukInstitute for Condensed Matter Physics, National Ukrainian Academy of Sciences,
1 Svientsitsky Street, UA-290011 Lviv, Ukraine

E-mail: omelyan@icmp.lviv.ua

Received 3 May 2000

Abstract. A more general formulation of the collective-mode approach is proposed to describe the processes of dynamical polarization in liquids. It is based on a consistent inclusion of non-Markovian terms into the kinetic memory kernels. This has allowed us to reproduce quantitatively the entire frequency dependence of the dielectric functions and identify the primary polarization modes for an interaction site model of water over the whole wavelength range.

The method of extended collective modes (ECM), introduced [1, 2] and developed [3, 4] to study time correlation functions (TCFs) of simple fluids, is widely used for the investigation of dynamical properties of mixtures [5], magnetic liquids [6, 7], semiquantum helium [8], and other systems. Within the ECM framework, a TCF can be written as a sum of partial terms each of which is associated with the contribution of a collective mode. In principle, the number of modes is not limited, but can be restricted to the most significant excitations. For example, the generalized transport coefficients of a Lennard-Jones fluid are quantitatively evaluated in terms of two sound, one heat, and six kinetic modes [9].

Substantial progress in applying the ECM approach has been achieved for dipolar systems. Previously, Madden and Kivelson [10] were able to explain the different types of frequency dependence for the dielectric function $\epsilon(\omega)$ using the well-known three-variable theory (3VT). Recently, within the spirit of the ECM formalism, it has been shown how one can extend the 3VT to an arbitrary number n of variables [11, 12]. As was demonstrated for a Stockmayer model, an accurate representation of $\epsilon(k, \omega)$ can be obtained for any wavevectors k and frequencies ω within a 5VT employing two dipolaron, one Debye, and two kinetic modes [12]. Among other methods, we should particularly point out the extended hydrodynamic description by Bagchi and Chandra [13]. However, due to the complexities of hydrodynamic equations, explicit results for $\epsilon(k, \omega)$ can be derived only in specific regions of k and ω .

Until now, there have been no successful attempts to apply the ECM approach to more realistic interaction site models (ISMs). As was established [14] for the TIP4P model of water, the 3VT is rather unsatisfactory for evaluating $\epsilon(\omega)$. Moreover, it was predicted that adding the next higher-order (HO) variables, one cannot expect to obtain a rapidly converging approximation. Usually, the difficulties with a quantitative representation of $\epsilon(k, \omega)$ for ISMs are handled phenomenologically by involving adjustable physically meaningless parameters. For instance in reference [14], these parameters were found artificially by extracting the Debye

[†] Author to whom any correspondence should be addressed.

contribution from the full TCF and fitting $\epsilon(\omega)$ to the molecular dynamics (MD) results. A similar procedure was used for the calculation of the transport coefficients of the TIP4P model of water [15].

The dielectric relaxation of water was theoretically studied also by Wei and Patey (WP) [16], Kim *et al* [17], Bertolini and Tani [18] (within the 3VT), and others. The starting point of the WP theory (like the ECM approach) is the definition of static components for the pair CF. Then the TCFs are constructed by means of the Kerr approximation using a self-part of the collective TCF. The self-part is obtained by solving diffusion equations for a single molecule moving in a viscous fluid. However, such a theory can be applicable in the hydrodynamic regime (small k and ω) only, because the short-time response is not described by the diffusion equations. Kim *et al* [17] have generalized the WP theory by including a non-collisional response, but the effect of collisions with other molecules was treated implicitly within a number-conserving relaxation-time approximation. Obviously, this approximation is not valid for real water because of the low moments of inertia of the water molecule and the large torques.

The pattern is somewhat different within the ECM approach. We mention that the n VT considers a basic variable and its HO components to explicitly include free-motion ($n = 2$), collision ($n = 3$), and kinetic ($n > 3$) processes which are important at short times t (large ω). The scale of small and intermediate ω is reproduced (at any k) implicitly, assuming that the Markovian approximation can be applied to HO memory kernels. However, if the characteristic intervals of variation of the basic TCF at short and long times differ considerably and the long-tail (Debye) contribution to the correlation time is significant, such a reproduction will not work properly. This leads to the necessity of including non-Markovian terms in the kinetic memory kernels.

