Linear complex permittivity of isotropic polar fluids

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Abstract. An analytical formula for the linear complex permittivity of polar fluids is obtained from the averaged Dean-Kawasaki equation as a function of temperature, density and molecular dipole moment. The static results compare reasonably well with experimental data of some simple polar fluids in their liquid phase, while when the Kirkwood correlation factor is larger than unity, a thermally activated relaxation process appears in the dynamic response.

1. Introduction
The Kirkwood-Fröhlich theory of the linear static permittivity \( \varepsilon \) is the most successful one to explain a number of experimental data concerning the experimental behaviour of \( \varepsilon \) of polar fluids. In effect, this theory yields a formula linking \( \varepsilon \) to the molecular dipole moment in the liquid phase \( \mu_L \), the molecular density \( \rho_0 \), the absolute temperature \( T \) and the "Kirkwood correlation factor" \( g_K \). This formula is

\[
\frac{(\varepsilon - \varepsilon_\infty)(2\varepsilon + \varepsilon_\infty)}{3\varepsilon} = \frac{\rho_0 \mu^2}{3\varepsilon_0 k T} g_K, \tag{1}
\]

where \( k \) is the Boltzmann constant, \( \varepsilon_0 \) is the absolute vacuum permittivity, \( \varepsilon_0 = (36\pi)^{-1} \cdot 10^{-9} \text{ F} \cdot \text{m}^{-1} \) in MKSA units \([1]\) and \( \varepsilon_\infty \) is the dielectric constant of the Kirkwood-Fröhlich cavity, and loosely accounts on the distortional polarization mechanism and thereby the effect of the polarizability of the molecules. The molecular dipole moment in the liquid phase is itself given by

\[
\mu_L = \frac{\varepsilon_\infty + 2}{3} \mu_g, \tag{2}
\]

and \( \mu_k \) is the mean dipole moment of a single molecule in the ideal gas phase, thus allowing a deduction of \( g_K \) by experimental measurements of the static permittivity. The physical meaning of \( g_K \) is rather simple: if \( g_K > 1 \), the dipoles tend to orient parallel; if \( g_K < 1 \), the dipoles tend to orient antiparallel; and if \( g_K = 1 \), no orientation is preferred although the molecules interact via long range forces and torques.

From the theoretical point of view, \( g_K \) has been calculated via \textit{bona fide} estimates for various simple polar fluids by Oster and Kirkwood \([2]\) at room temperature, leading to excellent agreement with experiment. However, it is also known via experiment that generally, \( g_K \) is a temperature-dependent quantity which, most of the time and even for the simplest polar liquids, is computed via numerical simulation methods. In the dynamical case, the situation is...
even more dramatic because the dynamics of the internal field is generally unknown, and is also an unknown function of the linear complex permittivity $\varepsilon(\omega)$ [3]. The most complete equation linking $\varepsilon(\omega)$ to the molecular linear response has been given by Scaife [3]; however, in order to use this equation, a microscopic model must be suggested.

The purpose of this communication is first of all to show that the Kirkwood correlation factor can be calculated analytically for simplest polar fluids, leading to reasonably good agreement with experiment. Then, an analytical formula will also be given for the low-frequency linear complex permittivity for pure polar fluids, i.e. for $\varepsilon_\infty = 1$. All these calculations will be dealt with in the framework of the rotational Dean-Kawasaki equation derived by Cugliandolo et al. [4]. This analytical formula reveals a thermally activated relaxation process due to long-range interactions for $g_K > 1$; while, for $g_K < 1$, no thermally activated process occurs and the behaviour of the complex permittivity is mostly Debye-like.

2. Microscopic dipole dynamics

The collective tumbling dynamics of an assembly of long-range interacting dipoles may be described by the averaged rotational Dean-Kawasaki equation

$$2\tau_D \frac{\partial W}{\partial t}(\mathbf{u}, t) = \nabla_u \cdot [\nabla_u W(\mathbf{u}, t) + \beta W(\mathbf{u}, t) \nabla_u V_1(\mathbf{u}, t)] + \beta \nabla_u \cdot \int \nabla_u U_m(\mathbf{u}, \mathbf{u}', t) W_2(\mathbf{u}, \mathbf{u}', t)d\mathbf{u},$$

