PHYSICAL REVIEW E VOLUME 57, NUMBER 6 JUNE 1998

Generalized dipolar modes of a Stockmayer fluid in high-order approximations

I. P. Omelyan,* I. M. Mryglod, and M. V. Tokarchuk
Institute for Condensed Matter Physics, National Ukrainian Academy of Sciences, 1 Svientsitsky Street, UA-290011 Lviv, Ukraine

(Received 18 November 1997)

Generalized dipolar mode spectra of a Stockmayer fluid are evaluated over a wide scale of wavelengths up to a five-order approximation. The wave-vector- and frequency-dependent dielectric permittivity and dipole-moment time autocorrelation functions are calculated on the basis of analytical expressions using the dipolar modes. The obtained results are compared with those performed in lower-order approximations and with molecular dynamics data. It is shown that the five-variable description quantitatively reproduces the entire frequency dependence of the dielectric constant at arbitrary wave numbers. A relationship of the proposed theory with existing approaches is established.
[S1063-651X(98)09106-5]

PACS number(s): 47.65.+a, 67.55.Jd, 77.22.−d

I. INTRODUCTION

Dielectric relaxation in polar fluids was the subject of many investigations in theory [1–11], computer simulation [12–28], and pure experiment [29–33]. Despite such intensive studies, there is a lack of agreement between predicted and experimental results. Moreover, some key problems still remain unsolved, even in the simplest case when the fluid is treated as a system of point dipoles.

The calculation of dielectric quantities for dipolar systems by computer simulation is still considered a major challenge. This is given that very long trajectories are required to obtain reliable statistical accuracy, and because long-range contributions of the dipolar interaction must be taken into account within a finite-size sample to determine the dielectric constant unambiguously. The first correct calculation of dielectric properties for a Stockmayer fluid model was done by Pollock and co-workers [12–14] using the Ewald summation technique. Neumann and co-workers [18,19] proposed a self-consistent computer adapted theory suitable for the investigation of dielectric properties using reaction field geometry. It has been shown that adequate values for the bulk dielectric constant can be reproduced from computer experiments of a few hundred particles. Recently [28], the computer adapted theory has been developed to evaluate time-dependent dipole fluctuations at arbitrary wave numbers. As a result, the dielectric function of a Stockmayer fluid has been calculated by molecular dynamics (MD) simulations in a wide range of wave vectors and frequencies.

Among various theoretical schemes able to describe the processes of dielectric relaxation in dipolar fluids, we can point out two approaches, namely, the dipole-density formalism of Madden and Kivelson [3] and the extended hydrodynamic description, developed by Bagchi and Chandra [6]. The usual Navier-Stokes hydrodynamics [34], being valid in the infinite-wavelength limit and at great times, cannot be used at molecular length scales. In the extended hydrodynamic description, the microscopic operators of particle numbers, spatial and angular momenta densities, depending on translational and orientational positions of molecules, are considered as basic dynamical quantities [5]. These quantities satisfy modified equations which take into account processes with short and intermediate time scales as well. The microscopic operator of dipole density is obtained by averaging the number density over orientations of the molecules. In such a way, the dynamical polarization in a dense dipolar fluid can be investigated, provided reasonable forms of the dissipative kernels are available. However, due to the complexities of the hydrodynamic equations, explicit results can be derived if various mechanisms of dielectric relaxation are included separately from each other. As a consequence, these results can be applicable only in specific regions of wave vectors and frequencies [6].

In an alternative scheme [3], the polarization vector and its next two higher-order components are assumed to be a set of slow variables. In this so-called three-variable theory the orientational relaxation, inertial effects, and correlations due to the dipole-dipole interactions are involved in the consideration. As a result, the dipole-moment autocorrelation function is represented on time as the sum of three exponential terms which are associated with the corresponding mechanisms of dielectric relaxation. The frequency-dependent dielectric constant is described in terms of the third-order continued fraction. Time constants, appearing in the dissipative kernel are considered, as a rule, adjustable parameters. It is worth underlining that previous applications of this theory were restricted to the long-wavelength regime only [17,20].

Recently, the concept of generalized collective modes, used earlier for the investigation of nonequilibrium properties of simple fluids [35–37], was applied to dipolar systems, and actual computations were performed in the whole wave-vector range up to a three-mode description [38]. In particular, it was concluded that the three-variable prescription is sufficient to predict quantitatively the frequency dependence of dielectric quantities for Stockmayer fluids. But such a conclusion was based on calculations carried out with the help of a fitting procedure, because higher-order static correlation functions were not known. For this reason, it is not so obvious that the described above pattern indeed takes place.

In the present paper, the generalized dipolar mode spectra of a Stockmayer fluid are evaluated over a wide scale of wavelengths up to a five-order description, without involving

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*Author to whom correspondence should be addressed. Electronic address: nep@icmp.lviv.ua any adjustable parameters. In the framework of the proposed approach, the frequency dependence of dielectric quantities is determined by extended continued fractions to which the Markovian approximation is applied. As a result, using the dipolar modes, it is shown that the three-variable theory reproduces qualitatively the wave-vector- and frequency-dependent dielectric constant and only beginning from the five-order description can one talk about quantitatively reproducing over the whole range of varying wave numbers and frequencies. Moreover, we demonstrate that within the same approximation all time constants of memory kernels can be expressed in terms of static correlation functions, so that dynamic properties of the system are obtained using static fluctuations exclusively.

II. GENERAL THEORETICAL FRAMEWORK

A. Basic definitions

We shall deal with a dipolar fluid of N identical molecules enclosed in volume V. Let

$$\mathbf{M}(\mathbf{k},t)=\sum_{i=1}^{N}\mathbf{u}_i(t)e^{-i\mathbf{k}\cdot\mathbf{r}_i(t)} \tag{1}$$

be the primary dynamical variable, whose correlation function is of direct interest. The collective variable (1) presents, in fact, the spatial Fourier transform $\int_V\hat{\mathbf{M}}(\mathbf{r},t)e^{-i\mathbf{k}\cdot\mathbf{r}}d\mathbf{r}$ of the microscopic operator of dipole-moment density $\hat{\mathbf{M}}(\mathbf{r},t)=\sum_{i=1}^{N}\mathbf{u}_i(t)\delta[\mathbf{r}-\mathbf{r}_i(t)]$, where $\mathbf{r}_i(t)$ and $\mathbf{u}_i(t)$ denote the position and dipole moment, respectively, of molecule i at time t. This dynamical variable satisfies the equation of motion $d\mathbf{M}(\mathbf{k},t)/dt=L\mathbf{M}(\mathbf{k},t)$, where

$$\begin{aligned}L=&\sum_{i=1}^{N}\left(\mathbf{v}_i\cdot\frac{\partial}{\partial\mathbf{r}_i}+\mathbf{w}_i\times\mathbf{u}_i\cdot\frac{\partial}{\partial\mathbf{u}_i}\right)\\&-\sum_{i\neq j}^{N}\left(\frac{1}{m}\frac{\partial\varphi_{ij}}{\partial\mathbf{r}_i}\cdot\frac{\partial}{\partial\mathbf{v}_i}+\frac{1}{J}\mathbf{u}_i\times\frac{\partial\varphi_{ij}}{\partial\mathbf{u}_i}\cdot\frac{\partial}{\partial\mathbf{w}_i}\right)\end{aligned} \tag{2}$$

is the Liouville operator of the system, φ_{ij} denotes the intermolecular potential, $\mathbf{v}_i$ and $\mathbf{w}_i$ are the translational and rotational velocities, respectively, of molecule i with mass m and moment of inertia J. The formal solution of the equation of motion is $\mathbf{M}(\mathbf{k},t)=e^{Lt}\mathbf{M}(\mathbf{k},0)\equiv e^{Lt}\mathbf{M}(\mathbf{k})$.

