An exact integral formula for the Kirkwood correlation factor of isotropic polar fluids $g_K$ is derived from the equilibrium averaged rotational Dean equation, which as compared to previous approaches easily lends itself to further approximations. The static linear permittivity of polar fluids $\varepsilon$ is calculated as a function of temperature, density and molecular dipole moment in vacuo for arbitrary pair interaction potentials. Then, using the Kirkwood superposition approximation for the three-body orientational distribution function, we suggest a simple way to construct model potentials of mean torques considering permanent and induced dipole moments. We successfully compare the theory with the experimental temperature dependence of the static linear permittivity of various polar fluids such as a series of linear monohydroxy alcohols, water, tributyl phosphate, acetonitrile, acetone, nitrobenzene and dimethyl sulfoxide, by fitting only one single parameter, which describes the induction to dipole-dipole energy strength ratio. We demonstrate that comparing the value of $g_K$ with unity in order to deduce the alignment state of permanent dipole pairs, as is currently done is in many situations, is a misleading oversimplification, while the correct alignment state is revealed when considering the proper interaction potential. Moreover we show, that picturing H-bonding polar fluids as polar molecules with permanent and induced dipole moments without invoking any specific H-bonding mechanism is in many cases sufficient to explain experimental data of the static dielectric constant. In this light, the failure of the theory to describe the experimental temperature dependence of the static dielectric constant of glycerol, a non-rigid polyalcohol, is not due to the lack of specific H-bonding mechanisms, but rather to an oversimplified model potential for that particular molecule.

In summary, the equation of state of linear dielectrics may symbolically be written:

\[
f(\varepsilon, \varepsilon_\infty) = \frac{\beta \langle M^2 \rangle_0}{3\varepsilon_0 \upsilon}
\]

where the angular brackets $\langle \rangle_0$ denote a statistical average in the absence of any applied or directing field, $\beta = (kT)^{-1}$, $k$ is Boltzmann's constant, $T$ the absolute temperature, $\varepsilon_0$ is the permittivity at a frequency where the rotational mechanism of polarization has ceased to operate, the quantities $f(\varepsilon, \varepsilon_\infty)$ and $\langle M^2 \rangle_0$ are specified in Table below. In this Table, $\mu_0$ is the permanent molecular dipole moment in vacuo, $\rho_0$ is the number of molecules per unit volume, $\mathbf{M}$ is the vector sum of permanent molecular dipole moments in the cavity, $g_K$ is the Kirkwood correlation factor and $\mu_{\text{eff}}$ is an effective dipole moment. Here, we note that both the Kirkwood-Fröhlich and Wertheim theories agree when $\varepsilon_\infty = 1$, and agree to leading order in $\varepsilon_\infty/\varepsilon$ when $\varepsilon > \varepsilon_\infty$. For a polar substance like liquid water, the difference between both theories is unimportant. Thus, the problem of the calculation of the linear static permittivity of polar fluids is essentially reduced either to that of $g_K$, or, equivalently, to that of the linear orientational polarization response to external fields by means of statistical mechanics.

This does not imply that Kubo’s linear response theory, from which Eq. (1) specifically arises, should necessarily be applied to calculate $g_K$. Now, the Kirkwood correlation factor may be writ-
Table 1 Definition of quantities used in Eq. (1).

| Theory               | \( f(\varepsilon, \varepsilon_0) \) | \( g_0/\varepsilon_0 \) | \( \mu \) |
|----------------------|-------------------------------------|-------------------------|----------|
| Debye                | \( \varepsilon - \varepsilon_0 \)  | \( \delta_0 \) \( \beta \) \( \varepsilon_0 \) | \( \varepsilon_0 \) |
| Onsager              | \( \frac{(\varepsilon - \varepsilon_0)(2\varepsilon - \varepsilon_0)}{N} \) | \( \delta_0 \) \( \beta \) \( \varepsilon_0 \) | \( \varepsilon_0 \) |
| Kirkwood-Fröhlich   | \( \frac{(\varepsilon - \varepsilon_0)(2\varepsilon - \varepsilon_0)}{N} \) | \( \delta_0 \) \( \beta \) \( \varepsilon_0 \) | \( \varepsilon_0 \) |
| Wertheim             | \( \frac{(\varepsilon - \varepsilon_0)(2\varepsilon - \varepsilon_0)}{N} \) | \( \delta_0 \) \( \beta \) \( \varepsilon_0 \) | \( \varepsilon_0 \) |

where \( \delta_0 \) is always larger than (or equal to) unity. However, he reckoned that his MSA theory was too crude an approximation to describe the dielectric constant of polar fluids. Subsequent efforts to extend his approach in order to relax the hard sphere hypothesis (retaining Wertheim’s expansion for the pair correlation function in three components however) are summarized in the review of Stell et al. showing good agreement with various Monte-Carlo and molecular dynamics simulations, and even with integral equation theories of fluids such as the linear and quadratic hypernetted chain approximations to the hypernetted chain closure of the Ornstein-Zernike equation. Now, the point is that the predictions of the dielectric constant found from these theories are too large in regard to experimental data on various compounds (see Figure 22 of Ref. and the discussion which follows). We remark that in all these approaches, the one-body density is always assumed uniform, and does not depend on the rotational degrees of freedom of the molecule, so that the pair density is simply proportional to the pair distribution function, which in turn has trivial dependence regarding the rotational degrees of freedom of molecular pairs.

A few years ago, Zhang et al. have determined the Kirkwood radius, i.e., the radius at which the dielectric function \( \varepsilon(r) \) does no longer depend on the coordinates of a point \( r \) inside the liquid, for water using numerical simulations, developing an original approach. Then they used Wertheim’s fluctuation theory in order to determine \( \varepsilon \) for liquid water at room temperature. In that case, the use of Wertheim’s theory does not make any substantial difference compared to the Kirkwood-Fröhlich treatment, since in the liquid state, the dielectric constant of water is about 80, while at the same time, \( \varepsilon_0 \leq 2 \). Yet, in this work, the temperature dependence of \( \varepsilon \) is only vaguely mentioned.

Very recently, based on the work of Kawasaki and Dean, Cugliandolo et al. derived a stochastic nonlinear integro-differential equation governing the dynamics of the microscopic density of collective modes for Brownian dipoles. In doing so, they ignored inertial effects, but included translational as well as rotational degrees of freedom of the molecules. Furthermore, their equation when averaged over the probability density of realizations of the local noises, reduces at equilibrium to the first approach. Then they used Wertheim’s fluctuation theory in order to determine \( \varepsilon \) for liquid water at room temperature. In that case, the use of Wertheim’s theory does not make any substantial difference compared to the Kirkwood-Fröhlich treatment, since in the liquid state, the dielectric constant of water is about 80, while at the same time, \( \varepsilon_0 \leq 2 \). Yet, in this work, the temperature dependence of \( \varepsilon \) is only vaguely mentioned.

In 1971, Wertheim proposed a statistical treatment based on a nontrivial extension of the Mean Spherical Approximation (MSA). In effect, using the hard-sphere condition for the pair distribution function and the Random Phase Approximation (RPA) for the direct pair correlation function, he was able to solve the Ornstein-Zernike equation and obtained a very elegant solution for the static permittivity of purely polar fluids, which can be easily computed. Later, he extended his statistical theory to assemblies of polar and polarizable molecules and obtained essentially the same formula with some nuances. We note in passing that in Wertheim’s approach, it is even possible to formally define a Kirkwood correlation factor by inserting his expression for \( \varepsilon \) in his fluctuation theory with \( \varepsilon_0 = 1 \), with the result that
vacuo $\mu_e$, the molecular density $\rho_0$ and temperature $T$. They further qualitatively compared the outcomes of their theory with the experimental temperature dependence and numerical simulations of $\epsilon$ of water and methanol and found that agreement between their theoretical findings and experimental data was relatively satisfactory. In order to derive their analytical formula, they used both the Ornstein-Zernike route\(^{18}\) and the Kirkwood superposition approximation applied to the orientational pair distribution function\(^{18}\) together with the averaged rotational Dean equation in order to derive the relevant Kirkwood potential of mean torques. The moment method used in References\(^{17,18}\) is a general method of attack when the interaction potential is specified. However, it makes the detailed comparison of the theory with experiment rather cumbersome, due to its restriction to one specific interaction potential.

In order to improve on this first approach, it is the purpose of the present work to derive a formula for the Kirkwood correlation factor that does not depend on any approximation made in solving the first member of the rotational Yvon-Born-Green hierarchy, but itself represents a good starting point for further approximations. An integral formula will then be obtained in the context of Kirkwood's superposition approximation, allowing $g_K$ to be calculated for arbitrary pair interaction potentials of forces and torques. Then, our theoretical results will be compared with experimental data concerning a series of primary linear alcohols, water, glycerol, tributyl phosphate (TBP), acetonitrile, acetone, nitrobenzene and dimethyl sulfoxide (DMSO).

