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Kinetic Yvon-Born-Green theory of the linear dielectric constant and complex permittivity of isotropic polar fluids

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The theory of the linear static dielectric constant and linear complex permittivity of isotropic polar fluids is formulated starting from the coupled Langevin equations describing the rototranslational dynamics of long-range interacting molecules with thermal agitation and subjected to external forces and torques. To this aim, adequate reduced densities are introduced and equations governing their dynamics derived. In the equilibrium zero frequency limit, integral expressions for the Kirkwood correlation factor g_K are given, transparently showing that the popular method consisting in comparing g_K with 1 in order to deduce pair dipolar ordering has no serious theoretical grounding. In the dynamical situation, the complex permittivity spectrum of a simple liquid is shown to exhibit an infinite discrete set of relaxation times, some of which may have thermally activated behavior. The theory is also shown to contain all previous results derived in the area provided molecular inertial effects are ignored, so restricting the range of validity of the theory to frequencies much below the far-infrared region. Finally, the theory can be adapted without much effort to relaxation of interacting magnetic nanoparticles for which *macroscopic* magnetic anisotropy arising from the assembly of nanoparticles is neglected.

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I. HISTORICAL BACKGROUND AND MOTIVATION

A. Historical background

The theory of the electric polarization of polar fluids was initiated by Debye a century ago [1] and therefore has a long history. It is nowadays well known that the Debye theory cannot *quantitatively* account for experimental data because his theory pertains to extremely dilute situations where intermolecular interactions are neglected. The statics was greatly improved by Onsager [2], whose theory removes the undesirable ferroelectric Curie point of the Debye-Lorentz theory, so allowing in principle to deduce the dipole of a single molecule μ from the measurement of the Snell-Descartes refractive index $\mathfrak{n}$ and that of the static dielectric constant ε. Yet, for a number of substances, μ was not predicted properly by Onsager's theory. For example, in order to get *quantitative* agreement between theory and experimental measurements on liquid water, one has to multiply the true individual molecular dipole moment by a factor of three, while for many polar liquids, it is found using Onsager's theory that μ has nonphysical temperature dependence.

Three years later, Onsager's static formula was improved by Kirkwood [3]. In particular, he found that in order to recover *quantitative* agreement between theory and experiment, μ^2 has to be multiplied by a positive factor, g_K, reflecting intermolecular dipole pair statistical orientational correlations (therefore pair dipole orientation order), hence the name "Kirkwood correlation factor" for g_K. The Kirkwood theory was finally rigorously justified by Fröhlich [4], and all this is well summarized in Brown's review on dielectrics [5]. To date, the so-called Kirkwood-Fröhlich theory is the most successful one in order to interpret the experimental values of the dielectric constant [6]. Moreover, since Onsager's theory can be used for dilute specimen to deduce accurate values of the molecular dipole moments (a good example is Malecki's experimental method [7]), the Kirkwood-Fröhlich equation is likewise used to obtain quantitative information on dipolar order by simply measuring the static dielectric constant ε in the pure liquid phase, the mass density of the fluid and the Snell-Descartes refractive index, having previously deduced the molecular dipole moment value from dilute measurements. We note also that when experimental values cannot be determined precisely, the individual molecular dipole moment can nowadays be obtained with the help of quantum *ab initio* calculations. Finally, tables of molecular dipole moments in the ideal gas phase exist [8].

Improvement of Debye's theory regarding the dynamics (i.e., the calculation of the complex permittivity $\varepsilon(\omega)$ resulting from the application of an alternating field of frequency ω) had to await the 1960s and the 1970s. It starts with the 1963 work of Zwanzig [9] who calculated the complex permittivity arising from interacting molecular dipoles located at the sites of a cubic lattice, thereby providing the first dynamical generalization of the Debye-Lorentz theory. Because Zwanzig's treatment handles interdipole interaction torques perturbatively, the resulting theory is not amenable to quantitative comparison with experiment. Nevertheless, Zwanzig's work unambiguously demonstrates that the spectrum of dielectric loss consists in an infinite discrete set of microscopic relaxation times, and therefore to a relaxation time distribution. This result is invaluable in view of the empirical approach to dielectric relaxation, which always involves a *continuous* relaxation time distribution that may be obtained *experimentally* [10]. We note in passing that this empirical approach is still widely used nowadays by any experimentalist in the area.

Logically, the next step is to generalize Onsager's theory of the static dielectric constant to dynamics. In a cornerstone paper, this was accomplished by Nee and Zwanzig [11]. In particular, these authors handled this theoretical problem by considering that the dipole not only lags behind the externally applied field, but also *lags behind the dynamical reaction field*. This last dipole lagging mechanism is called *dielectric friction* and is responsible for the *continuous* character of the distribution of relaxation times. In doing so, they were able to reproduce the dielectric loss of glycerol at −60 °C.

Because the Nee-Zwanzig theory does not reduce to the Kirkwood-Fröhlich one in the static limit, the dynamical theory still needed improvement. A culminating point in the history of dynamics modeling is the work of Madden and Kivelson [12]. Their work is important for many reasons, one of which being that their treatment of the statics yields the Kirkwood-Fröhlich theory in an unambiguous manner, with an integral formula for g_K. This integral formula for g_K was previously derived by Nienhuis and Deutch [13], and was later computed by a number of authors [14,15] using the Ornstein-Zernike (OZ) equation with various closures. One advantage of Madden and Kivelson's derivation is that much less theoretical effort is required in obtaining the aforementioned formula than other approaches [14,15]. The dynamics is then computed by stating the Mori continued fraction expansion [16] for the Fourier-Laplace transform of the dipole correlation function, allowing the frequency range to cover 12 decades, i.e., from zero frequency to the far-infrared region.