Let us consider an extended set of variables

$$\begin{aligned}&\{\mathbf{M}(\mathbf{k}),L\mathbf{M}(\mathbf{k}),L^2\mathbf{M}(\mathbf{k}),\ldots,L^{S-1}\mathbf{M}(\mathbf{k})\}\\&\quad\equiv\{L^{\alpha-1}\mathbf{M}(\mathbf{k})\},\quad\alpha=1,\ldots,S\end{aligned} \tag{3}$$

which includes, besides the basic dynamical quantity $\mathbf{M}(\mathbf{k})$, its time derivatives at $t=0$ up to $(S-1)$th order. It is necessary to note that due to isotropy of the system, longitudinal and transverse fluctuations are completely independent of one another and can be studied separately. Therefore, set (3) is formed by either longitudinal, $\mathbf{M}^L(\mathbf{k})$, or transverse, $\mathbf{M}^T(\mathbf{k})$, components of $\mathbf{M}(\mathbf{k})$. For more convenience of further presentation, we transform the extended set to the orthogonalized form

$$\mathcal{M}(\mathbf{k})=\{\mathcal{M}_1(\mathbf{k}),\mathcal{M}_2(\mathbf{k}),\mathcal{M}_3(\mathbf{k}),\ldots,\mathcal{M}_S(\mathbf{k})\}, \tag{4}$$

where $\mathcal{M}_1(\mathbf{k})=\mathbf{M}(\mathbf{k})$, $\mathcal{M}_2(\mathbf{k})=(1-\mathcal{P}_1)L\mathbf{M}(\mathbf{k}),\ldots,$ and $\mathcal{M}_S(\mathbf{k})=(1-\mathcal{P}_{S-1})L^{S-1}\mathbf{M}(\mathbf{k})$ and $\mathcal{P}_\alpha\ldots=\sum_{\beta=1}^{\alpha}\langle\ldots\mathcal{M}_\beta(-\mathbf{k})\rangle\langle\mathcal{M}_\beta(\mathbf{k})\cdot\mathcal{M}_\beta(-\mathbf{k})\rangle^{-1}\mathcal{M}_\beta(\mathbf{k})$ denotes the Mori-like projection operator [39]. The orthogonalized variables (4) constitute the matrix of time correlation functions (TCF's)

$$f_{\alpha\beta}(k,t)=\frac{\langle\mathcal{M}_\alpha(\mathbf{k})\cdot e^{Lt}\mathcal{M}_\beta(-\mathbf{k})\rangle}{\{2\}Nu^2}\equiv\mathbf{F}(k,t) \tag{5}$$

which is diagonal in the static limit $t\rightarrow0$, i.e., $f_{\alpha\beta}(k)=\delta_{\alpha\beta}f_{\alpha\alpha}(k)$, where $\langle\ \rangle$ denotes the equilibrium average, u designates the permanent magnitude of the molecule's dipole moment, and the multiplier $\{2\}$ is included in the case of transverse fluctuations only.

According to construction of the orthogonalized set, the functions $f_{\alpha\alpha}(k)$ can be found in terms of static correlation functions (SCF's) corresponding to the initial set (3), $g_{\alpha\beta}(k)=\langle L^{\alpha-1}\mathbf{M}(\mathbf{k})\cdot L^{\beta-1}\mathbf{M}(-\mathbf{k})\rangle/\{2\}Nu^2$, by the iterations

$$\xi_{\alpha\beta}(k)=g_{\alpha\beta}(k)-\sum_{\gamma=1}^{\beta-1}\frac{\xi_{\alpha\gamma}(k)\xi_{\beta\gamma}(k)}{f_{\gamma\gamma}(k)},$$

$$f_{\alpha\alpha}(k)=g_{\alpha\alpha}(k)-\sum_{\gamma=1}^{\alpha-1}\frac{\xi_{\alpha\gamma}^2(k)}{f_{\gamma\gamma}(k)} \tag{6}$$

with $f_{11}(k)=g_{11}(k)$ and $\alpha=2,3,\ldots,S$ and $\beta=1,2,\ldots,\alpha-1$, where it is understood that the sum on the right-hand side of the first equality of Eq. (6) must be omitted at $\beta=1$, and $\xi_{\alpha\beta}(k)=\langle L^{\alpha-1}\mathbf{M}(\mathbf{k})\cdot\mathcal{M}_\beta(-\mathbf{k})\rangle/\{2\}Nu^2$ denotes the auxiliary matrix. The orthogonalized procedure can be simplified significantly by taking into account that the basic function $g(k,t)\equiv f_{11}(k,t)$ is even with respect to time. Then one obtains that $g_{\alpha\beta}(k)$ [as well as $\xi_{\alpha\beta}(k)$] are equal to zero if $\alpha+\beta$ is an odd number, whereas nonzero elements can be expressed via their diagonal ones as $g_{\alpha\beta}(k)=(-1)^{|\alpha-\beta|/2}g_{\gamma\gamma}(k)$, where $\gamma=(\alpha+\beta)/2$.

The processes of dynamical polarization in the system can be described by TCF's (5). In particular, the longitudinal $\varepsilon_L(k,\omega)$ and transverse $\varepsilon_T(k,\omega)$ components of the wave-vector- and frequency-dependent dielectric permittivity are expressed via the first element $g(k,t)$ of the $S\times S$ square matrix $\mathbf{F}(k,t)$, as [28]

$$\begin{aligned}&\frac{\varepsilon_L(k,\omega)-1}{9y\varepsilon_L(k,\omega)}=g^L(k)-i\omega g^L(k,\omega),\\&\frac{\varepsilon_T(k,\omega)-1}{9y}=g^T(k)-i\omega g^T(k,\omega),\end{aligned} \tag{7}$$

where $y=4\pi Nu^2/9Vk_BT$ and k_B and T are the Boltzmann's constant and temperature of the system, respectively, $g(k,\omega)=\int_0^\infty g(k,t)e^{-i\omega t}dt\equiv\mathcal{L}_{i\omega}(g(k,t))$ and $\mathcal{L}_{i\omega}$ designates the Laplace transform.

B. Extended continued fractions

Using the memory function formalism, the matrix equation for equilibrium TCF's can be written as follows [35]:

$$\frac{\partial}{\partial t}\mathbf{F}(k,t)-\boldsymbol{\Omega}(k)\mathbf{F}(k,t)+\int_0^\infty \boldsymbol{\Gamma}(k,\tau)\mathbf{F}(k,t-\tau)d\tau=0. \tag{8}$$

In our case, due to the orthogonality of set (4), the matrix of memory kernels $\boldsymbol{\Gamma}(k,\tau)$ has one nonzero element only, namely, $\Gamma_{SS}(k,\tau)\equiv\Gamma_S(k,\tau)$, where

$$\Gamma_S(k,\tau)=\frac{\langle(1-\mathcal{P}_S)\mathcal{M}_{S+1}(\mathbf{k})\cdot\exp[(1-\mathcal{P}_S)L\tau](1-\mathcal{P}_S)\mathcal{M}_{S+1}(-\mathbf{k})\rangle}{\langle\mathcal{M}_S(\mathbf{k})\cdot\mathcal{M}_S(-\mathbf{k})\rangle}, \tag{9}$$

and

$$\boldsymbol{\Omega}(k)=\frac{\langle\mathcal{M}(\mathbf{k})\cdot L\mathcal{M}^+(\mathbf{k})\rangle}{\langle\mathcal{M}(\mathbf{k})\cdot\mathcal{M}^+(\mathbf{k})}$$

$$=\begin{pmatrix} 0 & -1 & 0 & 0 & 0 & \dots \\ \Omega_2 & 0 & -1 & 0 & 0 & \dots \\ 0 & \Omega_3 & 0 & -1 & 0 & \dots \\ 0 & 0 & \Omega_4 & 0 & -1 & \dots \\ 0 & 0 & 0 & \Omega_5 & 0 & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \end{pmatrix} \tag{10}$$

is the frequency matrix with the elements

$$\Omega_\alpha(k)=\frac{\langle\mathcal{M}_\alpha(\mathbf{k})\cdot\mathcal{M}_\alpha(-\mathbf{k})\rangle}{\langle\mathcal{M}_{\alpha-1}(\mathbf{k})\cdot\mathcal{M}_{\alpha-1}(-\mathbf{k})\rangle}\equiv\frac{f_{\alpha\alpha}(k)}{f_{\alpha-1\ \alpha-1}(k)}. \tag{11}$$