1 Kirkwood correlation factor from the equilibrium averaged rotational Dean equation

We consider an assembly of interacting polar molecules that are subjected both to thermal agitation and to uniform externally applied DC electric fields. The averaged rotational Dean equation at statistical equilibrium (time-independent regime) is\(^{16,17}\)

$$\nabla_u \left[ W_u V_1(u) + \beta W(u) \nabla_u V_1(u) \right] + \beta V_u \cdot \int \nabla_u U_m(u, u') W_2(u, u') \, du' = 0 \quad (5)$$

where $u$ is a unit vector along a molecular dipole moment of constant magnitude $\mu$, $W(u)$ is the one-body orientational probability density, $V_1(u) = -\mu \cdot E$ is a one-body potential containing the effect of the directing uniform electric field $E$, $U_m(u, u')$ is a space averaged orientational pair interaction potential, $W_2(u, u')$ is the orientational pair probability density. The integral in Eq. (5) is extended to the unit sphere of representative points of a dipole with constant magnitude $\mu$ and orientation $u'$. It is demonstrated in Appendix A that Eq. (5) is an exact one under the assumption of a translationally invariant system made of many interacting molecules. Then, using first-order perturbation theory it may easily be demonstrated that an integral representation of the Kirkwood correlation factor $g_K$ can be derived from Eq. (5) (see Appendix B). Thus, on fairly general grounds, we have:

$$g_K = 1 + \frac{\beta}{\cal G} \int \nabla_u U_m(u, u') \cdot \Phi(u, u') \, du/du' \quad (6)$$

with

$$\Phi(u, u') = W_2^{(0)}(u, u') \nabla_u P_2(u) - 9 W_2^{(1)}(u, u') \nabla_u P_1(u), \quad (7)$$

where $W_2^{(0)}$ is the field-free equilibrium pair probability density and $W_2^{(1)}$ its linear response counterpart, while $P_n(u)$ denotes the Legendre Polynomial of order $n$ of the component of the dipolar unit vector $u$ along the external electric field. Equation (6) is the rotational Dean (in fact, the rotational Yvon-Born-Green\(^{10}\)) representation of the Kirkwood correlation factor, and is a central result of our paper. We note that our result for $g_K$ does not depend on the number of neighbors of a "tagged" molecule and is therefore totally equivalent to Eq. (4). It is nevertheless impossible to obtain explicit results if one does not link $W_2^{(1)}(u, u')$ to $W_2^{(0)}(u, u')$. The general task is made complicated by the fact that the equation governing $W_2(u, u')$ involves the three-body orientational probability density $W_3(u, u', u'')$, the governing equation of which involves the four-body orientational probability density $W_4$ and so on, and for these distributions, the respective linear response to external fields must be calculated. Hence, one must make a choice in order to obtain explicit results, an aspect of which is discussed in Appendix C. If we use the Kirkwood superposition approximation for the three-body orientational distribution function\(^{10}\), then we may show that we have\(^{18}\)

$$W_2^{(1)}(u, u') = W_2^{(0)}(u, u') (u + u') \cdot e \quad (8)$$

where $e$ is a unit vector along the directing field, and where

$$W_2^{(0)}(u, u') = Z^{-1} e^{-\beta V_2^{(0)}(u, u')}, \quad (9)$$

where $Z$ is the partition function defined by

$$Z = \int e^{-\beta V_2^{(0)}(u, u')} \, du/du'. \quad (10)$$

$V_2^{(0)}(u, u')$ is an effective (rotational) pair potential given by\(^{18}\)

$$V_2^{(eff)}(u, u') = U_m(u, u') + U_{ia}(u) + U_{ai}(u') \quad (11)$$

while $U_{ia}(u)$ is obtained by solving the differential equations\(^{18}\)

$$\nabla_u U_{ia}(u) = \nabla_u U_m(u, u') \big|_{u'=u}. \quad (12)$$

Yet, in spite of its apparent simplicity, Eqs. (10) and (11) must be used with caution because the stationary points of $V_2^{(eff)}$ must at least approximately, if not exactly, be located at the same angles and must be of the same nature as those of $U_m$ so that both potentials describe the same physics. This was so far only vaguely described in the original work of Déjardin et al.\(^{18}\). Therefore, the necessary decorrelation procedure is described in Appendix 5. We can further use the expressions for the Legendre polynomials $P_n(\cos \vartheta)$ in order to obtain a tractable version of Eq. (6). This results in the following expression for $g_K$:

$$g_K = 1 + \frac{\beta}{\cal G} \int \Phi(u, u') W_2^{(0)}(u, u') \, du/du'. \quad (13)$$
where we have used Eq. (3), \( \cos \vartheta = \mathbf{u} \cdot \mathbf{e} \) in conjunction with Eq. (5) and where we have defined \( G(\mathbf{u}, \mathbf{u}') \) via the equation

\[
G(\mathbf{u}, \mathbf{u}') = \sin \vartheta \left( \cos \vartheta + \frac{3}{2} \cos \vartheta' \right) \frac{\partial U_m}{\partial \vartheta} (\mathbf{u}, \mathbf{u}')
\]

By steepest descents arguments, if the pair intermolecular interactions is large with respect to \( kT \), the value of \( g_K \) rendered by Eq. (12) depends on the location of the minima of \( V_{eff} \), therefore on the state of alignment of dipole pairs at equilibrium. However, in order to use this equation, \( U_m \) needs to be specified.

2 Construction of a model potential for electrostatic interactions

It is well-known that the inclusion of the effect of the polarizability of the molecules is a necessity in order to describe the polarization state at the molecular level. This means in particular that inclusion of the translational fluctuations (i.e. coupling between translational effects and the induced moment), makes it impossible to apply the Kirkwood-Fröhlich theory because then the back action of the reaction field is unknown. We therefore suggest, as an intermediate point of view between these two extreme situations, i.e., no polarizability effects and full inclusion of the latter, to average the true intermolecular interaction potential over translational and vibrational degrees of freedom of the molecules before using the Fröhlich internal field, so that the potential effectively becomes a function of the permanent dipole moment orientations only, and that this average still keeps a trace of polarizability effects. In other words, the task is therefore to encode, at least approximately, the molecular physical effects in the potential \( U_m \). To this aim, we write the pair interaction potential \( U_m \) as follows:

\[
\beta U_m(\mathbf{u}, \mathbf{u}') = \beta \int U_{int}(\rho, \mathbf{u}, \mathbf{u}') G(\rho)d\rho
\]

where \( \rho \) denotes both intermolecular distances and vibrational degrees of freedom, \( U_{int}(\rho, \mathbf{u}, \mathbf{u}') \) is the true pair intermolecular interaction potential and \( G(\rho) \) is the probability density of the translational and vibrational degrees of freedom (a similar average is defined in Appendix A). The precise result of integration indeed depends on the system under study. Formally, however, and without any loss of generality, we can expect this integral to have the following form:

\[
\beta U_m(\mathbf{u}, \mathbf{u}') = \sum_{n=1}^{\infty} a_n \phi_n(\mathbf{u}) \phi_n(\mathbf{u}')
\]

where \( \phi_n(\mathbf{u}) \) is a polynomial function of the direction cosines of \( \mathbf{u} \) of degree \( n \), the star denotes the complex conjugate and the expansion coefficients \( a_n \) are parameters which are chosen to match the physical reality as much as possible. In order to exploit further Eq. (14), we also require that \( \phi_n(\mathbf{u}) \) have the parity of their degree, i.e.

\[
\phi_n(-\mathbf{u}) = (-1)^n \phi_n(\mathbf{u})
\]

Hence, we may remark using Eqs. (14) and (15) that \( U_m(\mathbf{u}, \mathbf{u}') \) has the necessary property of global rotational invariance, i.e.

\[
U_m(-\mathbf{u}, -\mathbf{u}') = U_m(\mathbf{u}, \mathbf{u}')
\]

The simplest choice for \( \phi_1(\mathbf{u}) \) which encodes the correct dipole physics is

\[
\phi_1(\mathbf{u}) = \cos \vartheta
\]

so that the leading term of the series Eq. (14) is \( a_1 \cos \vartheta \cos \vartheta' \). According to the sign of \( a_1 \), this term has minima for parallel order or antiparallel order of the permanent dipoles, and represents the dipole-dipole interactions \( V_{dd} \). Hence, following for example Refs. [17,19] we have:

\[
a_1 = \mp \lambda
\]

where

\[
\lambda = \frac{\beta \rho_0 \mu^2}{3k_0}
\]

is the Debye susceptibility of ideal dipolar gases with individual permanent molecular dipole modulus \( \mu \). Thus we have

\[
\beta V_{dd}(\mathbf{u}, \mathbf{u}') = \mp \lambda \cos \vartheta \cos \vartheta'
\]

In order to account for the effect of the polarizability of the molecules and its probable coupling with the permanent dipole, we add the term \( n = 2 \) to Eq. (20), and use \( \phi_2(\mathbf{u}) = \cos^2 \vartheta \), which is the simplest choice we can make. This results in a term

\[
a_2 \cos^2 \vartheta \cos^2 \vartheta'
\]

This term loosely represents induction and dispersion terms. Nevertheless, because these interaction energy terms are in general not individually additive, this is very difficult to specify \( a_2 \) in terms of the polarizability exactly. Nevertheless, we may still write that \( a_2 \) is proportional to \( a_1 \), so that we have:

\[
a_2 = \mp \kappa \lambda
\]

resulting in the interaction energy term:

\[
\beta V_{indisp}(\mathbf{u}, \mathbf{u}') = \mp \kappa \lambda \cos^2 \vartheta \cos^2 \vartheta'
\]

where \( \kappa \) is a dimensionless parameter that may depend on the molecular density and temperature. However, in the following, we will consider it as a constant, the value \( |\kappa| \) giving the deviation to pure dipole-dipole interactions. The parameter \( \kappa \) can be taken positive or negative, and \( |\kappa| \) may exceed unity, meaning in the latter situation that the dipole-dipole interaction is not the most significant interaction in a given substance, which may happen if a given molecule has a tiny permanent dipole, typically less than 1 Debye. The overall electrostatic interaction \( U_m \) between dipole pairs is then written as follows:

\[
\beta U_m(\mathbf{u}, \mathbf{u}') = \beta V_{dd}(\mathbf{u}, \mathbf{u}') + \beta V_{indisp}(\mathbf{u}, \mathbf{u}')
\]
A generic expression for the Kirkwood potential of mean torques \( V_{2}^{\text{eff}} \) is not possible to obtain, see Appendix \( \text{[5]} \) for the practical determination of \( V_{2}^{\text{eff}} \) from \( U_{m} \) and \( U_{an} \). For \( \kappa = 0 \), we obtain the analytical results already derived elsewhere.\( \text{[21]} \) For \( \kappa \neq 0 \), this leads to 4 possible numerical values of \( g_{K} \). The notation for these values together with their corresponding interaction potentials are summarized in Table \( \text{[2]} \) below. In the next section, we discuss the theoretical \( g_{K} \) values rendered by these functions.

The choice we have made in Table \( \text{[2]} \) is such that when the theory is compared with experiment it generally renders a positive value of \( \kappa \), an exception being made in case of water, as will be shown in Paragraph \( \text{[4]} \). Unphysical situations have been eliminated according to the criteria mentioned in Ref. \( \text{[18]} \) and exposed in detail in Appendix \( \text{[5]} \).