Finally, the most accomplished step forward in the theory is that of Bagchi and Chandra [17], who reconsidered the problem from the point of view of generalized hydrodynamics. The main concern is that the statics and dynamics should arise from one and the same formalism for interacting dipoles, just as the Debye theory does for noninteracting ones. In effect, their theory is able to formally include all previously derived results [12,14,15] (statics and dynamics) within *one and the same* formalism. Moreover, the Bagchi-Chandra theory can be extended to intermediate to large wave vectors, therefore being the *first* prototype theory to be, at least in principle, applicable to all experiments which interpretation necessitate to invoke orientational relaxation processes in matter.

Now, before motivating our work, a word should be said on the general principles of calculation of the dielectric constant and complex permittivity themselves for the sake of readability.

B. Roadway to the calculation of the static dielectric constant and complex permittivity

The dielectric constant ε and complex permittivity $\varepsilon(\omega)$ (ω is the frequency at which the ac externally applied field oscillates) of a polar fluid are intensive quantities, by which we mean that they are independent of sample size and shape. Moreover, such quantities are defined at the *macroscopic* scale, where the Maxwell equations in matter hold, while at the *molecular* scale, those concepts are *meaningless* since molecules are embedded with *vacuum*.

In principle, it is not difficult to write down a microscopic expression for the polarization, since it is the (statistical average) vector sum of N molecular dipoles changing their orientations in the course of time, and contained in a volume $\mathfrak{V}$ divided through by the volume $\mathfrak{V}$. In zero applied field, this sum must vanish *at thermal equilibrium*.

Macroscopically, the linear polarization is proportional to the Maxwell field in the steady state regime where all transients have disappeared. For isotropic fluids, the coefficient of proportionality is termed the electric susceptibility $\chi(\omega)$, in turn linked to the linear complex permittivity $\varepsilon(\omega)$ by the equation $\varepsilon(\omega) = 1 + \chi(\omega)$. If the sample is bounded by a shape of second degree (i.e., the sample shape is ellipsoidal or spherical), then the Maxwell field and the externally applied field are related in a very simple manner. Moreover, in the spherical geometry, the Maxwell field and the externally applied field are *collinear* and oscillate at the same frequency. This point is important for further progress in the theory. Another important point is that the *macroscopic polarization* is also *uniform* in these geometries [6]. Then, since the linear polarization response to an external field (here "molecular") can always be calculated from statistical mechanics, and identified with the macroscopic polarization responsible for the orientational mechanism, the main question is to calculate the field seen by the molecules and to establish its relation to the *Maxwell* field *before any statistical mechanical calculation can be started*.

Onsager [2] was the first author to be able to compute this relation between the molecular and Maxwell fields. To accomplish this, he considered a spherical region much smaller than the size of the dielectric itself, and showed that in such a region (the cavity) the field which operates at a *tagged* dipole *is not the Maxwell macroscopic field*. If the cavity is empty (and made of vacuum) then the field inside the (spherical or ellipsoidal) cavity is rather a field proportional to it named the cavity field. If a dipole is inserted in the cavity, then the dipole polarizes *the surrounding dipoles outside the cavity*, and this outer region is treated as a *continuum* where precisely the concepts of dielectric constant and complex permittivity have a meaning. By back action (Newton's third law), the surroundings create in the spherical cavity a *uniform field* named the reaction field. This field is proportional to the instantaneous dipole [2] and is therefore *unable* to orient it. However, the reaction field is important when the molecular dipoles each consist of a permanent plus an induced dipole because it is the total dipole which interacts with the cavity plus reaction fields [6]. In particular, this allows one to single out the polarization mechanism which arises from the molecular polarizability, so that the statistical-mechanical calculation requires one to handle the *orientational mechanism of polarization in detail only*.

From a statistical mechanical point of view, the molecular orientational dipole response can be calculated as that resulting from an effective cavity field, that is, the directing field [6] which is still proportional to the Maxwell field for spherically shaped cavities. Since the proportionality constant involves ε and is known for spherical geometry, the linear polarization response can be computed as the *linear response to this field* [6] as it is one *external* to the cavity. Only when this equation linking the Maxwell and directing field is known can the problem be reduced to one of statistical mechanics, that is, the calculation of the linear response of an assembly enclosed in a volume $\upsilon \ll \mathfrak{V}$ which still contains a sufficient number of molecules. This last point is essential because it is at this condition that *the principles of statistical mechanics can still be applied inside the cavity of volume* υ. More sophisticated theories attempting to avoid the cavity trick in the static calculations [12,15] still lead to the same conclusion as that of Fröhlich and Kirkwood and *formally, to the same equation* (the square of the molecular dipole moment must be multiplied by a positive factor).