In the present letter, the terms desired are included within a mathematically rigorous framework. As a result, the correct dielectric response of the TIP4P model of water is obtained using a finite number of physically meaningful quantities. The primary polarization modes are identified as well.

Consider a polar fluid consisting of N rigid molecules each composed of M interaction sites. The microscopic vector of the longitudinal polarization density is of the form

$$\mathbf{P}(\mathbf{k}, t) = \frac{i\mathbf{k}}{k^2} \sum_{i=1}^N \sum_{a=1}^M q_a [e^{-i\mathbf{k} \cdot \delta_i^a(t)} - 1] e^{-i\mathbf{k} \cdot \mathbf{r}_i(t)} \quad (1)$$

where $\delta_i^a = \mathbf{r}_i^a - \mathbf{r}_i$ denotes the position of site a within molecule i relative to its centre of mass \mathbf{r}_i , and q_a is the site charge [19]. Using the TCF

$$f(\mathbf{k}, t) = \langle \mathbf{P}(\mathbf{k}, 0) \cdot \mathbf{P}(-\mathbf{k}, t) \rangle / N\mu^2$$

the longitudinal component of $\epsilon(k, \omega)$ can be evaluated as

$$1 - \epsilon_L^{-1}(k, \omega) = 4\pi N\mu^2 [f(k) - i\omega f(k, \omega)] / V k_B T$$

where T and V are the temperature and volume of the system, respectively, k_B is Boltzmann's constant, $\langle \rangle$ denotes the equilibrium averaging,

$$f(k, \omega) = \int_0^\infty f(k, t) e^{-i\omega t} dt \equiv \mathcal{L}_{i\omega}[f(k, t)]$$

is the Laplace transform, $f(k) = \lim_{t \rightarrow 0} f(k, t)$ the static CF (SCF), $\mu_i = \sum_a q_a \delta_i^a$ the dipole moment of the molecule, and $\mu = |\mu_i|$.

The collective variable (1) satisfies the equation $d\mathbf{P}(\mathbf{k}, t)/dt = \hat{L}\mathbf{P}(\mathbf{k}, t)$ of motion, where

$$\hat{L} = \sum_i \left[\mathbf{v}_i \cdot \frac{\partial}{\partial \mathbf{r}_i} - \frac{1}{m} \sum_{j;a,b} \frac{\partial \varphi_{ij}^{ab}}{\partial \delta_i^a} \cdot \frac{\partial}{\partial \mathbf{v}_i} + \mathbf{w}_i \times \sum_a \delta_i^a \cdot \frac{\partial}{\partial \delta_i^a} \right. \\ \left. - \mathbf{J}_i^{-1} \left(\mathbf{w}_i \times (\mathbf{J}_i \mathbf{w}_i) + \sum_{j;a,b} \delta_i^a \times \frac{\partial \varphi_{ij}^{ab}}{\partial \delta_i^a} \right) \cdot \frac{\partial}{\partial \mathbf{w}_i} \right]$$

is the Liouville operator of the system, φ_{ij}^{ab} denote the site-site intermolecular potentials, \mathbf{v}_i and \mathbf{w}_i are the translational and angular velocities, respectively,

$$\mathbf{J}_i = \sum_a m_a [(\delta_i^a \cdot \delta_i^a) \mathbf{1} - \delta_i^a \delta_i^a]$$

is the matrix of moments of inertia, m_a and $m = \sum_a m_a$ are the masses of site a and separate molecules, and $\mathbf{1}$ denotes the unit matrix. Since such an equation cannot be integrated exactly, we formally cast the solution in the form $\mathbf{P}(\mathbf{k}, t) = e^{\hat{L}t} \mathbf{P}(\mathbf{k})$, where $\mathbf{P}(\mathbf{k}) \equiv \mathbf{P}(\mathbf{k}, 0)$. The time dependence of $f(\mathbf{k}, t)$ at short times can be obtained using the Taylor series