### 3 Theoretical results

As already pointed out previously, the integral representation Eq. \( \text{(5)} \) of the Kirkwood correlation factor is equivalent to Eq. \( \text{(2)} \). The two equations differ in mathematical form simply because the starting point for their derivation is different. For example, Eq. \( \text{(2)} \) is obtained from the equilibrium linear response solution of the generalized Liouville equation, while our Eq. \( \text{(5)} \) is derived from the first member of the (rotational) Yvon-Born-Green hierarchy, which is a representation of the generalized Liouville equation when interactions are represented by pair interactions only.\( \text{[19]} \) Therefore, Eq. \( \text{(5)} \) is an exact one, provided that only pair interactions are considered. Although it is as difficult as Eq. \( \text{(2)} \) to evaluate exactly, it nevertheless lends itself to approximations in a much easier manner since it does not explicitly depend on the number of molecules in the cavity. As an example of a possible approximation, one may choose the mean field one for which we have \( W_{2}(u, u') = W(u)W(u') \) and use Eq. \( \text{(6)} \) for \( \kappa = 0 \), which yields: \( \text{[20,22]} \)

\[
g_{K} = \left( 1 \mp \frac{\lambda}{3} \right)^{-1} \tag{25}
\]

where the minus sign holds for parallel alignment and the plus sign holds for antiparallel alignment. Indeed, for parallel alignment, Eq. \( \text{(25)} \) produces a Curie point at \( \lambda = 3 \) which is undesirable here. Indeed, it has been shown elsewhere that Eq. \( \text{(25)} \) is valid for \( \lambda < 1 \), leading, for parallel alignment, to\( \text{[17]} \)

\[
g_{K} \approx 1 + \frac{\lambda}{3} \tag{26}
\]

In this context, the dielectric constant is given by\( \text{[18]} \)

\[
\varepsilon \approx 1 + \lambda \left( 1 + \frac{2\lambda}{3} \right) \tag{27}
\]

so that the Debye theory is recovered at weak densities, i.e., when \( \lambda < 1 \). If one uses the Kirkwood superposition approximation one obtains Eq. \( \text{(12)} \), the explicit evaluation of which in terms of the error function of the imaginary argument has been given elsewhere.\( \text{[17]} \)

Thus, we essentially have interaction energies \( U_{m} \), and four corresponding Kirkwood potentials of mean torques given in Table \( \text{[2]} \). This leads to four values \( g_{K}^{(1)} \), \( g_{K}^{(2)} \), \( g_{K}^{(1+1)} \) and \( g_{K}^{(1-1)} \) that reduce to previously derived results for \( g_{K} \) when \( \kappa = 0 \)\( \text{[21]} \), i.e., when \( V_{\text{indisp}} \) is neglected. The variation of \( g_{K}^{(1)} \) as a function of \( \lambda \) and \( \kappa \) is represented in Figures \( \text{[1]} \) and \( \text{[2]} \). One notices the substantial increase of the Kirkwood correlation factor as \( \kappa \) is increased from 0. The explanation is that in this situation, the induction term neither affects the location of the minima \((0, 0)\) and \((\pi, \pi)\), nor the location of the saddle point \((\frac{\pi}{2}, \frac{\pi}{2})\) of both \( U_{m} \) and \( V_{2}^{\text{eff}} \), but increases the energy barrier separating the two multidimensional minima in \( V_{2}^{\text{eff}} \), which in turn governs the pair equilibrium statistics. As a result, the parallel states \((0, 0)\) and \((\pi, \pi)\) are made even more (respectively less) probable for \( \kappa > 0 \) (respectively \( \kappa < 0 \)) than for \( \kappa = 0 \). This results in an increase (respectively a decrease) in the Kirkwood correlation factor with respect to the situation where \( \kappa = 0 \). As illustrated in Figure \( \text{[2]} \) the variation of \( g_{K}^{(1)} \) with \( \kappa \) for given \( \lambda \) is linear. This means that in this situation, the dipolar field has a trend to induce a dipole in the same direction as that of the alignment of the molecular permanent dipole moments. Thus, the bonds are slightly stretched, so the atomic charge distributions are more distant than in the absence of induced dipoles. The result is simply a proportion of \( g_{K} \) with \( \kappa \). We also note from Figures \( \text{[1]} \) and \( \text{[2]} \) that values of \( g_{K} < 1 \) are possible in spite of preferred parallel alignment of the permanent dipoles. Now, if too large negative \( \kappa \) values are used here, this causes \( g_{K}^{(1-)} \) to take unphysical negative or null values. The higher transcendental nature of the functions representing the integrals makes it difficult to precisely state the limiting \( \kappa \) value at which this occurs, nevertheless these integrals can be computed numerically. Therefore, if any negative \( \kappa \) value is to be applied when comparing the present theory with experiments, then one must guarantee the positiveness of \( g_{K}^{(1-)} \) in the whole temperature range where the species under study is in its liquid phase.

Figures \( \text{[4]} \) and \( \text{[5]} \) show the behavior of \( g_{K}^{(2-)} \) when \( \lambda \) and \( \kappa \) are varied. In this situation, the locations of the minima of \( V_{2}^{\text{eff}} \) are...
infinite orientation of dipole pairs at equilibrium obeys the double

the present model transverse modes are energy costless modes.

fied interaction potentials are azimuth-independent, so that in

the wells is not so well-defined in this situation, as our simpli-

ment dipoles is affected. The angle between a pair of dipoles in

V

alignment state is

The energy barrier separating

κ

is not linear at all. Here, a ten-

Thus, the strictly parallel equilibrium states are affected, and

pairs of dipoles form an angle at equilibrium, so that the pair

alignment state is

Fig. 2 Kirkwood correlation factor \( g_{K}^{1(-)} \) as a function of \( \kappa \) for various values of \( \lambda \).

affected in raising \( \kappa \), while the saddle point remains unchanged. Thus, the strictly parallel equilibrium states are affected, and pairs of dipoles form an angle at equilibrium, so that the pair alignment state is a canted one. The energy barrier separating the two minima is furthermore lowered and therefore the equilibrium states are less populated with respect to the situation where \( \kappa = 0 \). Altogether, this results in a decrease of \( g_{K} \). Unlike for \( g_{K}^{1(-)} \), the behavior of \( g_{K}^{2(-)} \) with \( \kappa \) is not linear at all. Here, a tentative explanation may be that the term \( V_{indip} \) fights non-trivially against the aligning effect of the permanent dipole moments due to \( V_{dd} \). Altogether, the equilibrium parallel alignment of permanent dipoles is affected. The angle between a pair of dipoles in the wells is not so well-defined in this situation, as our simplified interaction potentials are azimuth-independent, so that in the present model transverse modes are energy costless modes. Nevertheless, according to our model, we may state that the relative orientation of dipole pairs at equilibrium obeys the double

inequality:

\[
0 \leq \vartheta_{(u,w)} \leq 2 \arctan \frac{\sqrt{1+16\kappa^2} - 1}{\sqrt{2}} \tag{28}
\]

where the upper bound in Eq. (28) is equal to \( \Theta = \vartheta_{\min} + \vartheta_{\min}' = 2\vartheta_{\min} \) and \((\vartheta_{\min}, \vartheta_{\min}')\) is the location of one of the deepest symmetric minima of the corresponding Kirkwood potential of mean torques, while the lower bound is given by \( \vartheta_{\min} - \vartheta_{\min}' = 0 \). Thus, the relative orientation of dipole pairs may be larger than \( \pi/2 \), in spite of the fact that in this situation, \( g_{K} > 1 \). In order to illustrate this, we have plotted the quantity \( \Theta \) as a function of \( \kappa \) in Figure 3, where it becomes clear that \( \Theta \) may be larger than \( \pi/2 \) at some \( \kappa \) values.

This unusual result is explained by the very definition of \( g_{K} \), showing that Eq. (4) is an over-idealization of the real value of \( g_{K} \) given by Eq. (2). Hence, the Kirkwood estimate for \( g_{K} \) only applies to very special cases such as liquid water. Thus, in particular, \( g_{K} > 1 \) does not guarantee the parallel alignment of dipole pairs at equilibrium. In the next section we give a comparison of our calcula-
tions with the experimental temperature dependence of the static linear permittivity of tributyl phosphate in order to illustrate the situation we just described. The variation of $g_K^{1(+)}$ and $g_K^{2(+)}$ with $\lambda$ for various values of $\kappa$ are shown in Figures 6 and 7. These values of the Kirkwood correlation factor correspond to preferred antiparallel alignment when $\kappa = 0$. The most remarkable feature of $g_K^{1(+)}$ is that in this situation, the Kirkwood correlation factor is able to exhibit both $g_K$ values that are smaller and larger than 1, and that this happens at moderate values of $\lambda$. Furthermore, for $\kappa > 0$, $g_K^{1(+)}$ is able to render negative values of $g_K$ if $|\kappa|$ takes too large values, so that the same prescriptions as those given above for $g_K^{1(-)}$ apply to $g_K^{1(+)}$ when attempting a comparison with experimental data.

The variation of $g_K^{1(+)}$ and $g_K^{2(+)}$ with $\kappa$ is shown on Figures 8 and 9. As for $g_K^{2(-)}$, the variation of $g_K^{1(+)}$ with $\kappa$ is linear, so that the stretching of molecular bonds has the same effect as that for $g_K^{2(-)}$. In fact, here, the extra dipole is induced in the direction opposite to the permanent dipole alignment direction, leading to an overall increase of $g_K$, therefore to an increase of the dielectric constant with respect to the situation where $\kappa = 0$. At last, in this situation, the minima of the potential $V_2^{\text{eff}}$ are those of antiparallel alignment.

In contrast, the variation of $g_K^{2(+)}$ with $\kappa$ is not linear at all. Here, the explanation is different from the $\kappa$ behavior of variation of $g_K^{2(-)}$. In effect, for positive $\kappa$, the Kirkwood potential of mean torques $V_2^{\text{eff}}$ exhibits 2 pairs of unequal minima in a cycle of the motion of dipole pairs, located both at the parallel and antiparallel states. This altogether affects the $g_K$ value in a non-trivial way, depending on the $\lambda$ values. For negative $\kappa$, the equilibrium orientations of the permanent moments are spread over the range:
This is similar with the behavior of $g^K_2$ as in this situation, dipoles are induced in such a way that they are parallel. Here, $g^K_K$ is near 0.5, as if the induction term did not significantly affect orientational correlations.