Several ways are possible for handling the statistical mechanical calculation. As already alluded to above, the most general way of attack in the static situation is the equilibrium, time-independent generalized Liouville equation [18,19] which solution is invariably the many-body Maxwell-Boltzmann distribution. This allowed Fröhlich [4] to rationalize the notion of Kirkwood correlation factor and to provide a logical derivation of Kirkwood's theory. Unfortunately, the generalization to the time-dependent situation is very difficult from the generalized Liouville equation, because in this equation, the approach to statistical equilibrium is described in a very implicit manner. Nevertheless, the complex permittivity can be *formally linked* to the Fourier-Laplace transform of the time-dependent *equilibrium field free total dipole moment correlation function*, as shown by Klug, Kranbuehl, and Vaughan [20], Rivail [21], and Scaife [22]. We insist that this relation is completely formal and arises from the Liouville equation which is a *linear equation* (it can also be derived from the Kramers-Kronig relations [22–24]), and also on the fact that this correlation function approach is just a reformulation of first-order perturbation theory. Perturbation theory is the *safest method* to be applied when nonlinear kinetic equations are used to calculate the linear response. Experimentally, the use of such equation is similar with the one made for computing the Kirkwood correlation factor from experimental data [10]. In other words, the relation linking the complex permittivity to the Fourier transform of the time derivative of the total dipole correlation function is used to deduce the time dependence of the dipole correlation function in the absence of external fields; this correlation function is in turn the time response function of the dipolar system. The response function of the system can also be calculated by first-order perturbation theory, so that the correlation function approach can be bypassed entirely.

When the intermolecular interactions consist only of the superimposition of pair interaction terms, the generalized Liouville equation can be reduced to a set of partial differential-integral equations for the partial densities n_k defined in terms of the time-dependent solution of the Liouville equation $\mathfrak{F}$ by

$$\begin{aligned} n_k(\mathbf{q}_1, \dots, \mathbf{q}_k, t) \\ = \frac{N!}{(N-k)!} \int \mathfrak{F}(\mathbf{q}_1, \dots, \mathbf{q}_N, t) d\mathbf{q}_{k+1} d\mathbf{q}_{k+2} \cdots d\mathbf{q}_N \end{aligned} \tag{1}$$

with $k < N$ and $(\mathbf{q}_1, \dots, \mathbf{q}_N)$ denote the set of degrees of freedom and generalized momenta of the N-body system. The subsequent set, called the Bogolyubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy, reduces to a simpler set in configuration space [the Yvon-Born-Green (YBG) hierarchy] at thermodynamic equilibrium since the momenta are then assumed to reach their individual Maxwellian distribution [19]. Although the hierarchical process may seem simpler to handle, this is actually not so because (1) up to now and to the best of our knowledge nobody has succeeded in uncoupling the BBGKY hierarchy and (2) the approach to statistical equilibrium is as implicitly contained in the BBGKY hierarchy as it is in the generalized Liouville equation, the difference being however that in its original version, the BBGKY contains only pair interactions, while the Liouville equation contains *all many-body* ones. All this entails that relaxation mechanisms must always be explicitly stated in order to allow an initially excited system to reach its thermal equilibrium state.

A first route to handle dynamical many-body statistical mechanical problems is to use the generalized Liouville equation and to make an approximation regarding the propagator kernel by using the Mori-Zwanzig projection technique. After some approximation, this gives rise to the mode coupling theory (MCT), which is commonly used in glass science [19,25] for the sake of calculating intermediate scattering functions or structure factors of glasses and supercooled liquids. However, in this kind of theory, dynamics can be calculated only if it is assisted by the input of equilibrium conditions that are either imported from experimental data or equally well computed by an independent method. This is quite similar with the theory of Madden and Kivelson [12].

Another approach is classical dynamical density functional theory (DDFT) which is florishing in quite a number of areas nowadays (see Ref. [26] containing more than 1000 references, commenting on the ways to derive it, the approximations made in order to solve it, and the overwhelming number of its practical applications). As far as no approximation is stated on the dynamical excess free energy functional, DDFT is *formally exact* and in any case, contains *both* the statics and the dynamics in one and the same formalism. Moreover, the approach is physically appealing when derived from the Langevin stochastic equations of motion of the individual molecules. In addition, many well-grounded theoretical models can be constructed from DDFT as far as intermolecular interactions and thermal effects are involved. Finally, this is actually on that kind of approach that the Bagchi-Chandra theory is grounded, and therefore in our view this approach is by far more seducing than MCT ones, again because of its intuitive and physically appealing characters.

In the classical version (i.e., nonquantum-mechanical), there exist two kinds of DDFT that can be derived from the individual Langevin equations. The first is the deterministic approach put forward by Marconi and Tarazona [27]. The second one is stochastic and was derived by Dean [28]. The Dean equation is the exact one to start when handling a stochastic density functional theory approach, and contains Itô multiplicative noise. The Itô multiplicative noise is an important notion here, because unlike the Stratonovich one [29,30], this noise disappears when directly averaging the Dean equation over the distribution of realizations of the individual noises. Nevertheless, when averaging the Dean equation, one obtains the Marconi-Tarazona equation (10) [27], which is *exact*. This equation describes the overdamped dynamics of n_1 which contains a systematic diffusion term characteristic of the Einsteinian (overdamped) picture of Brownian motion augmented by an integral term involving n_2 and the interaction generalized force (i.e., minus the gradient of a pair interaction potential). Therefore, the equation which is obtained is one describing free diffusion (neglecting externally applied forces) of the one-body density augmented by interaction terms. Hence, this equation may be considered as a *fundamental result of DDFT* which is free from approximations. At statistical equilibrium, this equation reduces to the first member of the YBG hierarchy [26], so that DDFT *not only provides a specific mechanism to the approach of statistical equilibrium*, but also guarantees that the *correct thermal equilibrium state is attained*. If the exact formalism is maintained, then one may formally calculate any desired response to an external stimulus from this equation *at all perturbation orders of the external stimulus*. In the area of dielectrics, this is very important due to the recent finding of growing correlation lengths in nonlinear ac dielectric responses when some polar glass formers approach the glass transition [31].