In the Laplace representation, the integrodifferential equation (8) converts into the algebraic one

$$[i\omega\mathbf{I}-\boldsymbol{\Omega}(k)+\boldsymbol{\Gamma}(k,\omega)]\mathbf{F}(k,\omega)=\mathbf{F}(k), \tag{12}$$

where $\mathbf{I}$ is the unit matrix and $\mathbf{F}(k)=\lim_{t\to 0}\mathbf{F}(k,t)$ denotes the matrix of SCF's. Equation (12) is now solved analytically, and the result for first element of $\mathbf{F}(k,\omega)$ can be cast as the Sth-order continued fraction

$$g(k,\omega)=\cfrac{g(k)}{i\omega+\cfrac{\Omega_2(k)}{i\omega+\cfrac{\Omega_3(k)}{i\omega+\cdots\cfrac{\Omega_S(k)}{i\omega+\Gamma_S(k,\omega)}}}}. \tag{13}$$

In view of Eq. (6), more explicit expressions for elements (11) of the frequency matrix at $S\leqslant 5$ are

$$\Omega_2(k)=\frac{g_2(k)}{g(k)},$$

$$\Omega_3(k)=\frac{g(k)g_4(k)-g_2^2(k)}{g(k)g_2(k)}, \tag{14}$$

$$\Omega_4(k)=\frac{g(k)[g_2(k)g_6(k)-g_4^2(k)]}{g_2(k)[g(k)g_4(k)-g_2^2(k)]},$$

$$\Omega_5(k)=\frac{g_2(k)[g(k)g_4(k)g_8(k)+2g_2(k)g_4(k)g_6(k)-g_2^2(k)g_8(k)-g(k)g_6^2(k)-g_4^3(k)]}{[g(k)g_4(k)-g_2^2(k)][g_2(k)g_6(k)-g_4^2(k)]},$$

where

$$g_{2s}(k)=\frac{\langle L^s\mathbf{M}(\mathbf{k})\cdot L^s\mathbf{M}(-\mathbf{k})\rangle}{\{2\}Nu^2} \tag{15}$$

is the static Kirkwood factor of the $2s$th order ($s=0,1,\dots,S-1$), and $g_0(k)\equiv g(k)$.

It can be seen easily from Eq. (13) that the same function $g(k,\omega)$ is obtained within the $(S+1)$th order continued fraction as well if the memory functions obey the recurrent relation

$$\Gamma_S(k,\omega)=\frac{\Omega_{S+1}(k)}{i\omega+\Gamma_{S+1}(k,\omega)}. \tag{16}$$

The solution (13) leads to exact results at arbitrary order S, provided the corresponding memory functions Γ_S are precisely determined. However, such a prescription is rather a formal one, because the exact calculation (9) of the dissipative kernel constitutes, in general, an unresolvable problem. We shall now consider a question of how to perform this calculation approximately.

Let

$$\tau_S(k)=\min_{\alpha=1}^{S}\frac{\int_0^\infty t|f_{\alpha\alpha}(k,t)|dt}{\int_0^\infty |f_{\alpha\alpha}(k,t)|dt},$$

$$\tau_{S+1}(k)=\max_{\alpha=S+1}^{\infty}\frac{\int_0^\infty t|f_{\alpha\alpha}(k,t)|dt}{\int_0^\infty |f_{\alpha\alpha}(k,t)|dt} \tag{17}$$

be characteristic intervals of decaying in time of the autocorrelation functions from the S-order set and all the rest functions from higher-order sets, and $\gamma_S(k)=\tau_{S+1}(k)/\tau_S(k)$ be their ratio. We assume in advance that there exist dynamical processes in the system, corresponding to essentially different scales of time, and, therefore, beginning from a some number S, the ratio γ_S must become sufficiently small, i.e., $\gamma_S(k)\ll 1$ at arbitrary wave vectors. This assumption is justified provided that the S-order set (4) forms an almost complete slow set of dynamical variables. It is obvious that in this case the memory kernel (9), which is built on projected higher-order variables, decays in time faster than TCF's (5), i.e.,

$$\int_0^\infty \mathbf{\Gamma}(k,\tau)\mathbf{F}(k,t-\tau)d\tau\approx\int_0^\infty \mathbf{\Gamma}(k,\tau)d\tau\mathbf{F}(k,t)\equiv\mathbf{\Gamma}(k)\mathbf{F}(k,t). \tag{18}$$

Thus, on characteristic time scales of varying TCF's, the dissipative kernel can be considered as a δ function in time space, $\Gamma_S(k,\tau)\approx\Gamma_S(k)\delta(\tau)$, with the weight $\Gamma_S(k)\equiv\Gamma_S(k,\omega=0)$. In the frequency representation, relation (18) stays

$$\Gamma_S(k,\omega)\approx\Gamma_S(k), \tag{19}$$

that represents the well-known Markovian approximation [3,6].

The memory kernel $\Gamma_S(k)$ can be found in terms of elements (11) of the frequency matrix and the basic wave-vector-dependent correlation time

$$\tau_{\rm cor}(k)=\lim_{\omega\to 0}\frac{g(k,\omega)}{g(k)}=\int_0^\infty\frac{g(k,t)}{g(k)}dt, \tag{20}$$

putting $\omega\to 0$ in the S-order continued fraction (13). Then at different orders of the description we obtain the following result: $\Gamma_1(k)=1/\tau_{\rm cor}(k)$, $\Gamma_2(k)=\tau_{\rm cor}(k)\Omega_2(k)$, and ($n=2,3,\dots$)

$$\Gamma_{2n-1}(k)=\frac{1}{\tau_{\rm cor}(k)}\prod_{l=1}^{n-1}\frac{\Omega_{2(n-l)+1}(k)}{\Omega_{2(n-l)}(k)},$$

$$\Gamma_{2n}(k)=\tau_{\rm cor}(k)\Omega_2(k)\prod_{l=1}^{n-1}\frac{\Omega_{2(n-l)+2}(k)}{\Omega_{2(n-l)+1}(k)}. \tag{21}$$

It is worth mentioning that the frequency independence of the memory kernel in the S-order description does not concern the memory functions of lower orders, which depend on frequency, according to the recurrent relation (16).

Now we consider a more general formulation of the Markovian approximation in higher-order descriptions. As far as the ratio $\gamma_S(k)$ is small enough at a given value of S, it will also remain small at higher orders, or will even decrease with increasing S. If this statement indeed takes place, then not only the frequency dependence of $\Gamma_S(k,\omega)$ can be neglected, but also values of $\Gamma_S(k)$ will begin to depend almost not at all on the order S of the description. Then we can write that $\Gamma_{S+1}(k)\approx\Gamma_S(k)$ at sufficiently great values of S, and the basic correlation time (20) can be excluded from our consideration. Taking into account the explicit relations (21), and letting $\Gamma_1(k)=\Gamma_2(k)$, $\Gamma_2(k)=\Gamma_3(k),\dots$, $\Gamma_{2n-1}(k)=\Gamma_{2n}(k)$, $\Gamma_{2n}(k)=\Gamma_{2n+1}(k)$, where $n=2,3,\dots$, for the correlation time $\tau_{\rm cor}^{(s)}(k)$ in the sth approximation we obtain $\tau_{\rm cor}^{(1)}(k)=1/\sqrt{\Omega_2(k)}$, $\tau_{\rm cor}^{(2)}(k)=\sqrt{\Omega_3(k)}/\Omega_2(k),\dots$, and

$$\tau_{\rm cor}^{(2n-1)}(k)=\frac{1}{\sqrt{\Omega_2}}\prod_{l=1}^{n-1}\frac{\Omega_{2(n-l)+1}}{\sqrt{\Omega_{2(n-l)}\Omega_{2(n-l)+2}}},$$

$$\tau_{\rm cor}^{(2n)}(k)=\frac{\sqrt{\Omega_3}}{\Omega_2}\prod_{l=1}^{n-1}\frac{\sqrt{\Omega_{2(n-l)+1}\Omega_{2(n-l)+3}}}{\Omega_{2(n-l)+2}}. \tag{22}$$

Finally, substituting values (22) into expressions (21) for memory functions within the same order of the approximation, we obtain

$$\Gamma_{2n-1}(k)\approx\sqrt{\Omega_2}\prod_{l=1}^{n-1}\sqrt{\frac{\Omega_{2(n-l)+2}}{\Omega_{2(n-l)}}},$$

$$\Gamma_{2n}(k)\approx\sqrt{\Omega_3}\prod_{l=1}^{n-1}\sqrt{\frac{\Omega_{2(n-l)+3}}{\Omega_{2(n-l)+1}}}. \tag{23}$$

In such a way, in view of Eqs. (13), (14), and (23), the frequency dependence (7) of the dielectric constant can be reproduced using static correlation functions (15) exclusively.