### 4 Comparison with experimental data

In this section we compare our theoretical findings with experimental data. In order to do so, we use static dielectric permittivity values either from the literature, i.e., unless stated otherwise, values from Wohlfarth’s Landolt-Bornstein Tables, or from our own measurements and compare them to calculated values employing the theory described in the foregoing sections. In the Kirkwood-Fröhlich theory, the dielectric constant is given by:

$$\varepsilon = \frac{1}{4} \left( 3\lambda g^K_K + \varepsilon_w + \sqrt{8\varepsilon_w^2 + (3\lambda g^K_K + \varepsilon_w)^2} \right)$$

where

$$\lambda(T) = \frac{M_s(T)N_\lambda\alpha}{27M_{mol}\varepsilon_0 kT}$$

Here, $n$ is the mean refractive index of the fluid measured for the Sodium D spectral line and $M_s(T)$ is the experimentally measured temperature-dependent mass density of the polar fluid. Both quantities are sometimes extrapolated to the temperature of interest either via the equations given in the respective references or via a linear law fitted to the measured values. Furthermore, in Eq. (35), following Onsager, Kirkwood and Fröhlich, we set

$$\varepsilon_w(T) = n^2(T).$$

For some polar fluids we compute it from the Lorenz-Lorentz equation, i.e.: 

$$\frac{n^2(T) - 1}{n^2(T) + 2} = \frac{M_s(T)N_\lambda\bar{\alpha}}{3M_{mol}\varepsilon_0}$$

where $\bar{\alpha}$ is the mean molecular polarizability, taken from the literature.

The Kirkwood correlation factor $g^K$ in Eq. (34) is, according to our theory, dependent on $\lambda(T)$ and $\kappa$, and four different functions for $g^K(\lambda, \kappa)$ are possible according to Table 2. By substituting the respective $V_m$ and $V_{eff}$ as well as Eq. (3) into Eq. (12), the Kirkwood correlation factor is calculated by numerical integration.

As mentioned above, $\kappa$ can be regarded as a measure of the strength of the induction/dispersion-type interaction and is the only unknown parameter which is needed to calculate the theoretical Kirkwood correlation factor. It is expected that $\kappa$ is somehow related to the molecular polarizability $\bar{\alpha}$, however, in the current state of our theory, it can not be determined explicitly and thus it is left as the only fitting parameter to achieve agreement between theory and experiment. The choice between the four different representations of $g^K(\lambda, \kappa)$ is based upon some possibly existing foreknowledge about the preferred alignment from the literature and/or based upon the comparison of the theoretical and experimental temperature dependences of the static permittivity. Since the four $g^K(\lambda, \kappa)$ have distinct slopes depending on $\lambda(T)$, as can be seen in Figures 1-4, this results in an unambiguous assignment of one $g^K(\lambda, \kappa)$ to the respective polar fluid.

In the following subsections we discuss the comparison of theory and experiment for different classes of polar liquids. An overview of all substances under study, including all values needed to calculate the Kirkwood correlation factor is given in Table 3.

In this section we compare our theoretical findings with experimental data. In order to do so, we use static dielectric permittivity values either from the literature, i.e., unless stated otherwise, values from Wohlfarth’s Landolt-Bornstein Table, or from our own measurements and compare them to calculated values em-
ploying the theory described in the foregoing sections. In the Kirkwood-Fröhlich theory, the dielectric constant is given by:

\[ \varepsilon = \frac{1}{4} \left( 3\lambda g_K + \varepsilon_m + \sqrt{3\lambda g_K + \varepsilon_m^2 + 3\lambda^2 g_K^2 + \varepsilon_m^2} \right) \]  \hspace{1cm} (34)

where

\[ \lambda(T) = \frac{M_r(T)N_\lambda u^2_\lambda (n^2(T) + 2)^2}{27M_m_\text{mol} \varepsilon_0 kT} \]  \hspace{1cm} (35)

Here, \( n \) is the mean refractive index of the fluid measured for the Sodium D spectral line and \( M_r(T) \) is the experimentally measured temperature-dependent mass density of the polar fluid. Both quantities are sometimes extrapolated to the temperature of interest either via the equations given in the respective references or via a linear law fitted to the measured values. Furthermore, in Eq. (35), following Onsager, Kirkwood and Fröhlich,\(^{22,23}\) we set

\[ \varepsilon_m(T) = n^2(T). \]  \hspace{1cm} (36)

For some polar fluids we compute it from the Lorenz-Lorentz equation, i.e. :

\[ \frac{n^2(T) - 1}{n^2(T) + 2} = \frac{M_r(T)N_\lambda \bar{\alpha}}{3M_m_\text{mol} \varepsilon_0} \]  \hspace{1cm} (37)

where \( \bar{\alpha} \) is the mean molecular polarizability, taken from the literature.

The Kirkwood correlation factor \( g_K \) in Eq. (34) is, according to our theory, dependent on \( \lambda(T) \) and \( \kappa \), and four different functions for \( g_K(\lambda, \kappa) \) are possible according to Table 2. By substituting the respective \( U_m \) and \( V_{\text{eff}} \) as well as Eq. (9) into Eq. (12), the Kirkwood correlation factor is calculated by numerical integration.

As mentioned above, \( \kappa \) can be regarded as a measure of the strength of the induction/dispersion-type interaction and is the only unknown parameter which is needed to calculate the theoretical Kirkwood correlation factor. It is expected that \( \kappa \) is somehow related to the molecular polarizability \( \bar{\alpha} \), however, in the current state of our theory, it can not be determined explicitly and thus it is left as the only fitting parameter to achieve agreement between theory and experiment. The choice between the four different representations of \( g_K(\lambda, \kappa) \) is based upon some possibly existing foreknowledge about the preferred alignment from the literature and/or based upon the comparison of the theoretical and experimental temperature dependences of the static permittivity. Since the four \( g_K(\lambda, \kappa) \) have distinct slopes depending on \( \lambda(T) \), as can be seen in Figures 4,6,7, this results in an unambiguous assignment of one \( g_K(\lambda, \kappa) \) to the respective polar fluid.

In the following subsections we discuss the comparison of theory and experiment for different classes of polar liquids. An overview of all substances under study, including all values needed to calculate the Kirkwood correlation factor is given in Table 3.

4.1 Parallel alignment – Linear primary alcohols

We start with a series of linear primary alcohols with different alkyl-chain length, for which preferred parallel alignment of the dipole moments, which are located at the O–H group at one end of the carbon chain, is well known. Different values for this dipole moment of linear primary alcohols are found in the literature, and these values usually range between 1.65 and 1.70.\(^{24}\) Since the total dipole of a molecule is the sum of the dipole moments of its chemical bonds, and the C–H bonds are almost apolar, the permanent dipole moment of all linear primary alcohols should be the same in good approximation. An average value of 1.68 D has thus been chosen as the value of \( \mu_g \) for all the considered linear primary alcohols.

In Figure 10 the experimental static permittivities for all alkyl-chain lengths from methanol to octan-1-ol are shown as plain circles, together with the theoretical values calculated using \( g_K^{(1)} \) as solid lines.

As one can see, the agreement of the theoretical values with
Table 3 Parameters used in the computation of the static permittivity Eq. (34). Mean molecular polarizabilities from Ref. 24. Molecular dipole moments from Ref. 25 except (1) from Ref. 26 and (2) from Ref. 27 which is the value of the dipole moment of TBP in decalin, which is a nonpolar solvent that has no influence on the molecular TBP dipole. (1) We performed refractive index measurements between 10°C and 50°C using an Abbe refractometer.

| Compound      | μ(D) | δ(Å) | κ | gK | M(T) | n(T) |
|---------------|------|------|---|----|-----|-----|
| Methanol      | 1.68 | -    | 0.04 | g_k(1) | Ref. 28 | Ref. 29 |
| Ethanol       | 1.68 | -    | 0.05 | g_k(1) | Ref. 28 | Ref. 29 |
| Propan-1-ol   | 1.68 | -    | 0.22 | g_k(1) | Ref. 30 | Ref. 29 |
| Butan-1-ol    | 1.68 | -    | 0.35 | g_k(1) | Ref. 28 | Ref. 29 |
| Pentan-1-ol   | 1.68 | -    | 0.5  | g_k(1) | Ref. 31 | Ref. 29 |
| Hexan-1-ol    | 1.68 | -    | 0.65 | g_k(1) | Ref. 32 | Ref. 29 |
| Heptan-1-ol   | 1.68 | -    | 1.05 | g_k(1) | Ref. 33 | Ref. 29 |
| Octan-1-ol    | 1.68 | -    | 1.5  | g_k(1) | Ref. 34 | Ref. 29 |
| Water         | 1.845 | 1.501 | -0.15 | g_k(1) | Ref. 28 | L-L. |
| Acetonitrile  | 3.92 | 4.44 | 0.345 | g_k(1) | Ref. 28 | L-L. |
| Nitrobenzene  | 4.02 | 12.26 | 0.67 | g_k(1) | Ref. 35 | L-L. |
| Acetone       | 2.88 | 6.27 | 0.83 | g_k(1) | Ref. 28 | L-L. |
| DMSO          | 3.96 | 7.97 | 0.73 | g_k(1) | Ref. 36 | Ref. 36 |
| TBP           | 2.69 | -    | 0.85 | g_k(1) | Ref. 37 | own(1) |
| Glycerol      | 2.67 | 7.80 | -0.3 | g_k(1) | Ref. 38 | own(1) |

Fig. 10 Experimental temperature dependence of the linear static permittivity of Methanol (1), Ethanol (2), Propan-1-ol (3), Butan-1-ol (4), Pentan-1-ol (5), Hexan-1-ol (6), Heptan-1-ol (7) and Octan-1-ol (8). Solid line : Theory. Dots : Experimental data from Reference 23. For heptan-1-ol, the experimental data are the same as those published by Vij et al.[39] at normal pressures. Inset : variation of κ with the number of carbon atoms nC in the alkyl chain.