$$e^{\hat{L}t} \mathbf{P}(\mathbf{k}) = \sum_{s=0}^{\infty} \frac{t^s}{s!} \hat{L}^s \mathbf{P}(\mathbf{k})$$

where $\hat{L}^s \mathbf{P}(\mathbf{k})$ are HO ($s \geq 1$) static components of $\mathbf{P}(\mathbf{k}, t)$. Taking into account that $f(\mathbf{k}, t)$ is an even function of t and restricting S to being a finite number, one finds

$$f(\mathbf{k}, t) \approx f(\mathbf{k}) - t^2 f_2(\mathbf{k})/2! + \dots (-1)^S t^{2S} f_{2S}(\mathbf{k})/(2S)!$$

where the $f_{2s}(\mathbf{k}) = \langle \hat{L}^s \mathbf{P}(\mathbf{k}) \cdot \hat{L}^s \mathbf{P}(-\mathbf{k}) \rangle / N\mu^2$ (with $f_0(\mathbf{k}) \equiv f(\mathbf{k})$) are non-zero SCFs ($s = 0, 1, 2, \dots, S$) corresponding to the set $\mathbf{P}(\mathbf{k}), \hat{L}\mathbf{P}(\mathbf{k}), \dots, \hat{L}^S \mathbf{P}(\mathbf{k})$.

The main idea of our approach is based on the introduction of a modified set, namely,

$$\hat{L}^{-S'} \mathbf{P}(\mathbf{k}), \dots, \hat{L}^{-1} \mathbf{P}(\mathbf{k}), \mathbf{P}(\mathbf{k}), \hat{L}\mathbf{P}(\mathbf{k}), \dots, \hat{L}^S \mathbf{P}(\mathbf{k}) \quad (2)$$

which includes besides the HO array $\hat{L}^s \mathbf{P}(\mathbf{k})$ of quantities, new lower-order (LO) components $\hat{L}^{-s'} \mathbf{P}(\mathbf{k})$ of the basic dynamical variable $\mathbf{P}(\mathbf{k})$, where $s' = 1, 2, \dots, S'$. The LO components are evaluated in accordance with the rule $\hat{L}\hat{L}^{-1} = \hat{1}$ with $\hat{1}$ being the unit operator. Then by definition

$$\hat{L}^{-s'} \mathbf{P}(\mathbf{k}, t) = \int_{C_{s'}}^t \hat{L}^{-s'+1} \mathbf{P}(\mathbf{k}, t') dt'$$

where the $C_{s'}$ are arbitrary constants. Unlike the HO variables which can be obtained explicitly by applying the Liouville operator, the LO quantities require the direct integration of the equation of motion, and, thus, they cannot be presented in an explicit form. For this reason, these quantities should be treated as quasivariabes.

Using set (2), one constructs the matrix

$$f_{\alpha\beta}(\mathbf{k}, t) = \langle L^\alpha \mathbf{P}(\mathbf{k}) \cdot e^{Lt} L^\beta \mathbf{P}(-\mathbf{k}) \rangle / N\mu^2 \equiv \mathbf{F}(\mathbf{k}, t)$$

of TCFs, where $\alpha, \beta = -S', -S' + 1, \dots, 0, \dots, S - 1, S$. As long as the usual ($\alpha, \beta \geq 0$) TCFs vanish at $t \rightarrow \infty$, it is quite natural to determine the constants $C_{s'}$ in such a way as to fulfil the condition $\lim_{t \rightarrow \infty} f_{\alpha\beta}(\mathbf{k}, t) = 0$ for all the elements of $\mathbf{F}(\mathbf{k}, t)$. Then integrating by parts, the LO SCFs can be expressed uniquely in terms of the basic function $f_{00}(\mathbf{k}, t) \equiv f(\mathbf{k}, t)$ as ($\alpha + \beta < 0$)

$$f_{\alpha\beta}(\mathbf{k}) = \frac{(-1)^{|\alpha+\beta|}}{(|\alpha+\beta|-1)!} \int_0^\infty t^{|\alpha+\beta|-1} f(\mathbf{k}, t) dt.$$