C. Generalized collective modes

In Sec. II B it was shown how to obtain analytic results for dynamical quantities in the frequency representation. However, in the Markovian approximation, Eq. (8) for TCF's can be solved analytically in time space as well. This equation can now be written as

$$\frac{\partial}{\partial t}\mathbf{F}^M(k,t)=-\mathbf{T}(k)\mathbf{F}^M(k,t), \tag{24}$$

where the generalized evolution operator $\mathbf{T}(k)=-\mathbf{\Omega}(k)+\mathbf{\Gamma}(k)$ is determined by the explicit expressions (10), (11), and (21) [or (23)] for $\mathbf{\Omega}(k)$ and $\mathbf{\Gamma}(k)$, respectively, and $\mathbf{F}^M$ indicates the matrix $\mathbf{F}$ of TCF's, calculated in the Markovian approximation.

Let $X_{\beta\gamma}(k)$ be an eigenvector associated with an eigenvalue $Z_\gamma(k)$ of the $\mathbf{T}(k)$ matrix, i.e.,

$$\sum_{\beta=1}^{S}T_{\alpha\beta}(k)X_{\beta\gamma}(k)=Z_\gamma(k)X_{\alpha\gamma}(k), \tag{25}$$

where $\alpha,\gamma=1,\dots,S$ and $T_{\alpha\beta}$ designate the elements of $\mathbf{T}$. Then the solution to differential equation (24) is of the form

$$f_{\alpha\beta}^M(k,t)=\sum_{\gamma=1}^{S}Q_\gamma^{\alpha\beta}(k)e^{-Z_\gamma(k)t}, \tag{26}$$

i.e., each element of the $\mathbf{F}^M$ matrix can be expressed as the sum of S Lorentzians which are connected with the generalized collective modes $Z_\gamma(k)$. The amplitudes $Q_\gamma^{\alpha\beta}$ are defined uniquely in terms of eigenvectors, using the initial condition $\lim_{t\to 0}\mathbf{F}^M(k,t)=\mathbf{F}(k)$. The result is

$$Q_\gamma^{\alpha\beta}(k)=\sum_{l=1}^{S} X_{\alpha\gamma}(k)X_{\gamma l}^{-1}(k)f_{l\beta}(k), \qquad (27)$$

where the matrix $\mathbf{X}^{-1}$ is the inverse of $\mathbf{X}\equiv\{X_{\alpha\beta}\}$. The component $Q_\gamma^{\alpha\beta}(k)$ describes a partial contribution of the mode $Z_\gamma(k)$ into the time correlation function $f_{\alpha\beta}(k,t)$. Applying the Laplace transform to Eq. (26) yields the following result in frequency space:

$$f_{\alpha\beta}^M(k,\omega)=\sum_{\gamma=1}^{S}\frac{Q_\gamma^{\alpha\beta}(k)}{i\omega+Z_\gamma(k)}, \qquad (28)$$

which in the particular case $\alpha=\beta=1$ can be considered as an alternative representation of extended continued fractions (13) for $g(k,\omega)\equiv f_{11}(k,\omega)$ in the Markovian approximation (18). Result (26), obtained in the S-mode description, allows one to evaluate the $S\times S$ matrix of longitudinal and transverse TCF's (5).

From Eqs. (8) and (24) it can be shown easily that $\int_0^\infty dt\ \mathbf{F}^M(k,t)=\int_0^\infty dt\ \mathbf{F}(k,t)$ or, in other words, $\lim_{\omega\to 0}\mathbf{F}^M(k,\omega)=\lim_{\omega\to 0}\mathbf{F}(k,\omega)$ and, therefore, the Markovian approximation leads directly to exact results in the low-frequency limit. Moreover, from the initial condition $\mathbf{F}^M(k)=\mathbf{F}(k)$ [i.e., $f_{\alpha\alpha}^M(k)=f_{\alpha\alpha}(k)$, $\alpha=0,1,\ldots,S-1$], it follows that [37], if the S-mode approximation is used, time derivatives of the genuine $g(k,t)$ and approximated $g^M(k,t)$ functions coincide between themselves at $t=0$ up to the $2(S-1)$th order. For this reason, it is evident that in the hypothetical limit $S\to\infty$, the Markovian approximation exactly reproduces the original time correlation function $g(k,t)$ over the whole region of time and wave number for arbitrary dipolar systems.

III. INVESTIGATION OF A STOCKMAYER FLUID

In order to verify the proposed theoretical scheme, we considered the Stockmayer model of polar systems using the intermolecular potential $\varphi_{ij}=\varphi_{\rm LJ}(r_{ij})+\varphi_{\rm dd}(\mathbf{r}_{ij},\mathbf{u}_i,\mathbf{u}_j)$, where $\varphi_{\rm LJ}(r_{ij})=4\epsilon_{\rm LJ}[(\sigma_{\rm LJ}/r_{ij})^{12}-(\sigma_{\rm LJ}/r_{ij})^6]$ denotes the Lennard-Jones (LJ) part, $\varphi_{\rm dd}=-3(\mathbf{u}_i\cdot\mathbf{r}_{ij})(\mathbf{u}_j\cdot\mathbf{r}_{ij})/r_{ij}^5+(\mathbf{u}_i\cdot\mathbf{u}_j)/r_{ij}^3$ describes the dipole-dipole interactions, and $\mathbf{r}_{ij}=\mathbf{r}_i-\mathbf{r}_j$. Our numerical calculations were performed at a reduced density $n^*=\sigma_{\rm LJ}^3N/V=0.822$, a mean temperature $T^*=k_BT/\epsilon_{\rm LJ}=1.147$, a dipole moment $u^{*2}=u^2/(\epsilon_{\rm LJ}\sigma_{\rm LJ}^3)=3.0$, and a moment of inertia $J^*=J/(m\sigma_{\rm LJ}^2)=0.025$. The maximal order of extended continued fractions has been restricted to $S=5$.

According to the basic results (13), (14), (21), and (22), the knowledge of static correlation functions $g_{2s}(k)$ [Eq. (15)] is necessary at $s=0$–4 to investigate the frequency dependence of the dielectric permittivity and evaluate the generalized dipolar mode spectra within up to the five-order description. There are several possibilities to define the static correlation functions. The lowest-order function ($s=0$) presents the well-known Kirkwood factor $g(k)$ which is connected with the pair distribution function [19] and, therefore, can be calculated using one or another approach [12,15,16] of the equilibrium statistical mechanics. The Kirkwood factor of second order ($s=1$) has an analytical representation [38], $g_2^{L,T}(k)=(k_BT/3)[(2/J)+(k^2/m)]$. The higher-order functions ($s=2$–4) are related to the four-particle distribution function, and it is not a simple matter to predict them theoretically. Usually, they are considered as adjustable parameters. It is obvious, however, that in such a way these functions cannot be determined uniquely. Because of this, to avoid any additional uncertainties in the calculation of collective modes, and to observe the convergence of continued fractions in a pure form, we shall evaluate $g_{2s}(k)$ using the MD method. Details of our computer experiment are similar to those reported earlier [28].