The experimental ones is excellent for all linear primary alcohols over the whole temperature range where experimental data are available. The values of κ, which are chosen in order to achieve this agreement, are shown in the inset of figure 10. It is obvious that κ increases with increasing number of carbon atoms in the alkyl-chain, which indicates the increasing strength of the induction/dispersion-type interaction. Since the polarizability of a molecule increases with its molecular mass while the permanent dipole moment is the same for all molecules of this series, this finding is perfectly reasonable and underlines the importance of the induction/dispersion-type interaction for larger molecules. However, it is clear that the κ parameter does not depend linearly on the number of carbon atoms in the alkyl-chain, which shows that the latter parameter is not a trivial function of the polarizability, particularly as a result of non-additivity of induction-dispersion energies. Therefore, the determination of κ from molecular properties is beyond the scope of this work and thus is left as a fitting parameter.

As indicated by the use of g_k(1-), the preferred dipolar order in these substances is, as is well-known, the parallel one. The temperature dependence of the calculated Kirkwood order factor is shown in Figure 11 only for some of these substances for clarity.

Fig. 11 Experimental temperature dependence of the Kirkwood correlation factor of Methanol (1),1-Propanol (3), 1-Butanol (4) and 1-Octanol (8)
It is obvious that the slope of $g_K(T)$ is non-trivial and behaves distinctly different for various linear alcohols and it agrees with those found experimentally in the literature. Therefore, by adjusting the strength of the induction/dispersion-type interaction via $\kappa$, our theory is able to calculate the correct Kirkwood correlation factor and thus reproduces the experimental static permittivities.

### 4.2 Antiparallel alignment

In this subsection, we compare our theory with experimental static permittivities of substances, for which it is known from techniques other than dielectric spectroscopy, that they exhibit preferred antiparallel dipolar ordering. These substances are acetonitrile, nitrobenzene, acetone, and dimethyl sulfoxide (DMSO) and the comparison between experiment and theory is shown in figure 12. Experimental data for these substances are only available over a narrow temperature range. However, as can be seen in figure 13, the Kirkwood correlation factors hardly depends on temperature, thus this is not too great a drawback.

**Fig. 12** Experimental temperature dependence of the linear static permittivity of Acetonitrile(1), Acetone (2), Nitrobenzene (3) and DMSO (4). Solid line : Theory. Dots : Experimental points. DMSO data, including density and refractive index from Schläfer et al.

**Fig. 13** Theoretical temperature dependence of Kirkwood correlation factor of acetonitrile(1), acetone(2), nitrobenzene(3), and DMSO(4).

#### 4.2.1 Acetonitrile and Acetone

Our theoretical estimates of the static permittivity of acetonitrile (ACN) apparently deviate from the experimental data of Stoppa et al. at high temperatures, of at most 4.7%, while yielding good agreement at the lowest ones. Here, this is difficult to believe that the deviation between theory and experiment is due to a poor representation of intermolecular interactions as $\lambda$ takes rather low values at high temperatures. Yet, our theoretical findings remain not too far from the experimental data, and agree to some extent with the molecular dynamics data on the Kirkwood correlation factor of Koverga et al.

For ACN, the Kirkwood correlation factor remains almost temperature-independent between 10° and 60° Celsius, yielding $g_K \approx 0.82$. Since $g_K^{(+)}$ is used, the dipolar order is strictly antiparallel, as expected. These values agree reasonably well with the experimentally deduced values of Helambe et al. in the pure liquid phase.

Our theoretical estimates of the static permittivity of acetone are in good agreement with the experimental ones. We also find antiparallel order for acetone, using $g_K^{(+)}$ as a representative of $g_K$.

This substance exhibits the strongest temperature dependency of $g_K$ out of the four substances discussed in this subsection, as illustrated in Figure 13. Our values range between 1.22 at 20° Celsius and decreases to 1.19 at 50°. Our values are slightly above the value at 25° Celsius of pure acetone by Kumbharkhe et al., which is 1.02, while Vij et al. found the value 1.38. Our values are framed between both experimentally determined ones, and therefore, our theoretical findings may be considered as satisfactory for this substance in the considered temperature range. We emphasize that due to the relatively large value of $\kappa = 0.83$, the $g_K$ values of acetone are above unity, despite preferred anti-parallel alignment.

#### 4.2.2 Nitrobenzene and DMSO

The same notion is true for Nitrobenzene and DMSO, where a Kirkwood correlation factor of larger than one (see figure 13) reproduces the experimental data in figure 12 quite well, employing $g_K^{(+)}$, i.e. antiparallel alignment.

We emphasize here again that the expectation that antiparallel dipolar alignment has to result in a Kirkwood correlation factor of less than unity based on Eq. (4), has led for example Shikata et al. like many authors, to use a too high value of $\varepsilon_m = 3.5$, in order to obtain $g_K = 0.65 < 1$ for nitrobenzene. This procedure is misleading, because Eq. (4) is most of the time a poor approximation of (2) and results in some cases in somewhat arbitrary choices of $\varepsilon_m$, just to fulfill the expectations about the value of the Kirkwood factor in comparison with unity.

We also note here that great care must be taken regarding the frequency at which the dielectric constant is measured. If measurements are performed at a fixed frequency instead of measur-
ing a spectrum over several orders of magnitude in frequency, one has to be sure that this frequency is sufficiently low to neglect relaxation effects but also sufficiently high so that one also can neglect electrode polarization effects stemming from ionic impurities, which might be present in some occasions.

For example, in the case of DMSO we have compared our theoretical findings with the data of Schläfer et al. that report measurements of the static permittivity at a measuring frequency of 100 kHz. We were quite surprised that the data of Schläfer et al. were the only ones (see Reference) that we were able to interpret. Yet, they are the sole data of Reference which, in our opinion, truly reflect the static permittivity of DMSO, because all data but Schläfer’s were recorded at least at a ten times higher frequency, indicating that dipolar relaxation might play a role, rendering the measured permittivities not the static ones.

We note in passing that Schläfer et al. quote a dipole value of DMSO $\mu = 4.3 \pm 0.1 \text{D}$, using Onsager’s equation. In effect, we find that the Onsager dipole $\mu_0 \sqrt{\kappa}$ varies between 4.28 and 4.32 D, in agreement with the experimental one.

Finally, we remark that Onsager’s equation is generally most successful in polar substances with antiparallel order (one exception being liquid water) because as illustrated in Figure generally $\kappa$ has almost no temperature dependence. However, as explained by Coffey and later in Ref. this equation is difficult to understand from a microscopic point of view. Yet, it is useful because it yields a relatively good estimate of the dipole moment $\mu_0$ in many cases, for example, using Malecki’s method.

### 4.3 Special cases – Water, TBP, Glycerol

In this subsection we compare our theory to experimental values of three special liquids, namely water, glycerol and tributyl phosphate (TBP). The specialties of these substances will become clear in the following. Figure displays the experimental $\varepsilon$ values as points and the theoretical ones as solid lines for these three liquids.

#### 4.3.1 Water

A comparison of experimental static permittivities of water with an earlier stage of our theory was already given in Reference. Therein, the induction/dispersion-type interaction was not yet accounted for, the refractive index was kept temperature independent and $\varepsilon_0 = 1.03n^2$ was chosen. This leads to a disagreement with the experimental data at temperatures above 80°C. Here, the induction/dispersion effects together with inclusion of the temperature dependence of $n$ allows our theoretical findings to agree with experimental data across the whole temperature range. The $\kappa$ parameter was adjusted to -0.15 to achieve this agreement, indicating a slight reduction of the total effective dipole moment ($\varepsilon_0 + 2)\mu_0/3$. Moreover it indicates a specific equilibrium geometry of the water molecules in the liquid phase, which, however, is impossible to specify precisely in the present context.

The Kirkwood correlation factor of liquid water as a function of temperature is shown on Figure. For water, it is known that the experimental Kirkwood correlation factor is $K = 2.75$ at 0°C and decreases to $K = 2.49$ at $T = 83°C$, under the conditions that $\varepsilon_\infty = 1.05n^2$ and $\varepsilon_\infty$ is temperature-independent. In the present work, we find $K = 2.75$ at $T = 0°C$ and $K = 2.72$ at $T = 83°C$, however, under the condition $\varepsilon_\infty(T) = n^2(T)$, with $n^2$ obeying the Lorenz-Lorentz Eq. Since we use $\kappa_\infty$ as a representative of $\kappa$ for this substance, the dipolar order in water is the parallel one, in agreement with Kirkwood’s predictions. We also remark, that, incidentally, the $\kappa$ is basically independent of temperature, which clearly explains why Onsager’s equation works at room temperature for liquid water with values of $\varepsilon_\infty$ as large as 4.5. This exaggerated value of $\varepsilon_\infty$ has led many authors, including some of us, to treat $\varepsilon_\infty$ as a fitting parameter, in order to obtain values of $\kappa$ that comply with what is believed about dipolar order in water based on Kirkwood’s formula Eq. (4). Clearly, this procedure is misleading, because Eq. (4) is most of
the time a poor approximation of \( g \). Finally we note, that our calculations for \( g_K \) of water are also in agreement with the molecular dynamics (SPC/E) numerical simulations of van der Spoel et al. \(^{53}\)

### 4.3.2 TBP

Tributyl phosphate (TBP) is special in so far as it is the only substance – out of all we tested so far – where \( g_K^{(-1)} \) has to be employed to achieve agreement between theory and experiment. The experimental static permittivities, which are shown in figure 14, were obtained in our laboratory. Details of the experimental setup are described elsewhere. \(^{54}\) As can be seen in this figure, the theory is able to describe the experimental data over a temperature range of more than 260 K, and since the glass transition temperature of TBP is about \( T_g = -132^\circ \text{C} \), we may say that unlike what was stated in reference 17, the theory is sometimes able to predict correct values of the static permittivity even below the calorimetric \( T_g \).

The temperature variation of \( g_K \) for TBP is shown in Figure 15. Clearly, for this substance, \( g_K > 1 \). However, since \( g_K^{(-1)} \) is used here with \( \kappa = 0.85 \), the permanent dipole pair relative orientations continuously spread between 0 and 97 degrees, as obtained from Eq. 28. This means that both, parallel and antiparallel alignment of dipolar pairs are present in this substance.