It can be shown within the memory function formalism [3, 20] that the TCFs satisfy the generalized Langevin equation

$$[\mathbf{1}i\omega - \mathbf{\Omega}(k) + \mathbf{\Psi}(k, \omega)]\mathbf{F}(k, \omega) = \mathbf{F}(k) \tag{3}$$

where $\mathbf{\Omega}(k)$ and $\mathbf{\Psi}(k, \omega)$ denote the frequency and memory matrices, respectively, $\mathbf{F}(k) = \lim_{t \rightarrow 0} \mathbf{F}(k, t)$ and $\mathbf{F}(k, \omega) = \mathcal{L}_{i\omega}[\mathbf{F}(k, t)]$. One assumes in advance that at given values of S and S' , the matrix $\mathbf{F}(k, t)$ includes an almost complete set of slow TCFs. In this case we can apply the Markovian approximation $\mathbf{\Psi}(k, \omega) \approx \mathbf{\Psi}(k, \omega = 0)$. Then equation (3) is much simplified: $[\mathbf{1}i\omega + \mathbf{T}(k)]\mathbf{F}^{(S'S)}(k, \omega) = \mathbf{F}(k)$, and can be solved analytically. The result in time representation is

$$f_{\alpha\beta}^{(S'S)}(k, t) = \sum_{\gamma=-S'}^S g_{\gamma}^{\alpha\beta}(k) e^{-z_{\gamma}(k)t}$$

where z_{γ} is an eigenvalue corresponding to an eigenvector $x_{\alpha\gamma} \equiv [\mathbf{x}]_{\alpha\gamma}$ of the generalized evolution operator $\mathbf{T}(k) = -\mathbf{\Omega}(k) + \mathbf{\Psi}(k, \omega = 0) = \mathbf{F}(k)\mathbf{F}^{-1}(k, \omega = 0)$,

$$g_{\gamma}^{\alpha\beta}(k) = \sum_{l=-S'}^S x_{\alpha\gamma}(k)x_{\gamma l}^{-1}(k)f_{l\beta}(k)$$

where $T_{\alpha\beta}$ and $x_{\gamma l}^{-1}$ are the elements of matrices \mathbf{T} and \mathbf{x}^{-1} , respectively, and $\mathbf{F}^{(S'S)}$ denotes the TCFs in the Markovian approximation. Thus, each element of $\mathbf{F}^{(S'S)}(k, t)$ is expressed as a weighted sum of $S' + S + 1$ exponentials which are connected with the generalized collective modes $z_{\gamma}(k)$. More explicit expressions for $\mathbf{F}(k)$ and $\mathbf{F}(k, \omega = 0) \equiv \tilde{\mathbf{F}}(k)$ are ($S' = 2, S = 4$)

$$\mathbf{F}(k) = \begin{pmatrix} \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \boxed{\begin{matrix} \tau_3 & -\tau_2 & \tau_1 & -\tau_0 & f & 0 & -f_2 \\ \tau_2 & -\tau_1 & \tau_0 & -f & 0 & f_2 & 0 \\ \tau_1 & -\tau_0 & f & 0 & -f_2 & 0 & f_4 \\ \tau_0 & -f & 0 & f_2 & 0 & -f_4 & 0 \\ f & 0 & -f_2 & 0 & -f_4 & 0 & f_6 \\ 0 & f_2 & 0 & -f_4 & 0 & f_6 & 0 \end{matrix}} & \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & -f_2 & 0 & f_4 & 0 & -f_6 & 0 & f_8 & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \end{pmatrix}$$

$$\tilde{\mathbf{F}}(k) = \begin{pmatrix} \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \tau_4 & -\tau_3 & \tau_2 & -\tau_1 & \tau_0 & -f & 0 & \dots & \dots \\ \dots & \boxed{\text{the framed submatrix of } \mathbf{F}(k)} & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \end{pmatrix}$$

where

$$\tau_{\nu}(k) = \frac{1}{\nu!} \int_0^{\infty} t^{\nu} f(k, t) dt$$

is the correlation time of ν th order ($\nu = 0, 1, \dots, 2S'$).