We note that it is necessary to distinguish correlation functions, obtained directly in simulations for finite samples $G_s(k)$ from infinite-system functions $g_s(k)$. As was shown previously, additional transformations to obtain $g(k)$ from $G(k)$ are necessary, namely, $g(k)=[1/G(k)+D(k)]^{-1}$, where $D(k)$ takes into account details of simulations [28]. Moreover, the lowest-order time correlation functions, related to infinite and finite systems, obey the equality

$$\frac{1}{g(k)-i\omega\mathcal{L}_{i\omega}(g(k,t))}=\frac{1}{G(k)-i\omega\mathcal{L}_{i\omega}(G(k,t))}+D(k). \qquad (29)$$

Performing the Taylor expansion of Eq. (29) over inverse frequencies at $\omega\to\infty$, it can been shown easily that higher-order static correlation functions of the infinite system can be defined as follows:

$$\begin{aligned} g_2(k)&=G_2(k),\\ g_4(k)&=G_4(k)+D(k)G_2^2(k),\\ g_6(k)&=G_6(k)+D(k)G_2(k)[G_4(k)+g_4(k)],\\ g_8(k)&=G_8(k)+D(k)\{G_4(k)g_4(k)\\ &\quad+G_2(k)[G_6(k)+g_6(k)]\}. \end{aligned} \qquad (30)$$

The finite-system functions $G(k)$, $G_2(k)$, and $G_4(k)$ were calculated directly in the simulations by definition (15), using Eq. (1) and the explicit expressions

$$\begin{aligned} L\mathbf{M}(\mathbf{k})&=\sum_{i=1}^{N}[\mathbf{w}_i\times\mathbf{u}_i-i\mathbf{u}_i(\mathbf{k}\cdot\mathbf{v}_i)]e^{-i\mathbf{k}\cdot\mathbf{r}_i},\\ L^2\mathbf{M}(\mathbf{k})&=\sum_{i=1}^{N}\{\dot{\mathbf{w}}_i\times\mathbf{u}_i+((\mathbf{w}_i\cdot\mathbf{u}_i)\mathbf{w}_i-\mathbf{w}_i^2\mathbf{u}_i)-\mathbf{u}_i(\mathbf{k}\cdot\mathbf{v}_i)^2\\ &\quad-i[2\mathbf{w}_i\times\mathbf{u}_i(\mathbf{k}\cdot\mathbf{v}_i)+\mathbf{u}_i(\mathbf{k}\cdot\dot{\mathbf{v}}_i)]\}e^{-i\mathbf{k}\cdot\mathbf{r}_i} \end{aligned} \qquad (31)$$

for higher-order dynamical variables, where $\dot{\mathbf{v}}_i\equiv L\mathbf{v}_i=-(1/m)\Sigma_{j(j\neq i)}^N\partial\varphi_{ij}/\partial\mathbf{r}_i\equiv(1/m)\mathbf{f}_i$ and $\dot{\mathbf{w}}_i\equiv L\mathbf{w}_i=-(1/J)\Sigma_{j(j\neq i)}^N\mathbf{u}_i\times\partial\varphi_{ij}/\partial\mathbf{u}_i\equiv(1/J)\mathbf{K}_i$ denote the translational and

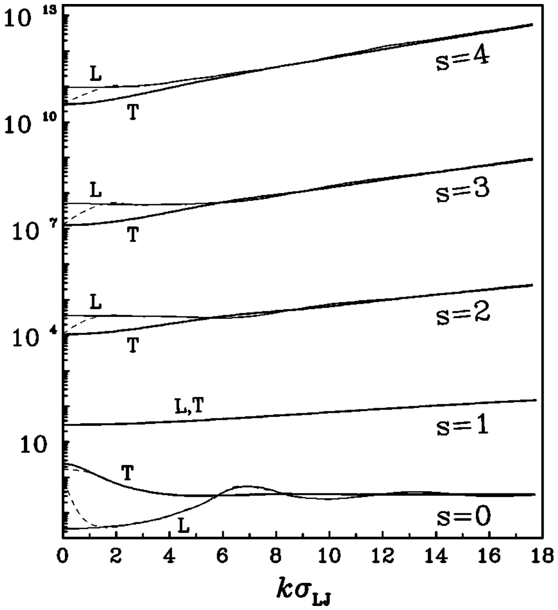

FIG. 1. Transverse (T) and longitudinal (L) components of the s-order static Kirkwood factors ($s=0$–4) for a Stockmayer fluid at $n^*=0.822$ and $T^*=1.147$. The MD data for the finite system are shown as dashed curves. The infinite-system Kirkwood factors are plotted by solid curves. Note that the transverse functions, corresponding to finite and infinite systems, are practically indistinguishable, excepting the case $s=0$.

rotational accelerations, respectively. In view of very complicated structures for $L^3\mathbf{M}(\mathbf{k})$ and $L^4\mathbf{M}(\mathbf{k})$, the highest-order static correlation functions $G_6(k)$ and $G_8(k)$ were evaluated numerically in terms of twofold and fourfold time derivatives of the function $G_4(k,t)$ at $t=0$, i.e., $G_6(k) = -\partial^2 G_4(k,t)/\partial t^2|_{t=0}$ and $G_8(k)=\partial^4 G_4(k,t)/\partial t^4|_{t=0}$. The evaluation of $G_6(k)$ and $G_8(k)$ was carried out with the help of a special procedure to reduce numerical errors to a minimum.

The longitudinal $g^L_{2s}(k)$ and transverse $g^T_{2s}(k)$ components of the infinite-system functions $g_{2s}(k)$ [as well as $G^{L,T}_{2s}(k)$] obtained in such a way are displayed in Fig. 1 at $s=0$–4 in units of τ_σ^{-2s}, where $\tau_\sigma=\sigma_{\rm LJ}(m/\epsilon_{\rm LJ})^{1/2}$. The components $g^{L,T}_{2s}(k)$, as autocorrelation static functions, are positively defined at arbitrary wave numbers. In the limit of great wave vectors they can be calculated analytically, namely, $\lim_{k\to\infty} g^{L,T}_{2s}(k)=(-1)^s \partial^{2s} g_G(k,t)/\partial t^{2s}|_{t\to 0}$, where $g_G(k,t)=\frac{1}{3}\exp(-ak^2t^2)$ denotes the limiting Gaussian transition of $g^{L,T}(k,t)$ at $k\to\infty$, and $a=k_BT/2m$ [38]. In particular, $g^{L,T}(k)\to\frac{1}{3}$, $g^{L,T}_2(k)\to\frac{2}{3}ak^2$, $g^{L,T}_4(k)\to 4a^2k^4$, $g^{L,T}_6(k)\to 40a^3k^6$, and $g^{L,T}_8(k)\to 560a^4k^8$. It is interesting to point out that higher-order functions differ from lower-order ones considerably. This indicates existing dynamical processes in the system, which correspond to essentially different scales of time.

The result of Fig. 1 allows us immediately to check our assumption about the possibility to express the correlation time in terms of static correlation functions. The corresponding calculations (22) of the correlation time $\tau^{(s)}_{\rm cor}(k)$ performed in different approximations ($s=1$–4) as well as exact values (20) obtained by the MD method are presented in Figs. 2(a) and 2(b) for the cases of longitudinal and transverse fluctuations, respectively. As we can see from the figures, the four-order approximation already reproduces values of $\tau_{\rm cor}(k)$ not only qualitatively but even quantitatively over the whole region of wave numbers.

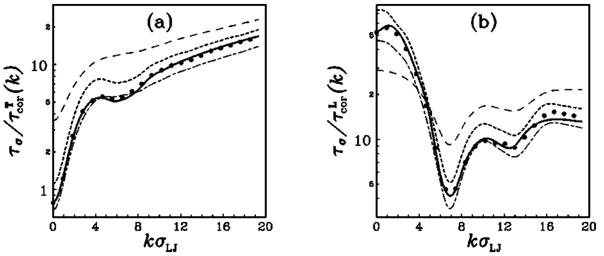

FIG. 2. Transverse (a) and longitudinal (b) components of the correlation time for the Stockmayer fluid. The results in one-, two-, three-, and four-order approximations are plotted by long-dashed, long-short-dashed, short-dashed, and solid curves, respectively. The exact values are presented as circles.