A Kirkwood correlation factor of less than unity was obtained in a different study by Saini et al. \(^7\) and thus needs a comment: The value of the molecular dipole moment \( \mu_K \) of tributyl phosphate (TBP) used in their study is 3.1 D, which is the value of TBP dissolved in carbon tetrachloride. Although this solvent is non-polar, it still affects the value of \( \mu_K \) as it has a non-negligible effect on the phosphoryl group. \(^{24}\) We used the value of 2.60 D, which is obtained in an octane solution and is almost identical to the value obtained in a decalin solution \(^{29}\) both unpolar solvents without influence on the TBP molecules.

Moreover, in the work of Saini et al., \( \varepsilon_{\infty} \approx 5 \) was used, which is far off from \( \varepsilon_{\infty} = n^2 \). This value was read off the spectrum at frequencies lower than the strong secondary relaxation, which is clearly due to molecular reorientation. Thus, this choice is not justified in our opinion and leads together with the too high dipole moment to a \( g_K \) value present in this substance.

The value 3.32 D of undiluted TBP quoted by Petkovic et al. \(^{27}\) is the one compatible with Onsager's equation at room temperature. If we use the Onsager dipole \( \mu_K \sqrt{g_K} \) with our calculated \( g_K \), we find 3.27 D at room temperature, which is rather close to Petkovic’s result.

### 4.3.3 Glycerol

As can be seen in Figure 14, the experimental data points of glycerol cannot be described by our theory at all. Here, we show the calculated values for \( g_K^{(-1)} \), however, also no other representation of \( g_K \) is able to reproduce the experimental values with physically reasonable values of the parameters.

Often, the specificity of H-bonding is invoked in order to explain disagreement between theory and experiment. This is not so here, since H-bonding specific mechanisms are not needed at all in order to obtain agreement between theory and experiment for linear primary alcohols and water, both prominent examples of H-bonding liquids. Rather, we believe that the disagreement is explained by the oversimplification of the interaction potential Eq. (24) which, in effect, pertains to molecules having their permanent dipole moment fixed with respect to a given axis of symmetry of the molecule. Thus, due to the floppyness of the glycerol molecules, and due to the fact that comparable contributions to the overall dipole moment are located in different positions in the molecule, the situation for glycerol is quite different. Owing to this reason, we believe that the interaction energy landscape is much too simple to capture the main physics which is necessary for the theoretical description of the temperature dependence of the dielectric constant of this polar fluid. We note, that seemingly good agreement between theory and experiment with the potential (24) can be obtained across the whole temperature range using the unphysical assumption \( \varepsilon(T) = 0.5n^2(T) \) together with \( g_K = g_K^{(-1)} \) and \( \kappa = 0.45 \). The relation \( \varepsilon(T) = 0.5n^2(T) \) used in such a fit actually reveals that the reason of our failure indeed lies in the oversimplification of the intermolecular interaction potential Eq. (24) and the resulting Kirkwood potential of mean torques \( \varepsilon^{\text{eff}} \) rather than in the specific H-bonding mechanism, which is not accounted for. Therefore, we state that glycerol is a non-simple polar fluid, where the intermolecular interaction is not appropriately represented in our theory and thus, the substance is out of scope of the present work.

## 5 Summary of results and perspectives

In this work, we have derived an integral formula for the Kirkwood correlation factor of polar fluids, Eq. \( 6 \) from the equilibrium rotational averaged Dean equation \( 5 \). This equation has a lot of advantages over Eq. \( 2 \), the first one being that it is independent on the number of (nearest) neighbors, the second one being the fact that it easily lends itself to tractable approximations. For example, in the Kirkwood superposition approximation, one immediately obtains a tractable expression for the correlation factor, namely Eq. \( 12 \). Then we suggest how to construct a model potential for the electrostatic interaction that not only includes the permanent electric dipoles but also in the next order some induction/dispersion-like effects. Finally, for each case of preferred parallel or antiparallel alignment of permanent dipoles and their modification by induced polarization, two different Kirkwood potentials of mean torques are deduced, for which Eq. \( 12 \) is solved to yield respective temperature dependent values of the static dielectric constant and the Kirkwood correlation factor. The models only contain physical quantities, like density, permanent dipole moment and refractive index or molecular polarizability, respectively, that are independently accessible by experiment. Only one single material specific and temperature independent parameter enters the calculation, which is connected to the molecular polarizability, that cannot be calculated from the latter in a straightforward manner and thus needs to be a fitting parameter. In that way, we are able to quantitatively compare the calculated values of \( \varepsilon(T) \) with experimental data, and it turns out that the derived model potentials seem to capture the underlying main physics of different system classes to a rather good accuracy, at least from the point of view of a static dielectric constant.
measurement.

A first important result from these calculations is the observation that a parallel alignment of the dipole pairs does not necessarily imply $g_K > 1$, and similarly an anti-parallel alignment of dipole pairs does not strictly imply $g_K < 1$ either. Rather, such alignment states are local minima of the effective pair interaction orientational potential of mean torques, for which not only permanent but also induced dipole moments play a decisive role. For example, applying Eq. (28) to TBP, we find that pairs of dipoles in this polar substance have a trend to make angles between 0 and $\theta^\circ$, explaining quantitatively the value of $g_K \approx 2$ of TBP near its glass transition temperature and beyond.\(^{54}\)

We also discuss several examples of preferred antiparallel alignment, not only for acetone, where $g_K < 1$ is found as expected, but also for acetone, nitrobenzene and dimethyl sulfoxide, where despite the antiparallel alignment clearly $g_K > 1$ due to the non-negligible influence of the molecular polarizability. This again underlines that the usual arguments relating parallel ($g_K > 1$) and antiparallel ($g_K < 1$) alignments based on Eq. (4) is an oversimplification which hampers comparison of the results found from linear dielectric measurements concerning dipolar alignment with those obtained from other characterization techniques.

As examples for a preferred parallel alignment of dipoles we have investigated a series of linear monohydroxy alcohols, where our theory reproduces the experimental $\epsilon(T)$ for the full series from methanol to octanol with the importance of the polarizability component increasing with molecular volume, as expected. But also the static permittivity of liquid water from the melting temperature to the boiling point shows excellent agreement with the theory. This is quite remarkable, as the theory does not explicitly contain any particular H-bonding related mechanism. Thus, the idealization of a molecule which consists of its permanent and induced dipole moments only is enough to explain the temperature dependence of the static dielectric constant of these hydrogen bonding liquids as first Debye, Kirkwood and Fröhlich assumed.\(^{11,23}\)

Interestingly, the situation is different for the polyalcohol glycerol. Here, apparently our model for the pair potential deduced equilibrium properties. Moreover, one may also try to extend the present model to dynamics, similar to previous work both in linear and nonlinear responses. Finally, one could also think of applying the present calculations to suspensions of magnetic nanoparticles similar to what was already pointed out previously.\(^{18,21}\)

The development of the theory in all of these directions is currently in progress.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank Profs. Yu. P. Kalmykov (Perpignan) and F. Affouard (Lille) for helpful conversations. T. B., F. P. and A. H. gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft under grant No. BL 1192/3.

Appendix A : Derivation of Eq. (5)

We consider an assembly of interacting molecules that are subjected to thermal agitation and external forces and torques. A description of such a system may be described by the averaged rototranslational Dean equation, which is

$$\frac{\partial W}{\partial t} (\mathbf{r}, \mathbf{u}, t) = D_T \nabla_r \cdot \mathbf{j}_r (\mathbf{r}, \mathbf{u}, t) + D_R \nabla_u \cdot \mathbf{j}_u (\mathbf{r}, \mathbf{u}, t)$$

(40)

where $D_T$ and $D_R$ are the translational and rotational bare diffusion coefficients, $\nabla_r$ is the usual del operator, $\nabla_u$ is the del operator acting on the unit sphere of representative points describing the orientation of a molecule and the vectors $\mathbf{j}_r$ and $\mathbf{j}_u$ are defined by

$$\mathbf{j}_r (\mathbf{r}, \mathbf{u}, t) = \nabla_r W (\mathbf{r}, \mathbf{u}, t) + \beta W (\mathbf{r}, \mathbf{u}, t) \nabla_r V_1 (\mathbf{r}, \mathbf{u}, t)$$

$$+ \beta \int \nabla_r U_{\text{int}} (\mathbf{r}, \mathbf{u} , \mathbf{u}' , t) W_2 (\mathbf{r}, \mathbf{u} , \mathbf{u}' , t) d\mathbf{u}'$$

(41)
where $U_{int}$ is a generalized pair interaction potential between two molecules with positions $(r, r')$ and orientations $(u, u')$, $W(r, u, t)$ and $W_2(r, u, u', t)$ are the one body and pair probability densities respectively, and $\beta = (kT)^{-1}$, $k$ being Boltzmann’s constant and $T$ the absolute temperature. The pair interaction $U_{int}$ has the property of translational invariance, and this means that we have

$$U_{int}(r, u, r', u') = U_{int}(r - r', u, u').$$

(43)

It follows that the pair density $W_2$ has also this property, viz.

$$W_2(r, u, r', u', t) = W_2(r - r', u, u', t)$$

(44)

There is also a general property which links $W_2$ to $W$. This property is

$$W_2(r, u, r', u', t) = W(r, u, t)W(r', u', t)g(r, u, r', u', t)$$

(45)

where $g$ is the dynamical pair distribution function. This last function has also the translational invariance property, viz.

$$g(r, u, r', u', t) = g(r - r', u, u', t)$$

(46)

Hence by Eqs. (44)- (46), it follows that we have

$$W_2(r - r', u, u', t) = W(r, u, t)W(r', u', t)g(r - r', u, u', t)$$

(47)

which ensures translational invariance of $W_2$ only if $W$ has no $r$ dependence, so that we have

$$W_2(r - r', u, u', t) = W(u, t)W(u', t)g(r - r', u, u', t)$$

(48)