C. Motivation

The Nee-Zwanzig theory [11], although allowing one to interpret dynamical glycerol data at −60 °C, does not reduce to the Kirkwood-Fröhlich equation at statics, and this is therefore a serious drawback of the theory. Moreover, it is not obvious to understand how short-range intermolecular forces and torques can be related to dielectric friction [23] in the context of their theory. The same holds true for the Madden-Kivelson theory [12] because the equilibrium and dynamical quantities are, in practice, computed independently. The Bagchi-Chandra theory is clearly a DDFT; however, the analytical computations have been achieved only in the mean spherical approximation (MSA) for uniform one-body density as a reference state, and therefore it is meaningless to *quantitatively* compare the outcomes of their analytical calculations with experimental data *save in dilute situations*. Moreover, using other approximations such as Percus-Yevick (PY) or hypernetted chain (HNC) approximations in the Bagchi-Chandra theory [17] leads to calculations that become analytically intractable, making it difficult to extract simple meaningful physical information (we leave apart the degree of arbitrariness of the MSA, PY, and HNC approximations). In fact, the rototranslational theory starting from the individual Langevin equations has been given by Cugliandolo *et al.* [32] quite recently in the context of stochastic DDFT as applied to dipolar relaxation, and the relation to previous theories discussed. Averaging their equation over the distribution of realizations of the individual noises reduces this equation to a rototranslational version of the Marconi-Tarazona equation (10) [27], which in turn becomes the Bagchi-Chandra theory if the interactions are computed from a Taylor functional expansion of a free excess energy functional and the pair density is factorized as a product of one-body densities.

The rototranslational Dean equation derived by Cugliandolo *et al.* [32] when averaged over the realizations of the individual noises links n_1 to n_2. While it is possible to derive an equation for n_2 from the Langevin individual equations, this is *never* made in approximate DDFT approaches [26]. However, in contrast with the equation for n_1, ignoring the integral terms involving n_3 in the equation for n_2 does *not* lead to a diffusion equation for n_2. Rather, it leads to a Fokker-Planck equation which drift involves the pair interaction potential. As such, it contains important information regarding microscopic relaxation processes and pair interactions that is not explicitly contained in the equation for n_1. If an equation for n_3 is derived, the same holds true, *viz.*, ignoring n_4 integral terms does not lead to a simple diffusion equation, rather to a Fokker-Planck equation which is similar with that for n_2 if only pair interactions are considered. To the best of our knowledge, considering both equations for n_1 and n_2 and making approximations on the n_2 equation for solving the equation for n_1 has never been considered in the past, save recently on an example, which allows analytical formulas to be obtained for both the Kirkwood correlation factor and complex permittivity spectrum [33,34]; good agreement for statics with both experimental data regarding the temperature dependence of the dielectric constant of water and methanol and numerical simulations was found [33]. Good qualitative agreement with many experimental data was found in the dynamical version [34]. Nevertheless, we believe it worthwhile presenting a formal theory because dielectric data have been available for long for various simple polar liquids of different nature, and therefore it is a chance to quantitatively test at least thermal equilibrium results against well-established experimental data, rather than testing them against numerical simulations [26]. However, before achieving this task, a number of theoretical calculations are necessary and it is the purpose of this paper to present them, together with an application to linear dielectric relaxation of dense polar fluids (the approach here is termed kinetic YBG theory) as an example of practical application. Computational results and comparison of the outcomes of the static theory with experimental data are given elsewhere [35].

The paper is organized as follows. Sections II–IV are devoted to a quite lengthy, but necessary derivation of theoretical statistical mechanical results. Section III introduces equations and derivations pertaining to statistical mechanics of polar fluids contained in a finite but sufficiently large volume. A one-time spatial density correlation function is introduced, which coincides with the distinct part of the Van Hove correlation function [36] at some instants of time, but deviates from it at other instants. This function is demonstrated to be the relevant one for evaluating the mean torques to which the molecular dipoles are subjected for the sake of interpreting a dielectric relaxation experiment in Secs. V and VI. Section IV is devoted to a derivation of a kinetic equation for the orientational pair probability density, then Sec. V provides an approximate Fokker-Planck equation for this orientational pair probability density, and achieves separation of rotational and translational timescales. Section VI applies the formalism derived in Secs. II–V to linear dielectric relaxation, establishes clearly the range of validity of the Bagchi-Chandra calculations and shows that their theory is actually a benchmark one for dilute polar fluids. The Onsager-Cole equation [37] is also rationalized and shown to be valid when intermolecular torques are *ignored* in the statistical mechanical calculation, so that Onsager's equation which is its zero-frequency limit has the same range of validity, *viz.,* in the dilute situation. Moreover, in this section, the relation to previous work concerning the Kirkwood correlation factor is given. Section VII discusses the results obtained and their formal transposition to macroscopically isotropic ferrofluids. Finally, Sec. VIII summarizes the work, emphasizes new results and concludes. Again, because the present work is lengthy, the numerical results and comparison with experimental data are presented elsewhere [35].