The generalized dipolar mode spectra in two-, three-, four-, and five-order descriptions are shown in Fig. 3. In the case of transverse fluctuations [subsets (a) and (b) of the figure], we can clearly identify the diffusive mode $D_1(k)$ which is well separated from all the rest of modes over a wide wave-vector range. This mode converges rapidly to its genuine value with an increasing order of the approximation, so that it is already reproduced quantitatively at small wave numbers within the two-order description. As far as the five-order description is used, we can talk about the quantitative reproducing at intermediate and great wave vectors as well. The appearance of the $D_1(k)$ mode is caused by the diffusive

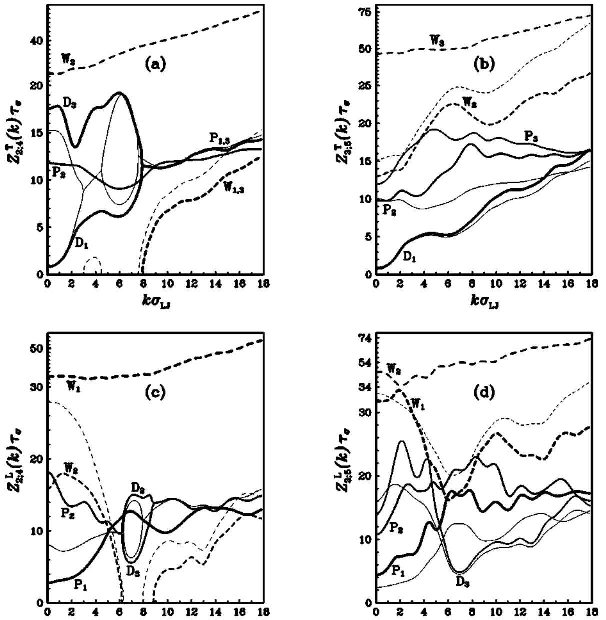

FIG. 3. Generalized dipolar mode spectra of the Stockmayer fluid: transverse [(a) and (b)] and longitudinal [(c) and (d)] modes in four- [(a) and (c)] and five- [(b) and (d)] order descriptions. The pure diffusive modes and real and imaginary parts of propagating modes are marked by the symbols D, P, and W, respectively. For the purpose of comparison the results in two- and three-mode approaches are shown in (a) and (c) and (b) and (d) by the thinnest curves.

mechanism of dielectric relaxation in polar systems, and only this mechanism is considered in the well-known Debye theory. Neglecting the dipole-dipole interactions, as done originally by Debye, it can been found that in the infinite-wavelength limit $\lim_{k\to 0} D_1(k) = 2D_R$, where D_R is the rotational diffusion coefficient. Applying the extended hydrodynamic approach, Bagchi and Chandra improved this result and obtained $D_1(k) = (2D_R + D_T k^2)[1 + (N/V)c(k)]$, where D_T is the translational diffusion coefficient, and $c(k)$ denotes a component of the spherical harmonic expansion of the two-particle direct correlation function [6]. The last result is valid not only for dilute systems but also for dense gases and liquids; however, it can be used at small wave vectors exclusively. Our scheme provides the possibility to define $D_1(k)$ in terms of the Kirkwood factor and its higher-order components at arbitrary values of the wave number.

It is worth remarking that the diffusive mode, as the mode with the lowest real part, makes the main contribution to the TCFs and dielectric quantities in an almost whole domain of k space, especially at small wave vectors. That is why the single-relaxation-time approximation for dipole-moment fluctuations, $\sim e^{-D_1(k)\,t}$, which is used in the Debye theory, can be applied here. This approximation works well in the overdamped limit of great times t and small frequencies ω, where the inertial motions of the liquid molecules are not important. To describe the region of intermediate values of t and ω properly, it is necessary to consider higher-order modes. The next two propagating modes $P_2(k) \pm iW_2(k)$ arise additionally, beginning from the three-order approach. The three- and higher-order descriptions explicitly include the free-motion effects in terms of $g_2(k)$, and correlations due to interactions via the torque-torque $\langle \Sigma_{i,j} \mathbf{K}_i \cdot \mathbf{K}_j \rangle$ and force-force $\langle \Sigma_{i,j} \mathbf{f}_i \cdot \mathbf{f}_j \rangle$ (at $k \neq 0$) fluctuations in terms of $g_4(k)$ [see Eq. (31)]. Within the four-order approximation the secondary diffusive mode $D_3(k)$ appears at small k. It separates into two new propagating modes $P_3(k) \pm iW_3(k)$ when the order of the approximation is increased to five, whereas the previous two propagating modes are moderately corrected. The four- and five-mode descriptions consider higher-order kinetic processes which are important at very small times (very great frequencies) and great wave-vector values. The transverse propagating modes describe an oscillation behavior of time polarization fluctuations. However, it is hard to observe these oscillations because they damp significantly during their time periods, i.e., $P_2(k) \sim W_2(k)$ and $P_3(k) \sim W_3(k)$.

For the longitudinal fluctuations [subsets (c) and (d) of Fig. 3], the pattern is quite different. Here we can easily distinguish two propagating modes $P_1(k) \pm iW_1(k)$. Contrary to the case of transverse fluctuations, these modes exhibit a quasiparticle feature at not very great wave numbers, where $P_1(k) \ll W_1(k)$. They should be associated with dipolarons [14] (analogous to the well-known plasmons in Coulomb systems), where $W_1(k)$ and $P_1(k)$ define the frequency and damping of the dipolaron excitations, respectively. As one can see from the figures, the dipolaron mode has already been predicted within the two-order description which includes the correct inertial short time behavior of polarization fluctuations. If dipole-dipole interactions are neglected, the dipolaron frequency can be defined approximately [6] as $\lim_{k\to 0} W_1(k) = 4\pi N u^2 / VJ \approx 35.2\ \tau_\sigma^{-1}$ that is very close to the values $27.8\tau_\sigma^{-1}$, $33.0\tau_\sigma^{-1}$, $35.5\tau_\sigma^{-1}$, and $31.7\tau_\sigma^{-1}$ obtained by us at $S=$ 2, 3, 4, and 5, respectively. The secondary oscillation process is reproduced by the next two complex-conjugated modes $P_2(k) \pm iW_2(k)$ at $S=4$. Finally, in the five-order description, the pure diffusive mode $D_3(k)$ appears additionally.

The dipolarons are expected to occur for systems with large permittivities where a rapid reorientation of dipoles takes place. They were found for the first time by Pollock and Alder [14], investigating Stockmayer fluids in a somewhat different thermodynamic point and with smaller values of the particle's dipole moment than in the present work. Analysis of the dipolaron oscillations in Ref. [14] was limited, in fact, by small values of the wave vector. The dipolaron frequency was estimated as that providing the maximum of the imaginary part of $1/\varepsilon_L(k,\omega)$. Computations have shown, however, that such an estimation gives correct values of the dipolaron frequency for small wave numbers only [28].

In our approach, the inequalities $P_1(k) \lesssim W_1(k)$, $P_2(k)$, and $D_3(k)$ can be considered as a condition of existing the dipolaron oscillations. This condition is satisfied as far as $k^* \equiv k\sigma_{\mathrm{LJ}} \lesssim 4$. With increasing wave-vector values the diffusive processes begin to dominate, especially at $k^* \sim 7$, where $D_3(k)$ is much less than all the other modes. This feature is visible in all the orders of the approximations as well. For example, in the four-order description the propagating modes $P_2(k) \pm iW_2(k)$ are separated into two pure diffusive modes $D_2(k)$ and $D_3(k)$ within a small region near $k^* \sim 7$, where the longitudinal component $g^L(k)$ of the Kirkwood factor has the sharp maximum (see Fig. 1).

In view of the behavior of dipolar modes, the whole region of wave vectors can be split into several characteristic intervals. In the first one the lowest-lying dipolar modes are well separated from the rest of others, and this separation is observed as long as $k^* \lesssim 2$ (the so-called extended hydrodynamic regime). In this interval the Debye-like theory can be applied to transverse dipole-moment fluctuations, whereas the longitudinal component of the dielectric permittivity can be predicted by two complex-conjugated dipolaron modes. In the second range of intermediate wave numbers, $2 \lesssim k^* \lesssim 12$, all the modes are mixed between themselves in a very complicated manner (especially in the case of longitudinal fluctuations). To describe the dynamical behavior of dielectric quantities in this range, it is necessary to involve additional higher-order modes, except for the subinterval $6 \lesssim k^* \lesssim 8$, where the longitudinal diffusive mode dominates over all the rest of modes, similar to the behavior of transverse modes in the extended hydrodynamic regime. Finally, in the so-called free-motion regime, $k^* \lesssim 12$, all the modes tend to their own linear asymptotes to reproduce the Gaussian time shape $g_G(k,t)$ of dipole-moment fluctuations.