It is necessary to stress that the Markovian approximation used for expanded set (2) does not concern the usual memory kernels $\Gamma_S(k, \omega)$ corresponding to the HO array $\hat{L}^S \mathbf{P}(k)$. Indeed, solving the system (3) of linear equations with respect to $f(k, \omega)$, the desired result

can be cast as the S 'th-order continued fraction

$$f^{(S'S)}(k, \omega) = \frac{f(k)}{i\omega + \frac{\Omega_1(k)}{i\omega + \frac{\Omega_2(k)}{i\omega + \cdots + \frac{\Omega_S(k)}{i\omega + \Gamma_{S'S}(k, \omega)}}}} \quad (4)$$

where $\Omega_1(k) = f_2(k)/f(k)$, $\Omega_2(k) = [f(k)f_4(k) - f_2^2(k)]/[f(k)f_2(k)]$, and so on [12] are HO elements of the frequency matrix, and

$$\Gamma_{S'S}(k, \omega) = \frac{a_0^{(S)}(k) + za_1^{(S)}(k) + \cdots + z^{S'}a_{S'}^{(S)}(k)}{1 + zb_1^{(S)}(k) + \cdots + z^{S'}b_{S'}^{(S)}(k)} \quad (5)$$

is the HO memory kernel $\Gamma_S(k, \omega)$ in the S' 'th approximation ($z \equiv i\omega$). We see that at $S' \neq 0$ the function $\Gamma_{S'S}$ depends on frequency in a characteristic way and, therefore, describes significantly non-Markovian effects. The multipliers for $S = 0$ and $S' = 0, 1, \dots$ are

$$\begin{aligned} a_0^{(0)} &= 1/\tilde{\tau}_0 \\ a_1^{(0)} &= (\tilde{\tau}_0^3 - 2\tilde{\tau}_0\tilde{\tau}_1 + \tilde{\tau}_2)/(\tilde{\tau}_0\tilde{\tau}_1 - \tilde{\tau}_0^3) \\ b_1^{(0)} &= (\tilde{\tau}_0\tilde{\tau}_2 - \tilde{\tau}_1^2)/(\tilde{\tau}_0\tilde{\tau}_1 - \tilde{\tau}_0^3) \end{aligned}$$

and so on, where $\tilde{\tau}_s(k) = \tau_s(k)/f(k)$. For any $S > 0$ they are calculated using the recursion relations

$$\begin{aligned} a_0^{(n+1)} &= \Omega_{n+1}/a_0^{(n)} \\ b_1^{(n+1)} &= a_1^{(n)}\Theta^{(n)}/((a_0^{(n)})^3 + a_0^{(n)}\Theta^{(n)}) \\ a_1^{(n+1)} &= b_1^{(n+1)}\Omega_{n+1}/a_0^{(n)} - 1 - \Theta^{(n)}/(a_0^{(n)})^2 \end{aligned}$$

and so on for $S' = 2, 3, \dots$, where $n = 0, 1, \dots, S - 1$, and $\Theta^{(n)} = [a_1^{(n)} - a_0^{(n)}b_1^{(n)}]\Omega_{n+1}$. This ensures the validity of the expansion

$$f(k, \omega) \approx \tau_0 - i\omega\tau_1 + (i\omega)^2\tau_2 - \cdots + (i\omega)^{2S'}\tau_{2S'}$$

at $\omega \rightarrow 0$ for $f^{(S'S)}(k, \omega)$.