II. GENERALITIES

We consider as a model monomolecular fluid an assembly of N interacting polar molecules contained in a volume υ, such that its number density $\rho_0 = N/\upsilon$ is constant at given temperature and pressure. Each molecule labeled i has its center of mass located at $\mathbf{r}_i(t)$ at time t and carries a rigid dipole $\boldsymbol{\mu}_i(t)$ of constant magnitude μ and orientation specified by unit vector $\mathbf{u}_i(t)$ such that $\boldsymbol{\mu}_i(t) = \mu\mathbf{u}_i(t)$. The system of molecules is moreover subjected to externally applied forces and torques (described by a generalized one-body potential V_1) and thermal agitation. For simplicity, we neglect inertial effects and assume that intermolecular forces and torques can be derived from a scalar potential V_{int} made of a superposition of pair interaction terms U_{int}, *viz.,*

$$V_{\text{int}}(\mathbf{r}_1, \mathbf{u}_1, \dots, \mathbf{r}_N, \mathbf{u}_N) = \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i} U_{\text{int}}(\mathbf{r}_i - \mathbf{r}_j, \mathbf{u}_i, \mathbf{u}_j). \tag{2}$$

For purposes which will appear later in Sec. VI, we assume that V_1 is spatially uniform, so that $V_1(\mathbf{r}, \mathbf{u}, t) = V_1(\mathbf{u}, t)$. With the above assumptions, the rototranslational tumbling motion of the molecules is described by the overdamped Langevin equations [32], *viz.*

$$\dot{\mathbf{r}}_i(t) = -\frac{1}{\gamma}\sum_{j\neq i}\int \nabla_{\mathbf{r}_i(t)} U_{\text{int}}(\mathbf{r}_i(t) - \mathbf{r}_2, \mathbf{u}_i(t), \mathbf{u}_2)\hat{\rho}_j(\mathbf{r}_2, \mathbf{u}_2, t)\, d\mathbf{r}_2\, d\mathbf{u}_2 + \frac{\mathbf{f}_i(t)}{\gamma} \tag{3}$$

and

$$\dot{\mathbf{u}}_i(t) = -\frac{1}{\zeta}\sum_{j\neq i}\int \nabla_{\mathbf{u}_i(t)} U_{\text{int}}(\mathbf{r}_i(t) - \mathbf{r}_2, \mathbf{u}_i(t), \mathbf{u}_2)\hat{\rho}_j(\mathbf{r}_2, \mathbf{u}_2, t)\, d\mathbf{r}_2\, d\mathbf{u}_2 - \frac{1}{\zeta}\nabla_{\mathbf{u}_i(t)} V_1(\mathbf{u}_i(t), t) + \frac{\boldsymbol{\lambda}_i(t)\times\mathbf{u}_i(t)}{\zeta}, \tag{4}$$

where γ and ζ are, respectively, the phenomenological translational and rotational friction coefficients, $\mathbf{f}_i(t)$ and $\boldsymbol{\lambda}_i(t)$ are the white noise Gaussian random force and torque acting at molecule i, and

$$\rho_i(\mathbf{r}_1, \mathbf{u}_1, t) = \delta(\mathbf{r}_1 - \mathbf{r}_i(t))\delta(\mathbf{u}_1 - \mathbf{u}_i(t)). \tag{5}$$

The noise force and torque $\mathbf{f}_i(t)$ and $\boldsymbol{\lambda}_i(t)$ obey the statistical properties

$$\overline{\mathbf{f}_i(t)} = \mathbf{0},$$
$$\overline{f_{i,a}(t)f_{j,b}(t')} = 2kT\gamma\delta_{ij}\delta_{ab}\delta(t-t')$$

and

$$\overline{\boldsymbol{\lambda}_i(t)} = \mathbf{0},$$
$$\overline{\lambda_{i,a}(t)\lambda_{j,b}(t')} = 2kT\zeta\delta_{ij}\delta_{ab}\delta(t-t'),$$

where the indexes (a, b) refer to Cartesian components of the time-dependent stochastic vectors $\mathbf{f}_i(t)$ and $\boldsymbol{\lambda}_i(t)$, and the overbar means an average over the distribution of the realizations of the noise forces and torques [29,30]. We also assume that

$$\overline{f_{i,a}(t)\lambda_{j,b}(t')} = 0.$$

Finally, without any loss of generality, we always interpret following Risken [29] and Coffey *et al.* [30] the Langevin equations (3) and (4) as Stratonovitch ones because the Stratonovitch definition allows one to use the ordinary rules of differential calculus. Instead of representing the system dynamics with Eqs. (3) and (4), we introduce the average one-body density of collective modes (referred to in this work as the one-body density) as follows:

$$n_1(\mathbf{r}_1, \mathbf{u}_1, t) = \overline{\hat{\rho}(\mathbf{r}_1, \mathbf{u}_1, t)} = \sum_{i=1}^{N}\overline{\rho_i(\mathbf{r}_1, \mathbf{u}_1, t)} \tag{6}$$

and write an equation for $n_1(\mathbf{r}_1, \mathbf{u}_1, t)$. This equation is [26,27]

$$\begin{aligned}\frac{\partial n_1}{\partial t}(\mathbf{r}_1, \mathbf{u}_1, t) = {} & D_T\nabla_{\mathbf{r}_1}\cdot\left(\nabla_{\mathbf{r}_1} n_1(\mathbf{r}_1, \mathbf{u}_1, t) + \beta\int \nabla_{\mathbf{r}_1} U_{\text{int}}(\mathbf{r}_1 - \mathbf{r}_2, \mathbf{u}_1, \mathbf{u}_2) n_2(\mathbf{r}_1, \mathbf{u}_1, \mathbf{r}_2, \mathbf{u}_2, t)\, d\mathbf{r}_2\, d\mathbf{u}_2\right)\\ & + D_R\nabla_{\mathbf{u}_1}\cdot[\nabla_{\mathbf{u}_1} n_1(\mathbf{r}_1, \mathbf{u}_1, t) + \beta n_1(\mathbf{r}_1, \mathbf{u}_1, t)\nabla_{\mathbf{u}_1} V_1(\mathbf{u}_1, t)]\\ & + \beta D_R\nabla_{\mathbf{u}_1}\cdot\int \nabla_{\mathbf{u}_1} U_{\text{int}}(\mathbf{r}_1 - \mathbf{r}_2, \mathbf{u}_1, \mathbf{u}_2) n_2(\mathbf{r}_1, \mathbf{u}_1, \mathbf{r}_2, \mathbf{u}_2, t)\, d\mathbf{r}_2\, d\mathbf{u}_2,\end{aligned} \tag{7}$$