Here, a word of caution is necessary. In effect, in writing (48), we are assuming that $W_2$ has units of inverse volume, while in Eqs. (44) and (45) $W_2$ has units of inverse squared volume. This implies, assuming that $W$ is normalized to unity that in writing Eq. (48), $g$ has units of inverse volume and can no longer be analyzed as a pair distribution function since the latter quantity must be dimensionless. Now, we require that $W_2$ should be normalized to unity since, rightly or wrongly, we have chosen to treat this quantity as a probability density. By writing $\rho = r - r'$, we have

$$\int W_2(\rho, u, u', t)d\rho du du' = 1$$

(49)

Then, by writing

$$g(\rho, u, u', t) = g_\rho(\rho, t)g_2(u, u', t)$$

(50)

and assuming that

$$\int W(u, t)W(u', t)g_2(u, u', t)dudu' = 1$$

(51)

then we immediately have

$$\int g_\rho(\rho, t)d\rho = 1,$$

(52)

implying the following relationship

$$g_\rho(\rho, t) = KG(\rho, t)$$

(53)

where $K$ is a constant, and $G$ is the dynamical spatial part of the generalized pair distribution function. Next we have the result

$$I_1 = \int \nabla_r U_{int}(r, u, r', u')W_2(r, u, r', u', t)dru'du'$$

$$= \frac{1}{2} \int \nabla_u U_{int}(\rho, u, u')W_2(\rho, u, u', t)d\rho du'$$

(54)

so that $\nabla_r I_1 = 0$ and the averaged rototranslational Dean equation takes the simpler form

$$\frac{\partial W}{\partial t}(u, t) = \beta D_T W(u, t)\nabla_x^2 V_1(u, t) + D_\theta \nabla_u \cdot j_\theta(u, t).$$

(55)

This equation looks inconsistent because of a spurious $r$ dependence. However, since $V_1$ is a single-particle potential arising from external sources, so that $-\nabla_r V_1$ represents the force seen by all the molecules of the ensemble (taken as identical). A further requirement is that the representative samples constituting the statistical ensemble which statistics is governed by $W$ be identical since the system is translationally invariant, therefore seeing the same external force (this would not be so if the system was not translationally invariant). Hence $V_1$ is at best linear in $r$, so that its Laplacian vanishes. It is then of little use to consider the $r$ dependence of $V_1$ in the rotational part. Therefore, $V_1$ is effectively $r$-independent, as a result of translational invariance. It follows that $j_\theta$ in Eq. (55) is given by

$$j_\theta(u, t) = \nabla_u W(u, t) + \beta W(u, t)\nabla_u V_1(u, t)$$

$$+ \beta \int \nabla_u U_{int}(\rho, u, u')W_2(\rho, u, u', t)d\rho du'$$

(56)

Hence, in a perfectly general fashion, Eq. (55) becomes

$$2\tau_0 \frac{\partial W}{\partial t} = \nabla_u \cdot (\nabla_u W(u, t) + \beta W(u, t)\nabla_u V_1(u, t))$$

$$+ \beta \int \nabla_u U_{int}(\rho, u, u')W_2(\rho, u, u', t)d\rho du'$$

(57)
where $2\tau_D = D_R^{-1}$ is the Debye relaxation time used in free rotational diffusion dielectric relaxation theory, and

$$
U_m(u, u', t) = \int U_m(\rho, u, u') g_\rho(\rho, t) d\rho
$$

(58)
is a mean interaction potential that contains orientational degrees of freedom only, and is a function of time (so that it also contains memory of structural relaxation). At last, we have introduced in Eq. (57) the rotational pair probability density $w_2$ as

$$
w_2(u, u', t) = W(u, t)W(u', t)g_2(u, u', t)
$$

(59)
At statistical equilibrium, we have

$$
\frac{\partial W}{\partial t} = 0
$$

(60)
and all quantities are time-independent in Eq. (57), so that Eq. (5) follows.

Appendix B: Derivation of Eq. (6)

In order to achieve this, we need Eq. (57) at equilibrium, where all quantities are time-independent. Thus we have

$$
\nabla_u \cdot [\nabla_u W(u) + \beta W(u) \nabla_u V_1(u)] + \beta \nabla_u \cdot \int \nabla_u U_m(u, u') w_2(u, u') du' = 0
$$

(61)
where $u$ is a unit vector along a molecular dipole moment of constant magnitude $\mu$, $W(u)$ is the one-body orientational probability density, $V_1(u) = -\mu u \cdot E$ is a one-body potential containing the effect of the directing electric field $E$ which is assumed uniform, The mean polarization in the direction of the directing field is given by

$$
\langle P \cdot e \rangle = \rho_0 \mu \langle (u \cdot e) W(u) \rangle
$$

(62)
where $\rho_0$ is the number of molecules per unit volume, $P$ is the polarization of the sample, $e$ is a unit vector along the directing field $E$, $P_1(z)$ is the first Legendre polynomial and the angular brackets denote a statistical average over $W(u)$. On multiplying Eq. (5) by the Legendre polynomial $P_n(u \cdot e)$ of order $n$ and integrating the resulting equation on the unit sphere of representative points of a dipole with orientation $u$, we arrive after some algebra at the set of moment equations

$$
n(n + 1) \langle P_n \rangle = \frac{n(n + 1) \xi}{2n + 1} \langle (P_{n-1}) - \langle P_{n+1} \rangle \rangle
$$

(63)
$$
- \beta \int \nabla_u U_m(u, u') \cdot \nabla_u P_n(u) w_2(u, u') du/du'
$$

write $P_n(u \cdot e) = P_n(u)$. In particular, for $n = 1$ and $n = 2$, Eqs. (63) read respectively

$$
\langle P_1 \rangle = \frac{\xi}{3} (1 - \langle P_2 \rangle)
$$

(64)
$$
- \frac{\beta}{2} \int \nabla_u U_m(u, u') \cdot \nabla_u P_1(u) w_2(u, u') du/du'
$$

$$
\langle P_2 \rangle = \frac{\xi}{3} \langle (P_1) - \langle P_3 \rangle \rangle
$$

(65)
$$
- \frac{\beta}{6} \int \nabla_u U_m(u, u') \cdot \nabla_u P_2(u) w_2(u, u') du/du'
$$

Now, Eqs. (64) and (65) pertain to response to arbitrary order in the field strength. However, we are solely interested in linear response. Hence we expand the various quantities involved in these equations in powers of the field strength and retain linear terms only. Explicitly, on using the following expansions

$$
\langle P_n \rangle = \langle P_n \rangle^{(0)} + \xi \langle P_n \rangle^{(1)} + \ldots
$$

(66)
$$
w_2(u, u') = w_2^{(0)}(u, u') + \xi w_2^{(1)}(u, u') + \ldots
$$

(67)
Eqs. (64) and (65) become the perturbation equations

$$
\langle P_1 \rangle^{(0)} = \frac{\beta}{2} \int \nabla_u U_m(u, u') \cdot \nabla_u P_1(u) w_2^{(0)}(u, u') du/du'
$$

(68)
$$
\langle P_2 \rangle^{(0)} = \frac{\beta}{6} \int \nabla_u U_m(u, u') \cdot \nabla_u P_2(u) w_2^{(0)}(u, u') du/du'
$$

(69)
which is the interaction torque balance equation in the absence of directing field at equilibrium,

$$
\langle P_1 \rangle^{(1)} = \frac{1}{3} (1 - \langle P_2 \rangle^{(0)})
$$

(70)
$$
- \frac{\beta}{2} \int \nabla_u U_m(u, u') \cdot \nabla_u P_1(u) w_2^{(1)}(u, u') du/du'.
$$
We can now use Eqs. (69) and (70) to obtain the equation

\[ \langle P_1(u) \rangle^{(1)} = \frac{1}{3} + \frac{\beta}{18} \int \nabla_u U_m(u, u') \cdot \Phi(u, u') d\mu / d\mu', \]  

(71)

where

\[ \Phi(u, u') = w_2^{(0)}(u, u') \nabla_u P_2(u) - 9 w_2^{(1)}(u, u') \nabla_u P_1(u). \]  

(72)

Now, on using Eqs. (62), (66) with \( n = 1, \) (68), and equating the resulting linear microscopic polarization with \( (\varepsilon - \varepsilon_w)E_M \) \( (E_M \) being the Maxwell field amplitude), we have

\[ \rho_0 \mu_0 \langle P_1 \rangle^{(1)} = (\varepsilon - \varepsilon_w)E_M. \]

Finally, on combining the above equation with Eqs. (71) and (72) we have

\[ (\varepsilon - \varepsilon_w) \frac{\partial E_M}{\partial \varepsilon} = \lambda \left( 1 + \frac{\beta}{6} \int \nabla_u U_m(u, u') \cdot \Phi(u, u') d\mu / d\mu' \right) \]

(73)

The derivative in the left-hand side of Eq. (73) can be written using Fröhlich’s field, viz.

\[ \frac{\partial E_M}{\partial \varepsilon} = \frac{2 \varepsilon + \varepsilon_w}{3 \varepsilon} \]  

(74)

By identification with Eq. (1) and using Table 1 we obtain the following integral representation for \( g_k \), viz.

\[ g_k = 1 + \frac{\beta}{6} \int \nabla_u U_m(u, u') \cdot \Phi(u, u') d\mu / d\mu' \]

(75)

which is Eq. (6), where in the body text we have used the notation \( W_2^{(0)} \) in lieu and in place of \( w_2^{(0)} \).

Decoration of the third body and the meaning of Eqs. (10) AND (11)

In this Appendix we detail the decorrelation procedure followed by Déjardin et al.18 in order to compute \( V_2^{\text{eff}} \) from \( U_m \) as a lot of mathematical-physical tricks are only vaguely alluded to in their paper.