From the above, it becomes clear that the first $2S$ -fold derivatives at $t = 0$ and the $2S'$ time integral moments for the actual $f(k, t)$ and approximated $f^{(S'S)}(k, t)$ functions coincide. In such a way, the time dependence of $f(k, t)$ is reproduced for arbitrary t . It is worth emphasizing that function (5) at $\omega \rightarrow 0$ fulfils the truncated Taylor series

$$\bar{\Gamma}_{S'S}(k, \omega) = \Gamma_S + \omega \frac{\partial \Gamma_S}{\partial \omega} + \cdots + \frac{\omega^{2S'}}{(2S')!} \frac{\partial^{2S'} \Gamma_S}{\partial \omega^{2S'}} \quad (6)$$

of the exact memory kernel $\Gamma_S(k, \omega)$. Note, however, that the straightforward extension (6) of the Markovian approximation distorts the correct short-time behaviour of $f(k, t)$, because the condition $\lim_{\omega \rightarrow \infty} \Gamma_S(k, \omega)/\omega = 0 = \lim_{\omega \rightarrow \infty} \Gamma_{S'S}/\omega$ is broken for $\bar{\Gamma}_{S'S}$.

Our numerical calculations were performed for the TIP4P model [21] at $mN/V = 1 \text{ g cm}^{-3}$ and $T = 293 \text{ K}$. In order to avoid additional uncertainties, the required input quantities $f_{2s}(k)$ and $\tau_s(k)$ were computed exactly by means of MD simulations (the MD details are similar to those reported in reference [19]). Generally speaking, such quantities might be obtained within a microscopic theory. For instance, $f(k)$ is directly connected with static components of the pair CF [22], whereas the $f_{2s}(k)$ at $s > 2$ are also reduced to them by low-order decoupling approximations ($f_2(k)$ is evaluated analytically [23]). Like in the WP theory, the pair CF can be determined by solving the integral equations within

the reference-hypernetted-chain approximation [16]. The correlation times $\tau_\nu(k)$ define the non-Markovian behaviour of kinetic memory kernels (5). From physical point of view, such a behaviour is caused by the diffusion processes which determine the shape of $f(k, t)$ at long times. Therefore, the quantities $\tau_\nu(k)$ can be calculated by solving diffusion equations (like those presented in reference [16]) and they should be closely related to rotational and translational diffusion coefficients. Alternatively, the correlation times can be expressed in terms of SCFs using the relations $a_0^{(S+1)} \approx a_0^{(S)}$, $a_1^{(S+1)} \approx a_1^{(S)}$, $b_1^{(S+1)} \approx b_1^{(S)}$, and so on for sufficiently large S . These relations constitute a system of non-linear equations for $\tau_\nu(k)$ which can be solved numerically. The above problems are beyond the scope of the present study and will be considered elsewhere.

Examples of the normalized $\Phi(k, t) \equiv f(k, t)/f(k)$ TCFs obtained within the usual ($S' = 0$) and non-Markovian ($S' = 1$) approximations for $S = 2, 4$, and 6 are shown in figure 1 in comparison with MD data of reference [19]. The most striking features of $f(k, t)$ are damped very fast librational oscillations at short times, which further transform into an almost pure decay at intermediate intervals, and, finally, into a very slow exponential Debye