where $\beta = (kT)^{-1}$ and D_T and D_R are respectively the bare translational and rotational diffusion coefficients given by

$$D_T = \frac{kT}{\gamma}, \qquad D_R = \frac{kT}{\zeta}, \tag{8}$$

and

$$n_2(\mathbf{r}_1, \mathbf{u}_1, \mathbf{r}_2, \mathbf{u}_2, t) = \sum_i \sum_{j\neq i} \overline{\rho_i(\mathbf{r}_1, \mathbf{u}_1, t)\rho_j(\mathbf{r}_2, \mathbf{u}_2, t)} \tag{9}$$

is the pair density of collective modes. Equation (7) is well known [26] and is at the basis of the development of, for example, the usual deterministic DDFT description of the many-body statistical problem. This equation reduces to Berne's basic diffusion equation [38] as well as that of Bagchi and Chandra [17] when the mean-field approximation $n_2(\mathbf{r}_1, \mathbf{u}_1, \mathbf{r}_2, \mathbf{u}_2, t) \approx n_1(\mathbf{r}_1, \mathbf{u}_1, t)n_1(\mathbf{r}_2, \mathbf{u}_2, t)$ is used in Eq. (7). It may be remarked that in the absence of interactions described by the integral terms and in the absence of externally applied forces, Eq. (7) reduces to a rototranslational diffusion equation [26].

From Eqs. (3) and (4), it is possible to derive an equation of motion for n_2. This equation is

$$\begin{aligned}\frac{\partial n_2}{\partial t}(\mathbf{r}_1, \mathbf{u}_1, \mathbf{r}_2, \mathbf{u}_2, t) = {}& D_T \sum_{i=1}^{2} \nabla_{\mathbf{r}_i} \cdot [\nabla_{\mathbf{r}_i} n_2(\mathbf{r}_1, \mathbf{u}_1, \mathbf{r}_2, \mathbf{u}_2, t) + \beta n_2(\mathbf{r}_1, \mathbf{u}_1, \mathbf{r}_2, \mathbf{u}_2, t)\nabla_{\mathbf{r}_i} V_2(\mathbf{r}_1 - \mathbf{r}_2, \mathbf{u}_1, \mathbf{u}_2, t)]\\ &+ D_R \sum_{i=1}^{2} \nabla_{\mathbf{u}_i} \cdot [\nabla_{\mathbf{u}_i} n_2(\mathbf{r}_1, \mathbf{u}_1, \mathbf{r}_2, \mathbf{u}_2, t) + \beta n_2(\mathbf{r}_1, \mathbf{u}_1, \mathbf{r}_2, \mathbf{u}_2, t)\nabla_{\mathbf{u}_i} V_2(\mathbf{r}_1 - \mathbf{r}_2, \mathbf{u}_1, \mathbf{u}_2, t)]\\ &+ \beta D_T \sum_{i=1}^{2} \nabla_{\mathbf{r}_i} \cdot \int \nabla_{\mathbf{r}_i} U_{\text{int}}(\mathbf{r}_i - \mathbf{r}_3, \mathbf{u}_i, \mathbf{u}_3) n_3(\mathbf{r}_1, \mathbf{u}_1, \mathbf{r}_2, \mathbf{u}_2, \mathbf{r}_3, \mathbf{u}_3, t)\, d\mathbf{r}_3\, d\mathbf{u}_3\\ &+ \beta D_R \sum_{i=1}^{2} \nabla_{\mathbf{u}_i} \cdot \int \nabla_{\mathbf{u}_i} U_{\text{int}}(\mathbf{r}_i - \mathbf{r}_3, \mathbf{u}_i, \mathbf{u}_3) n_3(\mathbf{r}_1, \mathbf{u}_1, \mathbf{r}_2, \mathbf{u}_2, \mathbf{r}_3, \mathbf{u}_3, t)\, d\mathbf{r}_3\, d\mathbf{u}_3,\end{aligned} \tag{10}$$

where

$$V_2(\mathbf{r}_1 - \mathbf{r}_2, \mathbf{u}_1, \mathbf{u}_2, t) = U_{\text{int}}(\mathbf{r}_1 - \mathbf{r}_2, \mathbf{u}_1, \mathbf{u}_2) + V_1(\mathbf{u}_1, t) + V_1(\mathbf{u}_2, t) \tag{11}$$

is the two-body potential describing interactions between two molecules with degrees of freedom $(\mathbf{r}_1, \mathbf{u}_1)$ and $(\mathbf{r}_2, \mathbf{u}_2)$ augmented by externally applied fields, and

$$n_3(\mathbf{r}_1, \mathbf{u}_1, \mathbf{r}_2, \mathbf{u}_2, \mathbf{r}_3, \mathbf{u}_3, t) = \sum_{i=1}^{N} \sum_{j\neq i} \sum_{k\neq j\neq i} \overline{\rho_i(\mathbf{r}_1, \mathbf{u}_1, t)\rho_j(\mathbf{r}_2, \mathbf{u}_2, t)\rho_k(\mathbf{r}_3, \mathbf{u}_3, t)} \tag{12}$$

is the three-body density of collective modes.