(3)

where $\nabla_u$ is the del operator on the unit sphere, $\tau_D$ is the Debye relaxation time, $\beta = (kT)^{-1}$, $W$ and $W_2$ are respectively the one-body and pair orientational probability densities on the unit sphere, $U_m$ is a pair interaction potential and $V_1(\mathbf{u}, t) = -\mu \mathbf{F}_l(t) \cdot \mathbf{u}$ is the mean electrostatic orientational energy due to the electric field $\mathbf{F}_l(t)$ (i.e. the orientational electrostatic energy seen by a molecule). As written, Eq. (3) is a particular rotational, non-inertial Fokker-Planck (Schmoluchowski) equation forced by pair interactions. Furthermore, it has been shown [5] that, in the usual Kirkwood superposition approximation, $W_2$ obeys the effective two-body Fokker-Planck equation

$$2\tau_D \frac{\partial W_2}{\partial t}(\mathbf{u}, \mathbf{u}', t) = \nabla_u \cdot \left[ \nabla_u W_2(\mathbf{u}, \mathbf{u}', t) + \beta W_2(\mathbf{u}, \mathbf{u}', t) \nabla_u V_2^{\text{eff}}(\mathbf{u}, \mathbf{u}', t) \right] + \nabla_{\mathbf{u}'} \cdot \left[ \nabla_{\mathbf{u}'} W_2(\mathbf{u}, \mathbf{u}', t) + \beta W_2(\mathbf{u}, \mathbf{u}', t) \nabla_{\mathbf{u}'} V_2^{\text{eff}}(\mathbf{u}, \mathbf{u}', t) \right],$$

(4)

where $V_2^{\text{eff}}(\mathbf{u}, \mathbf{u}') = V_2(\mathbf{u}, \mathbf{u}', t) + U_{\text{an}}(\mathbf{u}) + U_{\text{an}}(\mathbf{u}')$ [5] and where $U_{\text{an}}(\mathbf{u}) = U_{\text{an}}(-\mathbf{u})$ is a one-particle potential that loosely describes the effects of three-body orientational correlations on a pair of dipoles with orientations $(\mathbf{u}, \mathbf{u}')$. In this approximation, $U_{\text{an}}(\mathbf{u})$ verifies the equation [5]

$$\nabla_u U_{\text{an}}(\mathbf{u}) = (\nabla_u U_m(\mathbf{u}, \mathbf{u}'))|_{\mathbf{u}' = -\mathbf{u}}.$$  

(5)

For the model pair interaction potential

$$\beta U_{\text{in}}(\mathbf{u}, \mathbf{u}') = +\lambda \cos \theta \cos \theta',$$

(6)

we have two possibilities for $V_2^{\text{eff}}(\mathbf{u}, \mathbf{u}', t)$ [5], viz.

$$\beta V_2^{\text{eff}}(\mathbf{u}, \mathbf{u}', t) = -\frac{\lambda}{2} (\cos \theta \pm \cos \theta')^2 - \xi_\ell(t) (\cos \theta + \cos \theta'),$$

(7)

where $\theta$ and $\theta'$ are the colatitudes of the dipoles having orientations $(\mathbf{u}, \mathbf{u}')$ in the laboratory frame, $\lambda = (\rho_0 \mu_0^2)/(3\varepsilon_0 kT)$ and $\xi_\ell(t) = \beta \mu_0 F_\ell(t)$. 

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3. Statics
In this case \( \partial W_0 / \partial t = 0 \). Then it has been shown that according to the sign chosen in Eq. (6), the Kirkwood correlation factor was given by [6]

\[
g_{\text{K}}((\lambda)) = \frac{\sqrt{2\pi \lambda^2}(15 + 4\lambda)\text{erfi}(\sqrt{2\lambda}) + 4(2 - \lambda)e^{2\lambda} - 16(3 + 5\lambda)}{60(\lambda - \lambda e^{2\lambda} + \sqrt{2\pi \lambda^2}\text{erfi}(\sqrt{2\lambda}))},
\]

where the superscript \((-)\) is associated with the minus sign in Eqs (6). If the plus sign is chosen in these equations, we have instead

\[
g_{\text{K}}^{(+)}((\lambda)) = \frac{1}{12}\left(8 - 4\lambda + \frac{\sqrt{2\pi \lambda}\text{erfi}(\sqrt{2\lambda}) + 4\lambda}{1 - e^{2\lambda} + \sqrt{2\pi \lambda^2}\text{erfi}(\sqrt{2\lambda})}\right),
\]

where, in both Eqs (8) and (9), \text{erfi}(z) = i \text{erf}(-iz) is the error function of imaginary argument. Either Eq. (8), either Eq. (9), may be injected into the Kirkwood-Fröhlich Eq. (1), which negative root is indeed rejected.

4. Dynamics
The dynamical aspects corresponding to the approximation dealt with here has been worked out for purely polar fluids only (\( \varepsilon_\infty = 1 \)). The Scaife equation [3] results in

\[
\frac{(\varepsilon(\omega) - 1)(2\varepsilon(\omega) + 1)}{3\varepsilon(\omega)} = 3\lambda A_1^{(1)}(\omega),
\]

where [5]

\[
A_1^{(1)}(\omega) \approx \frac{1 + \lambda(b_{3,1}^{(0)} - b_{1,1}^{(0)})/5}{3(1 + i\omega\tau_D)} + \frac{\lambda}{3} \frac{B_{0,1}^{(1)}(0) - B_{2,1}^{(1)}(0)}{(1 + i\omega\tau_D)(1 + \lambda/3 + i\omega\tau_D)},
\]