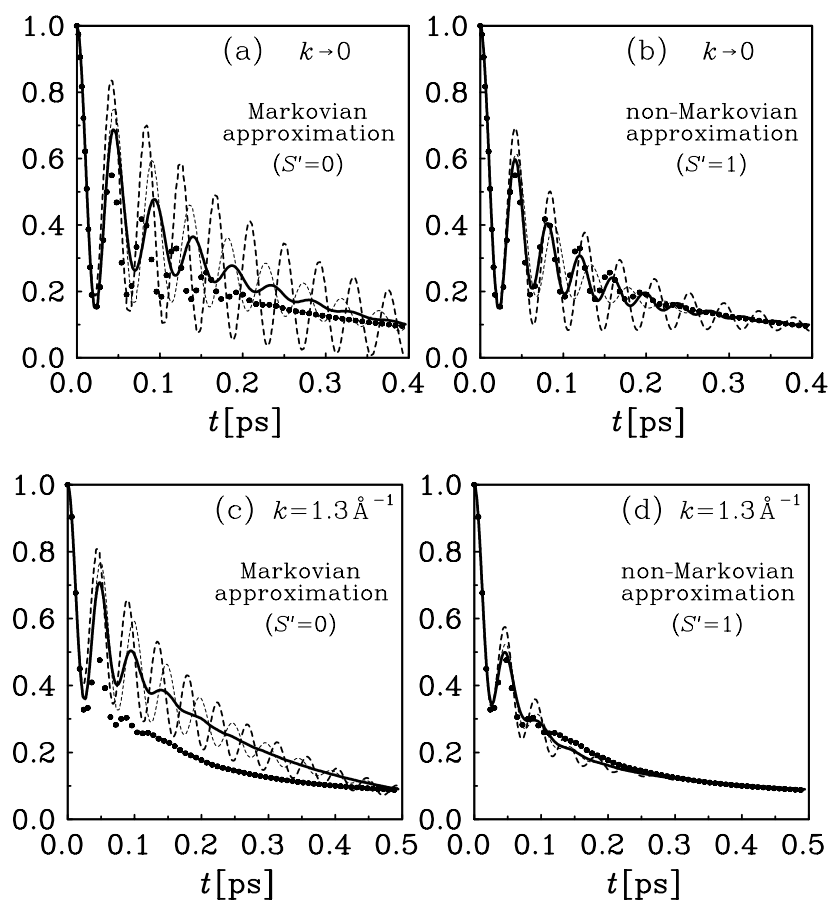


Figure 1. The longitudinal polarization TCFs of the TIP4P model of water, reproduced within the usual ($S' = 0$, subsets (a), (c)) and non-Markovian ($S' = 1$, (b), (d)) approximations. The results corresponding to $S = 2, 4$, and 6 are plotted as long-dashed, short-dashed, and solid curves, respectively. The MD data are shown as circles.

relaxation at long times. As we can see, the 3VT (corresponding to $S' = 0$ and $S = 2$ in our notation) is unable to describe these features satisfactorily. Such a statement remains valid even if the extra-order counterparts the 5VT ($S' = 0$, $S = 4$) and 7VT ($S' = 0$, $S = 6$) are involved. On the other hand, applying the 3VT' (when $S' = 1$ and $S = 2$) we can talk about a qualitative reproduction of $f(k, t)$ not only for very short times but also for intermediate and long timescales. Moreover, including the non-Markovian effects allows one to speed up considerably the convergence of continued fractions, with the outcome that the results corresponding to the 5VT' ($S' = 1$, $S = 4$) and 7VT' ($S' = 1$, $S = 6$) begin to be practically indistinguishable from the MD data. A similar pattern was observed for $\epsilon_L(k, \omega)$.

The polarization mode spectrum reproduced by the 3VT' is presented in figure 2. We have identified two propagating modes, $z_L(k) = \sigma_L(k) \pm i\omega_L(k)$, and two purely real modes, $z_{1,2}(k) \equiv \sigma_{1,2}(k)$. The propagation modes describe the librational excitations in fluctuations of the polarization density as damped waves $\sim e^{-\sigma_L(k)t} e^{-i\omega_L(k)t}$, with ω_L and σ_L being the frequency and damping coefficient, respectively. Such excitations exhibit a quasiparticle behaviour at small $k < 2 \text{ \AA}^{-1}$, where $\sigma_L(k) \ll \omega_L(k)$. The librational oscillations are caused by the fast rotational motion of particles in the averaged electric field of their neighbours. These oscillations vanish at $k > 3 \text{ \AA}^{-1}$ when $\sigma_L(k) \sim \omega_L(k)$. The relaxing character of the intermolecular torques is described by the Debye-like mode $\sigma_2(k) \sim 1/\tau_0(k)$ which should be associated with the secondary relaxation process $\sim e^{-\sigma_2(k)t}$ at intermediate times. The last, fourth mode $\sigma_1(k)$ must be related to the primary long-time Debye relaxation. Because $\sigma_1^{-1}(k) \gg \sigma_2^{-1}(k)$ (at not very great k), this mode cannot be reproduced by n VTs. Within n VT's, the Debye contribution to $f(k, t)$ is $g_D(k)e^{-\sigma_1(k)t}$, where the amplitude and damping coefficient can be estimated with a great precision at small k as $g_D \approx \tau_1^3/\tau_2^2$ and $\sigma_1 \approx \tau_1/\tau_2$. For $k > 6 \text{ \AA}^{-1}$, when $\sigma_1(k) \sim \sigma_2(k) \approx \sigma_L(k)$, the non-Markovian effects can be neglected and the description by simple n VTs may be appropriate.