It can be remarked that in contrast with Eq. (7), Eq. (10) does not reduce to a simple diffusion equation if integral and external field terms are ignored, but rather to a two-body Fokker-Planck (Smoluchowski) equation [29]. We do not write an equation for n_3 because as mentioned in the Introduction, the situation for this equation is the same as the one for n_2. Hence all the information we need is contained in Eqs. (7) and (10). Furthermore, in the time-independent situation, these equations reduce to the first two members of the YBG hierarchy. Hence, the above approach to rototranslational relaxation may be termed as a "kinetic YBG approach" to rototranslational relaxation.

Now the mean polarization of a volume υ containing N molecules of a monomolecular fluid in the direction of an externally applied field may be written as

$$\mathfrak{P}(t) = \frac{\mu}{\upsilon} \int (\mathbf{u}_1 \cdot \mathbf{e}) n_1(\mathbf{r}_1, \mathbf{u}_1, t)\, d\mathbf{r}_1\, d\mathbf{u}_1, \tag{13}$$

where $\mathbf{e}$ is a unit vector in the direction of the externally applied field. By inspection of this equation, it is clear that $n_1(\mathbf{r}_1, \mathbf{u}_1, t)$ is of little interest because $(\mathbf{u}_1 \cdot \mathbf{e})$ does not involve $\mathbf{r}_1$ explicitly. It is therefore worthwhile introducing the one-body orientational probability density $W_1(\mathbf{u}_1, t)$ defined by

$$W_1(\mathbf{u}_1, t) = \frac{1}{N} \int_{\upsilon} n_1(\mathbf{r}_1, \mathbf{u}_1, t)\, d\mathbf{r}_1 \tag{14}$$

so that Eq. (13) may be written in terms of $W_1(\mathbf{u}_1, t)$ as

$$\mathfrak{P}(t) = \rho_0 \mu \int (\mathbf{u}_1 \cdot \mathbf{e}) W_1(\mathbf{u}_1, t)\, d\mathbf{u}_1. \tag{15}$$

This equation is the expression of the microscopic polarization used by Debye [1], with the difference that in Debye's theory, the effects of intermolecular interactions on $W_1(\mathbf{u}_1, t)$ are entirely neglected. In writing Eq. (15), we assume following Debye, Onsager, Kirkwood, and Fröhlich [1–4] that ρ_0

is a constant at given temperature and pressure through the whole fluid. By integrating Eq. (7) with respect to $\mathbf{r}_1$ over an arbitrary large volume υ and making use of Gauss's theorem, we directly obtain an equation for $W_1(\mathbf{u}_1, t)$, *viz.*,

$$\frac{\partial W_1}{\partial t}(\mathbf{u}_1, t) = D_R \nabla_{\mathbf{u}_1} \cdot \left(\nabla_{\mathbf{u}_1} W_1(\mathbf{u}_1, t) + \beta W_1(\mathbf{u}_1, t) \nabla_{\mathbf{u}_1} V_1(\mathbf{u}_1, t) + \frac{\beta}{\rho_0} \int \nabla_{\mathbf{u}_1} U_{\text{int}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2) n_2(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t|N, \upsilon) d\mathbf{r} d\mathbf{u}_2 \right), \tag{16}$$

where

$$n_2(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t|N, \upsilon) = \frac{1}{\upsilon} \int_{\upsilon} n_2\left(\mathbf{R} + \frac{\mathbf{r}}{2}, \mathbf{u}_1, \mathbf{R} - \frac{\mathbf{r}}{2}, \mathbf{u}_2, t\right) d\mathbf{R} \tag{17}$$

is the pair density for two molecules having relative position $\mathbf{r}$ with dipole pairs oriented at $(\mathbf{u}_1, \mathbf{u}_2)$ at time t *given that N molecules are contained in* υ, and where $\mathbf{R}$ and $\mathbf{r}$ are respectively the coordinates of the center of mass of a pair of molecules and the relative position coordinates of a pair of molecules, *viz.*,

$$\mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2), \qquad \mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2. \tag{18}$$

Equation (16) generalizes Eq. (7) of Ref. [41] to the full configuration space of the dipole orientations. In fact, Eq. (16) is the one from which $\mathfrak{P}(t)$ is to be calculated. In order to achieve this task, clearly an equation for $n_2(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t|N, \upsilon)$ is to be derived as a first step. As we shall see, this will allow for a number of simplifications.

III. SOME EXACT RESULTS

We show in this section that a number of exact results can be obtained from Eq. (10) without making any extra hypotheses and allows us to justify some assumptions made in previous work [33,34]. We begin by deriving an equation for $n_2(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t|N, \upsilon)$.