Examples of the normalized, time correlation functions $\Phi_{L,T}(k,t) \equiv g^{L,T}(k,t)/g^{L,T}(k)$, obtained in two-, three-, and five-mode descriptions, are presented and compared with the MD data [28] in Fig. 4. As we can see from the figure, the transverse component $\Phi_T(k,t)$ exhibits an almost pure damped feature over a wide range of wave numbers. In the case of longitudinal fluctuations this is valid for intermediate and great wave-vector values only. At small wave vectors, the longitudinal dipole-moment fluctuations are described by

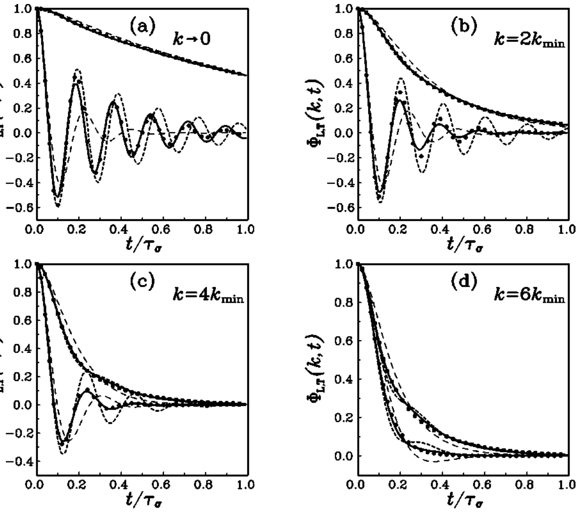

FIG. 4. The normalized time autocorrelation functions of the dipole-moment fluctuations for the Stockmayer fluid at some fixed values of wave number, where $k_{\rm min}=2\pi/\sqrt[3]{V}=0.927/\sigma_{\rm LJ}$. The MD data for longitudinal and transverse components are shown as circles and squares. The results of two-, three-, and five-mode descriptions are plotted by the corresponding long-dashed, short-dashed, and solid curves, respectively.

strong dipolaron oscillations with a slight damping. Such a behavior of $\Phi_{L,T}(k,t)$ is completely in line with the predictions of the generalized dipolar modes approach. The transverse TCF's are reproduced satisfactorily even within the three-mode description. The longitudinal oscillations are described in this case as well, but only qualitatively. At the same time, the approximated and genuine TCF's begin to be indistinguishable when the order of the description is increased to five.

A pattern similar to that presented for TCF's is observed for the wave-vector- and frequency-dependent dielectric permittivity $\varepsilon_{L,T}(k,\omega)=\varepsilon'_{L,T}(k,\omega)-i\varepsilon''_{L,T}(k,\omega)$. Our calculations, carried out in one-, two-, three- and five-order approximations for the longitudinal $\varepsilon_L(k,\omega)$ and transverse $\varepsilon_T(k,\omega)$ components are shown in Figs. 5 and 6, respectively, in comparison with the MD data of Ref. [28]. We note that in the infinite-wavelength limit $\lim_{k\to 0}\varepsilon_{L,T}(k,\omega)=\varepsilon(\omega)$. It can easily be seen that within the Debye-like theory $(S=1)$ the dielectric permittivity can be well reproduced in the hydrodynamic limit (low frequencies and wave numbers). With increasing wave-vector and frequency values this theory fails, especially in the case of longitudinal fluctuations. In the three-mode approximation we can talk about a qualitative description. Finally, within the five-order approach the entire frequency dependence of the dielectric permittivity is described quantitatively at arbitrary wave vectors (the deviations from MD data do not exceed a few percent). This merely means that the five variables constitute an almost complete set of slow quantities, and the Markovian approximation begins to be almost exact. Therefore, the extended continued fractions (13) converge rapidly with an increasing order of the approximation, and the hypothesis of an abbreviated description is in an excellent accord.

IV. CONCLUDING REMARKS

It has been established that dielectric relaxation in a dipolar fluid can be successfully studied within the generalized mode method. The proposed approach can be considered as an extension of the three-variable theory of Madden and Kivelson [3] to arbitrary numbers of dynamical variables. Our scheme for the computation of dipolar modes is presented in a form that is very convenient to actual applications. In particular, all necessary input quantities are, in fact, static Kirkwood factors of different orders. The static factors can be determined by either equilibrium theories or direct computer simulations. This has allowed us both to avoid any fitting procedures and to evaluate the generalized dipolar-mode spectra of a Stockmayer fluid over the whole scale of wavelengths up to the five-order description. It has been shown on the basis of direct calculations that the five-variable theory enables one to define the dielectric permittivity of a dipolar fluid quantitatively at arbitrary wave-vector and frequency values.

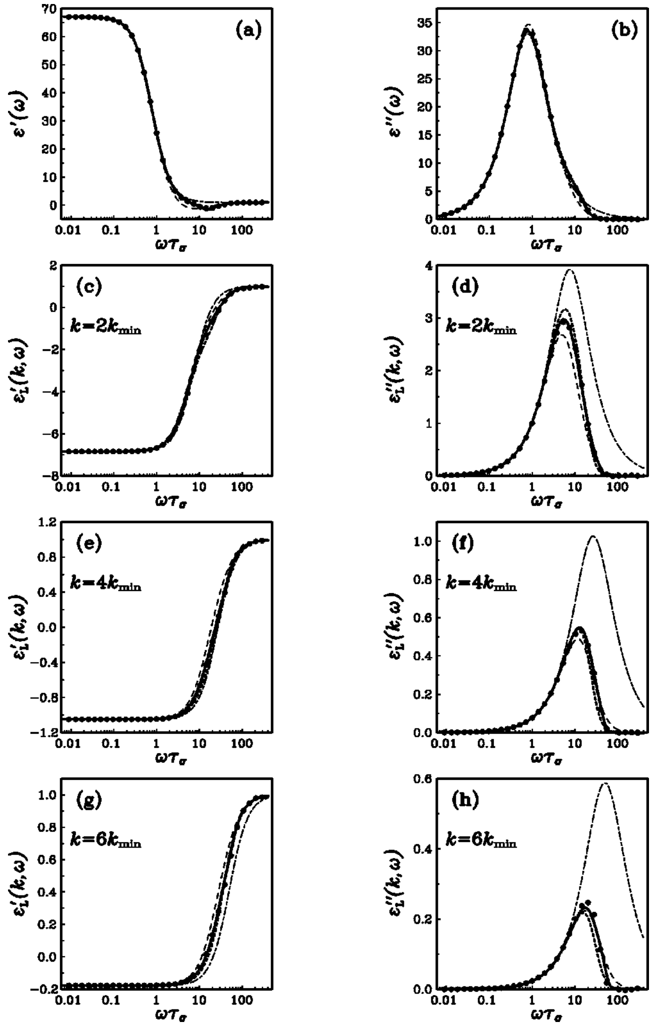

FIG. 5. The frequency dependence of the longitudinal dielectric permittivity for the Stockmayer fluid at infinite [(a) and (b)] and finite [(c)–(h)] wavelengths. The MD data are shown by circles. The results obtained within one-, two-, three-, and five-mode descriptions are plotted by long-short-, long-, short-dashed, and solid curves, respectively.