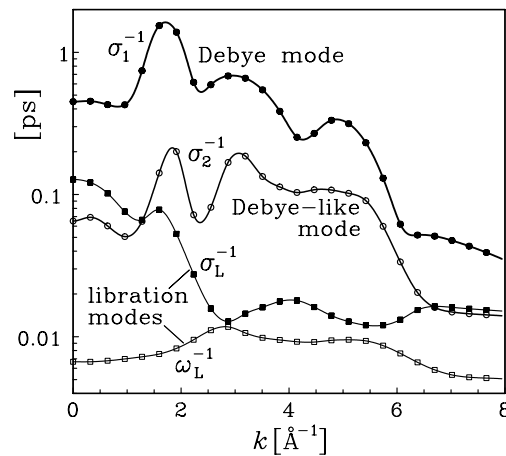


Figure 2. The most significant polarization modes of the TIP4P model of water.

References

- [1] Bruin C, Michels J P J, van Rijs J C, de Graaf L A and de Schepper I M 1985 *Phys. Lett. A* **110** 40
- [2] de Schepper I M, Cohen E G D, Bruin C, van Rijs J C, Montfrooij W and de Graaf L A 1988 *Phys. Rev. A* **38** 271
- [3] Mryglod I M, Omelyan I P and Tokarchuk M V 1995 *Mol. Phys.* **84** 235

- [4] Mryglod I M and Omelyan I P 1995 *Phys. Lett. A* **205** 401
- [5] Bryk T M, Mryglod I M and Kahl G 1997 *Phys. Rev. E* **56** 2903
- [6] Mryglod I M, Tokarchuk M V and Folk R 1995 *Physica A* **220** 325
- [7] Mryglod I, Folk R, Dubyk S and Rudavskii Yu 2000 *Physica A* **277** 389
- [8] Montfrooij W, de Graaf L A and de Schepper I M 1992 *Phys. Rev. B* **45** 3111
- [9] Mryglod I M and Omelyan I P 1997 *Mol. Phys.* **91** 1005
Mryglod I M and Omelyan I P 1997 *Mol. Phys.* **92** 913
- [10] Madden P and Kivelson D 1984 *Adv. Chem. Phys.* **56** 467
- [11] Omelyan I P 1997 *Physica A* **247** 121
- [12] Omelyan I P, Mryglod I M and Tokarchuk M V 1998 *Phys. Rev. E* **57** 6667
- [13] Bagchi B and Chandra A 1991 *Adv. Chem. Phys.* **80** 1
- [14] Neumann M 1986 *J. Chem. Phys.* **85** 1567
- [15] Bertolini D and Tani A 1995 *Phys. Rev. E* **51** 1091
Bertolini D and Tani A 1995 *Phys. Rev. E* **52** 1699
- [16] Wei D and Patey G N 1989 *J. Chem. Phys.* **91** 7113
Wei D and Patey G N 1990 *J. Chem. Phys.* **93** 1399
- [17] Kim S H, Vignale G and DeFacio B 1992 *Phys. Rev. A* **46** 7548
- [18] Bertolini D and Tani A 1992 *Mol. Phys.* **75** 1047
Bertolini D and Tani A 1992 *Mol. Phys.* **75** 1065
- [19] Omelyan I P 1998 *Mol. Phys.* **93** 123
- [20] Mori H 1965 *Prog. Theor. Phys.* **33** 423
Mori H 1965 *Prog. Theor. Phys.* **34** 399
- [21] Jorgensen W L, Chandrasekhar J, Madura J D, Impey R W and Klein M L 1983 *Chem. Phys.* **79** 926
- [22] Bopp P A, Kornyshev A A and Sutmann G 1996 *Phys. Rev. Lett.* **76** 1280
- [23] Omelyan I P 1999 *Mol. Phys.* **96** 407