It was implicitly suggested by Déjardin et al.18 that even if it is a priori impossible to truncate the BBGKY (for Bogolyubov-Born-Green-Kirkwood-Yvon) hierarchical process14, yet it is possible to decide to stop the aforementioned process at rank \( p \) by making appropriate hypotheses concerning the \( (p+1) \)-body orientational density, in particular by analyzing all partial densities as probability densities. They further showed that at rank \( p = 2 \), the corresponding equilibrium BBGKY member could be mapped upon an equilibrium two-body Smoluchowski equation after the decorrelation of the third body from the two others has been achieved. To this aim, they introduced the Kirkwood potential of mean torques \( V_2^{\text{eff}} \) having the essential (but vague) constraint of grossly (if not exactly) describing the same physics as that contained in \( U_m \). This means in particular that the location and nature of the stationary points of \( V_2^{\text{eff}} \) should approximately, if not exactly, be the same as those of \( U_m \). Of course, this implies that \( V_2^{\text{eff}} \) must have the essential property of global rotational invariance, viz.

\[ V_2^{\text{eff}}(-u, -u') = V_2^{\text{eff}}(u, u') \]

(76)

Furthermore, it has been shown by Déjardin et al.18 that

\[ V_2^{\text{eff}}(u, u') = U_m(u, u') + V_c(u, u') \]

(77)

where the complementary term \( V_c \) obeys the exact partial differential equations

\[ \nabla_u V_c(u, u') = \int \nabla_u U_m(u, u'') W^{(0)}(u'') \frac{g_3(u, u', u'')}{g(u, u')} d\mu '' \]

(78)

and

\[ \nabla_u V_c(u, u') = \int \nabla_u U_m(u', u'') W^{(0)}(u'') \frac{g_3(u, u', u'')}{g(u, u')} d\mu '' \]

(79)

where \( g_3 \) denotes the orientational three-body distribution function, \( g \) is the two-body distribution function and \( W^{(0)} \) obeys Eq. (5) with \( V_1 = 0 \). From the global rotational invariance of \( V_c \), we must have

\[ g_3(-u, -u', u'') = g_3(u, u', u'') \]

(80)

and indeed,

\[ g(-u, -u') = g(u, u') \]

(81)

provided \( u \) and \( u' \) are describing the orientation of a pair of molecules belonging to the same representative sample of a statistical ensemble. Next, since generally \( U_m \) consists of a superposition of \( n \) terms, we can write with obvious notations

\[ U_m(u, u') = \sum_{i=1}^{n} U_m^{(i)}(u, u') \]

(82)

so that we can also postulate that \( V_c \) also consists of a superposition of \( n \) terms, viz.

\[ V_c(u, u') = \sum_{i=1}^{n} V_c^{(i)}(u, u') \]

(83)
and

\[ V_u V_c^{(i)}(u, u') = \int V_u U_{c0}^{(i)}(u', u'') W^{(i)}(u'') \frac{g_3(u, u', u'')}{g(u, u')} \, du'' \]  

(84)

It indeed follows that both \( V_c \) and \( V_{\text{eff}} \) can be determined term by term. The statistical ensemble we are interested in is therefore one made of identical samples of three interacting bodies, i.e., the one depicted in Figure 16.

![Fig. 16 Decorrelation step (a) -step 0-: A schematic representation of a statistical ensemble made of samples of identical interacting three dipoles.](image)

Then the decorrelation procedure consists in writing the Kirkwood superposition approximation (KSA) for \( g_3 \) and examining further some of the consequences of this approximation. Thus, the KSA is [10]

\[ g_3(u, u', u'') \approx g(u, u')g(u', u'')g(u, u'') \]  

(85)

This superposition approximation is the result of approximating the three-body interaction potential as a superposition of pair interactions, due to the impossibility to even write an exact analytical expression for this three-body interaction. It has several immediate consequences, the first one being

\[ g_3(-u, -u', u'') \approx g(u, u')g(-u', u'')g(-u, u'') \]  

(86)

This last equation is difficult to interpret in statistical and physical terms because \( g(-u, u') \) and \( g(-u', u'') \) are a priori unknown. If no extra hypothesis is made on the behavior of the third body. One reasonable hypothesis is to assume that a dipole with orientation \( u'' \) is subtracted from the influence of a pair of dipoles with orientations \( (u, u') \) so that a representative triplet of the initial ensemble depicted in Figure 16 \((u, u', u'')\) is split into a doublet \((u, u')\) and a singlet \((u'')\). This is depicted in Figure 17.

![Fig. 17 Decorrelation step (b): in each statistical representative of the ensemble, the dipole with orientation \( u'' \) is taken away from the influence of the interacting pair with orientations \( (u, u') \), splitting the statistical representative into a doublet and a singlet.](image)

At this stage, the newly generated ensemble is no longer an ensemble onto which a probability density can be defined so easily, because this new ensemble is not made of identical non-interacting representatives, so that statistics are not easy on such an ensemble, or impossible. In order to recover a statistical ensemble from this newly generated ensemble, the sole chance we have is to consider pairs of split triplets a typical pair of which is such that for one sample \( u'' \) will coincide with \( u \) and in the other \( u'' \) will coincide with \( u' \). This decomposition is partly depicted in Figure 18.

![Fig. 18 Decorrelation step (c): the dipole with orientation \( u'' \) in one sample is under the influence of the dipole with orientation \( u'' \) of an other statistical sample. These two dipoles form a pair with orientations \((u, u')\) so that two triplets of interacting bodies form three pairs of interacting bodies.](image)

Hence a pair of triplets interacting through some three-body interaction effectively form three identical doublets interacting.
through an effective two-body interaction $V^{\text{eff}}$. The structure of this final newly formed ensemble is depicted in Figure 19.

![Diagram](image_url)

**Fig. 19** Decorrelation step (d): the statistical ensemble made of interacting triplets has become an effective statistical ensemble made of pairs interacting via the effective pair potential $V^{\text{eff}}$.

This implies three important consequences. First, now the ensemble is made of identical representative samples of interacting pairs through $V^{\text{eff}}$ and each sample does not interact with one another, so that statistics in the sense of usual statistical mechanics can be made. This consequence is extremely important for further purposes. The second one may be expressed via the two equations

$$g(u, u'') = 1$$  \hspace{1cm} (87)

if $(u)$ and $(u'')$ are orientations of dipoles which do not belong to the same representative of the newly formed statistical ensemble, and

$$g(u, u'') = e^{-\beta U_m(u, u'')}$$  \hspace{1cm} (88)

if $(u)$ and $(u'')$ are orientations belonging to the same representative of the newly formed statistical ensemble. Using the KSA and the two above equations, then we have

$$\nabla_u V^{(i)}(u, u') \approx \int \nabla_u U^{(i)}_m(u, u'') W^{(0)}(u'') d\omega''$$  \hspace{1cm} (89)

and

$$\nabla_{u'} V^{(i)}(u, u') \approx \int \nabla_{u'} U^{(i)}_m(u', u'') W^{(0)}(u'') d\omega''$$  \hspace{1cm} (90)

so that in the KSA, $V^{(i)}$ can be written down as a sum of single-body potentials $U^{(i)}_m$, viz.

$$V^{(i)}(u, u') = U^{(i)}_m(u) + U^{(i)}_m(u')$$  \hspace{1cm} (91)

since Eqs. (89) and (90) have identical mathematical form. Because $V_c$ has the global rotational invariance property, it immediately follows that $U^{(i)}_m(-u) = U^{(i)}_m(u)$  \hspace{1cm} (92)

The third immediate consequence in the decorrelation scheme proposed by Déjardin et al. is that in Eq. (89), one must set

$$W^{(0)}(u'') = \delta(u'' - u) = W^{(0)}(u'|u)$$  \hspace{1cm} (93)

where $W^{(0)}(u'|u)$ is a conditional probability density (therefore it conditionates the third body), while in Eq. (90), we must use

$$W^{(0)}(u'') = \delta(u'' - u') = W^{(0)}(u'|u')$$  \hspace{1cm} (94)

These last two equations finally yield Eq. (11), viz.

$$\nabla_u U^{(i)}_m(u) = \nabla_u U^{(i)}_m(u, u'') |_{u'' = u}$$  \hspace{1cm} (95)

Yet, this is an incomplete solution of the problem as if one takes Eq. (95) literally, then the reverse interaction torque is not explicitly included as possible solutions of the potential theory problem generated by Eqs. (77) and (78). This in turn may cause stationary points of $V^{\text{eff}}$ not to coincide with those of $U_m$. In order to show that the reverse torque is also included in Eq. (95) for a solution, we rewrite Eq. (89) as

$$\int (\nabla_u U^{(i)}_m(u) - \nabla_u U^{(i)}_m(u, u'')) \delta(u'' - u) d\omega'' = 0,$$

where Eq. (93) has been used. This in turn can be rewritten

$$\int (\nabla_{u''} U^{(i)}_m(u'') - \nabla_{u''} U^{(i)}_m(u'', u)) \delta(u'' - u) d\omega'' = 0,$$

Now, by Newton’s third law, we have

$$\nabla_{u''} U^{(i)}_m(u', u'') = -\nabla_u U^{(i)}_m(u, u'')$$  \hspace{1cm} (96)

so that we have

$$\int (\nabla_{u''} U^{(i)}_m(u'') + \nabla_{u''} U^{(i)}_m(u', u'')) \delta(u'' - u) d\omega'' = 0,$$

Hence leading to a second possibility for $U_m$, viz.

$$\nabla_u U^{(i)}_m(u) = -\nabla_u U^{(i)}_m(u, u'') |_{u'' = u}$$  \hspace{1cm} (97)

Hence, we interpret Eq. (95) as really meaning

$$\nabla_u U^{(i)}_m(u) = \pm \nabla_u U^{(i)}_m(u, u'') |_{u'' = u}$$  \hspace{1cm} (98)

where the $\pm$ sign in this last equation has nothing to do with the one we choose in a given $U^{(i)}_m$ term, and has to be interpreted as the lack of knowledge we have regarding the effect of the third body on the two others. As a consequence, this generates plethora of possibilities for $V^{\text{eff}}$ as all combinations of signs are possible.
However, all $V_2^{\text{eff}}$ expressions save one can be eliminated by using the two criteria a) $V_2^{\text{eff}}$ and $U_m$ must approximately describe the same physics (by investigating the nature and location of the stationary points for both potentials) and b) the resulting values of $g_K$ must be positive across the widest possible range of parameters involved in the expression for $U_m$. Again, all these considerations have been vaguely alluded to in the paper of Déjardin et al. For simplicity, these authors stated Eq. (55) only without the details given here.

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