In view of the importance of the problem of dynamical polarization in polar fluids, we would also like to discuss briefly the question of how the theoretical scheme we present

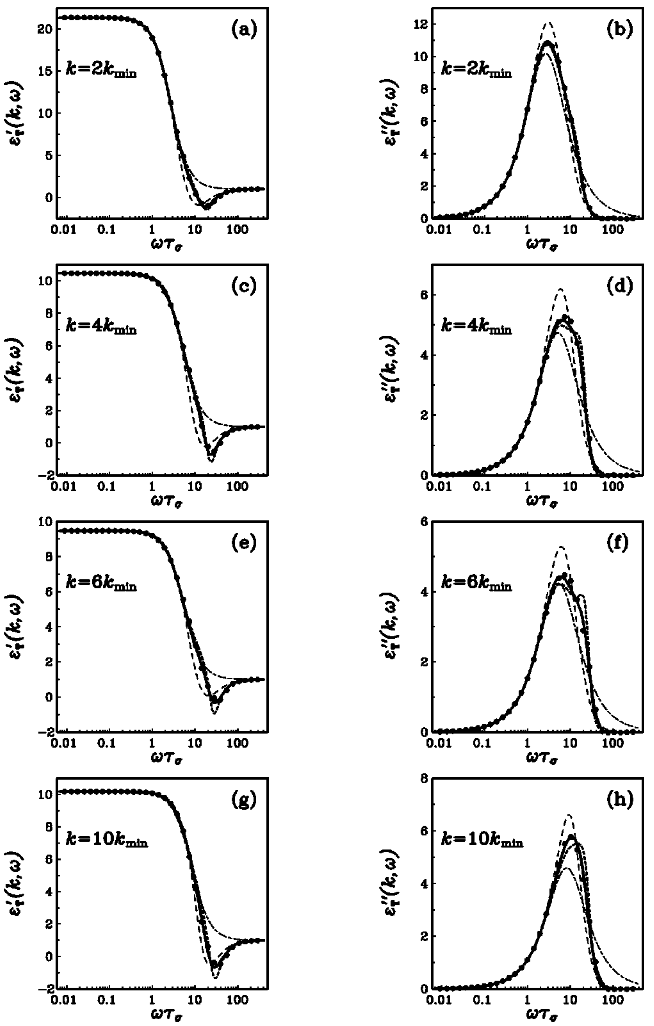

FIG. 6. The frequency dependence of the transverse dielectric permittivity for the Stockmayer fluid at finite wavelengths. The notations are the same as for Fig. 5.

is related to existing hydrodynamic approaches. As mentioned in Sec. I, the microscopic operators of number density $\hat{n}(\mathbf{r},\mathbf{\Theta})=\Sigma_{i=1}^{N}\delta(\mathbf{r}-\mathbf{r}_i)\delta(\mathbf{\Theta}-\mathbf{\Theta}_i)$, spatial momentum density $\hat{\mathbf{P}}(\mathbf{r},\Theta)=\Sigma_{i=1}^{N}m\mathbf{v}_i\delta(\mathbf{r}-\mathbf{r}_i)\delta(\mathbf{\Theta}-\mathbf{\Theta}_i)$, and angular momentum density $\hat{\mathbf{L}}(\mathbf{r},\mathbf{\Theta})=\Sigma_{i=1}^{N}J\mathbf{w}_i\delta(\mathbf{r}-\mathbf{r}_i)\delta(\mathbf{\Theta}-\mathbf{\Theta}_i)$ are involved within the widely cited approach of Bagchi and Chandra [6]. In this theory, fluctuations of the total energy density $\hat{e}(\mathbf{r},\mathbf{\Theta})=\Sigma_{i=1}^{N}e_i\delta(\mathbf{r}-\mathbf{r}_i)\delta(\mathbf{\Theta}-\mathbf{\Theta}_i)$, where $e_i=\frac{1}{2}(m\mathbf{v}_i^2+J\mathbf{w}_i^2+\Sigma_{j(j\neq i)}^{N}\varphi_{ij})$, are not taken into account due to the complexities of the hydrodynamic equations. The vector $\mathbf{\Theta}_i$ characterizes orientations of molecule i and, in the case of rigid nonpolarizable molecules, it can be associated with the unit vector directed along the particle's dipole moment, i.e., $\mathbf{\Theta}_i=\mathbf{u}_i/u$. Then the dipole-moment fluctuations can be reproduced on the basis of number-density correlations, using the relation $\hat{\mathbf{M}}(\mathbf{r},t)=u\langle\mathbf{\Theta}\ \hat{n}(\mathbf{r},\mathbf{\Theta},t)\rangle_{\mathbf{\Theta}}$, where the averaging is performed over orientations. Despite the fact that such an approach allows one, in principle, to describe the processes of dielectric relaxation in a dipolar fluid and connect them directly with thermodynamic and hydrodynamic properties, it is rather sophisticated and impractical in applications. The main results are yet to be obtained.

A somewhat different approach for describing the generalized hydrodynamics of dipolar systems was recently proposed in Ref. [40]. The main idea of this approach consists of the following. When the vector $\mathbf{M}(\mathbf{k})$ of the dipole density is included into the consideration as an orientational variable, it is no longer necessary to deal with the orientational dependence $\hat{\mathbf{Q}}(\mathbf{r},\mathbf{\Theta})\equiv\{\hat{n},\hat{\mathbf{P}},\hat{e},\hat{\mathbf{L}}\}$ of hydrodynamic variables. Then the basic set can be cast in the usual molecular form $\hat{\mathbf{Q}}(\mathbf{k})=\int_V\langle\hat{\mathbf{Q}}(\mathbf{r},\mathbf{\Theta})\rangle_{\mathbf{\Theta}}e^{-i\mathbf{k}\cdot\mathbf{r}}d\mathbf{r}\equiv\{n(\mathbf{k}),\ \mathbf{P}(\mathbf{k}),\ e(\mathbf{k}),\mathbf{L}(\mathbf{k})\}$, where $n(\mathbf{k})=\Sigma_{i=1}^{N}e^{-i\mathbf{k}\cdot\mathbf{r}_i}$, $\mathbf{P}(\mathbf{k})=\Sigma_{i=1}^{N}m\mathbf{v}_ie^{-i\mathbf{k}\cdot\mathbf{r}_i}$, $e(\mathbf{k})=\Sigma_{i=1}^{N}\langle e_i\rangle_{\mathbf{\Theta}_i}e^{-i\mathbf{k}\cdot\mathbf{r}_i}$, and $\mathbf{L}(\mathbf{k})=\Sigma_{i=1}^{N}J\mathbf{w}_ie^{-i\mathbf{k}\cdot\mathbf{r}_i}$. The advantage of such a representation lies in the evident simplification of the corresponding hydrodynamic equations. Moreover, owing to the conservation laws of the total number of particles, momenta and energy, the basic set $\mathbf{Q}(\mathbf{k})$ can be considered as a set of slow variables. For instance, time derivatives of $n(\mathbf{k})$, $\mathbf{P}(\mathbf{k})$, and $e(\mathbf{k})$ vanish, when $k\to 0$. Finally, for isotropic and spatially homogeneous systems, the dipole density $\mathbf{M}(\mathbf{k})$ does not correlate at equilibrium with basic hydrodynamic quantities in the static limit, i.e., $\langle\mathbf{M}(\mathbf{k})\cdot\mathbf{Q}(\mathbf{k})\rangle=0$.

For this reason, the dipole-density and hydrodynamic fluctuations can be considered separately from each other, as has been done in the present paper, when investigating dipole-moment fluctuations. We call the generalized collective modes related to these fluctuations dipolar modes, in order to distinguish them from the hydrodynamic modes concerning fluctuations of hydrodynamic quantities. At the same time, the generalized hydrodynamic modes of a dipolar system can be studied within the same scheme as in the case of simple fluids [35–37]. It is also worth remarking that correlations between the dipole-moment density and hydrodynamic quantities are not completely independent. Being absent at the basic level, however, they appear at higher orders of the description. This leads to additional non-Markovian effects when working within the dipole-density formalism. Nevertheless, these effects are taken into account in an effective way, including, besides the basis quantity $\mathbf{M}(\mathbf{k})$, its higher-order components (3) as well. The hydrodynamic correlations are included in the same way too. For example, the fluctuations of $L\mathbf{M}(\mathbf{k})$ [see Eq. (31)] can be expressed in terms of the correlations of spatial and angular momenta densities. Therefore, within the extended dipole-density formalism, the processes of dielectric relaxation are connected implicitly with hydrodynamic properties via higher-order static Kirkwood factors. The investigation of generalized hydrodynamic modes of a Stockmayer fluid, as well as an application of the proposed theory to more complicated interaction site models of polar fluids, will be presented in a separate publication.

ACKNOWLEDGMENTS

One of us (I.P.) would like to acknowledge the financial support of the President of Ukraine. I.M. also thanks the Österreichische Fonds zur Förderung der wissenschaftlicher Forschung (Project P12422TPH).

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