for \( g_K > 1 \), and

\[
A_1^{(1)}(\omega) \approx \frac{1 - \lambda(b_{3,1}^{(0)} - b_{1,1}^{(0)})/5}{3(1 + i\omega\tau_D)} - \frac{\lambda}{3} \left(1 + \frac{\lambda}{3}\right) \frac{B_{0,1}^{(1)}(0) - B_{2,1}^{(1)}(0)}{(1 + i\omega\tau_D)(1 + \lambda/3 + i\omega\tau_D)},
\]

for \( g_K < 1 \), those two ranges of \( g_K \) being associated with both signs in Eq. (6). In Eq. (11), \( \Lambda_1 \) is the smallest non-vanishing eigenvalue of the two-body Fokker-Planck equation (5) having Arrhenius behaviour at low temperatures while expressions for the coefficients \( b_{n,1}^{(0)}(0) \) and \( B_{n,1}^{(1)}(0) \) as functions of \( \lambda \) have been given elsewhere [6]. Moreover, \( A_1^{(1)}(\omega) \) has been computed exactly by solving Eq. (4) in term of matrix continued fractions, and the numerical result agrees in all respects with Eqs (11) and (12) [5].

5. Results and discussion
The various formulas we have obtained are particularly useful, first of all to analyze the behaviour of the Kirkwood correlation factor as a function of the density of the fluid and temperature. In our analysis, phase transitions are not permitted, so that, in principle, the formulas that we have obtained are relevant for the liquid phase only, with the provision that the limit \( \lambda \to 0 \) render results that pertain to a dilute system of dipoles. The explicit variation of the Kirkwood correlation factor as a function of \( \lambda \) together with its asymptotes has been represented elsewhere [5] and will not be reproduced here. Yet, comparison of our analytical results with the
Figure 1. $\varepsilon(T)$ for various simple polar fluids. Black, water ($\varepsilon_\infty = 1.82$); red, glycerol ($\varepsilon_\infty = 1.91$); blue, methanol ($\varepsilon_\infty = 2.10$); green, dichloromethane ($\varepsilon_\infty = 2.47$). Solid lines are our theoretical calculations. The dashed line is the empirical equation of Matyushov and Richert [7] for glycerol. The density of the liquid used is the experimental density.

experimental dependence of the dielectric constant of four "simple" polar fluids is represented on Figure 1 above.

One may see from this Figure that reasonable agreement between experiment and theory is obtained, and this without any fitting parameter. Here, we mention that contrarily to what was stated in [6], our analytic formula works well for glycerol provided the temperature considered is away from the glycerol glass transition temperature $T_g$. At low temperatures, we observe a clear deviation of our calculations with respect to experimental data. This is because our calculations do not account for higher correlations. This task has yet to be accomplished, and is in progress [8]. At high temperatures, better agreement can be obtained by evaluating the quantity $\varepsilon_\infty$ from the Lorenz-Lorentz equation, so allowing the temperature dependence of $\varepsilon_\infty$. These results will be published elsewhere [8].

We have also compared the results of our static calculations with numerical simulations of molecular dynamics and DFT types [6], and found that the agreement between theory and experiment was generally better for our calculations. This is because the Kirkwood-Fröhlich theory treats distortional polarization qualitatively only, while numerical simulations attempt to account for this effect in a detailed manner (see for example [9]). Our dynamical calculations propagate the statics that have been derived in [6]. However, the agreement between theory and experiment is generally not so good. For example, although it allows interpretation of the Debye absorption peak of water at 20 GHz or so in the range 0-35°C, however the high-frequency real part of the complex permittivity is too large for our complex polarizability model, yielding a plateau value that is in disagreement with experimental data. This suggests that the dynamics of the reaction field is not properly included in our calculations, and that specific memory effects due to the dynamics of the hydrogen-bonded network must be included in some way.

References
[1] Brown W F J 1956 Dielectrics (Handbuch der Physik vol 17) (Berlin, Germany: Springer)
[2] Oster G and Kirkwood J G 1943 J. Chem. Phys. 11 175
[3] Scaife B K P 1998 Principles of dielectrics 2nd ed (Oxford, UK: Clarendon)
[4] Cugliandolo L F, Dénardin P M, Lozano G S and van Wijland F 2015 Phys. Rev. E 91 032139
[5] Dénardin P M, Titov S V and Cornaton Y 2019 Phys. Rev. B 99 024304
[6] Dénardin P M, Cornaton Y, Ghesquière P, Caliot C and Brouzet R 2018 J. Chem. Phys. 148 044504
[7] Matyushov D V and Richert R 2016 J. Chem. Phys. 114 044102 suppl. Material
[8] Dénardin P M and Cornaton Y In preparation
[9] Zhang C, Hütter J and Sprik M 2016 J. Phys. Chem. Lett. 7 2696