A. Derivation of a kinetic equation for $n_2(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t|N, \upsilon)$

In order to achieve this derivation, we start from Eq. (10) and introduce the dynamical two-body and three-body dynamical distribution functions as follows:

$$G_2(\mathbf{r}_1, \mathbf{u}_1, \mathbf{r}_2, \mathbf{u}_2, t) = \frac{n_2(\mathbf{r}_1, \mathbf{u}_1, \mathbf{r}_2, \mathbf{u}_2, t)}{n_1(\mathbf{r}_1, \mathbf{u}_1, t) n_1(\mathbf{r}_2, \mathbf{u}_2, t)}, \tag{19}$$

$$G_3(\mathbf{r}_1, \mathbf{u}_1, \mathbf{r}_2, \mathbf{u}_2, \mathbf{r}_3, \mathbf{u}_3, t) = \frac{n_3(\mathbf{r}_1, \mathbf{u}_1, \mathbf{r}_2, \mathbf{u}_2, \mathbf{r}_3, \mathbf{u}_3, t)}{n_1(\mathbf{r}_1, \mathbf{u}_1, t) n_1(\mathbf{r}_2, \mathbf{u}_2, t) n_1(\mathbf{r}_3, \mathbf{u}_3, t)}. \tag{20}$$

These definitions are simple generalizations of the same functions in the time-independent situation [19]. Next, we change the variables $(\mathbf{r}_1, \mathbf{r}_2)$ in Eq. (10) into the variables $(\mathbf{R}, \mathbf{r})$. After lengthy but straightforward algebra, we arrive at the equation

$$\begin{aligned}
\frac{\partial n_2}{\partial t}(\mathbf{R}, \mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t) = {} & 2D_T \nabla_{\mathbf{R}} \cdot [\nabla_{\mathbf{R}} n_2(\mathbf{R}, \mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t) + \beta n_2(\mathbf{R}, \mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t) \nabla_{\mathbf{R}} \phi_2(\mathbf{R}, \mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t)] \\
& + \frac{D_T}{2} \nabla_{\mathbf{r}} \cdot [\nabla_{\mathbf{r}} n_2(\mathbf{R}, \mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t) + \beta n_2(\mathbf{R}, \mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t) \nabla_{\mathbf{r}} \phi_2(\mathbf{R}, \mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t)] \\
& + D_R \sum_{i=1}^{2} \nabla_{\mathbf{u}_i} \cdot [\nabla_{\mathbf{u}_i} n_2(\mathbf{R}, \mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t) + \beta n_2(\mathbf{R}, \mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t) \nabla_{\mathbf{u}_i} V_2(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t)] \\
& + \beta D_R \nabla_{\mathbf{u}_1} \cdot \int \nabla_{\mathbf{u}_1} U_{\text{int}}(\mathbf{r}', \mathbf{u}_1, \mathbf{u}_3) n_3\left(\mathbf{R} + \frac{\mathbf{r}}{2}, \mathbf{u}_1, \mathbf{R} - \frac{\mathbf{r}}{2}, \mathbf{u}_2, \mathbf{R} + \frac{\mathbf{r}}{2} - \mathbf{r}', \mathbf{u}_3, t\right) d\mathbf{r}'\, d\mathbf{u}_3 \\
& + \beta D_R \nabla_{\mathbf{u}_2} \cdot \int \nabla_{\mathbf{u}_2} U_{\text{int}}(\mathbf{r}', \mathbf{u}_2, \mathbf{u}_3) n_3\left(\mathbf{R} + \frac{\mathbf{r}}{2}, \mathbf{u}_1, \mathbf{R} - \frac{\mathbf{r}}{2}, \mathbf{u}_2, \mathbf{R} - \frac{\mathbf{r}}{2} - \mathbf{r}', \mathbf{u}_3, t\right) d\mathbf{r}'\, d\mathbf{u}_3,
\end{aligned} \tag{21}$$

where we have used for short the notation

$$n_2(\mathbf{R}, \mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t) = n_2(\mathbf{R} + \frac{\mathbf{r}}{2}, \mathbf{u}_1, \mathbf{R} - \frac{\mathbf{r}}{2}, \mathbf{u}_2, t)$$

and where

$$\nabla_{\mathbf{R}} \phi_2(\mathbf{R}, \mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t) = \frac{3}{8} \mathbf{I}_1(\mathbf{R}, \mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t) + \frac{5}{8} \mathbf{I}_2(\mathbf{R}, \mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t), \tag{22}$$

$$\nabla_{\mathbf{r}}\phi_2(\mathbf{R},\mathbf{r},\mathbf{u}_1,\mathbf{u}_2,t)=\nabla_{\mathbf{r}}U_{\mathrm{int}}(\mathbf{r},\mathbf{u}_1,\mathbf{u}_2)+\frac{3}{4}\mathbf{I}_1(\mathbf{R},\mathbf{r},\mathbf{u}_1,\mathbf{u}_2,t)-\frac{5}{4}\mathbf{I}_2(\mathbf{R},\mathbf{r},\mathbf{u}_1,\mathbf{u}_2,t). \tag{23}$$

Here $\mathbf{I}_1$ and $\mathbf{I}_2$ are the vectors defined by

$$\mathbf{I}_1(\mathbf{R},\mathbf{r},\mathbf{u}_1,\mathbf{u}_2,t)=\int\nabla_{\mathbf{r}'}U_{\mathrm{int}}(\mathbf{r}',\mathbf{u}_1,\mathbf{u}_3)n_1\left(\mathbf{R}+\frac{\mathbf{r}}{2}-\mathbf{r}',\mathbf{u}_3,t\right)\frac{G_3\left(\mathbf{R}+\frac{\mathbf{r}}{2},\mathbf{u}_1,\mathbf{R}-\frac{\mathbf{r}}{2},\mathbf{u}_2,\mathbf{R}+\frac{\mathbf{r}}{2}-\mathbf{r}',\mathbf{u}_3,t\right)}{G_2\left(\mathbf{R}+\frac{\mathbf{r}}{2},\mathbf{u}_1,\mathbf{R}-\frac{\mathbf{r}}{2},\mathbf{u}_2,t\right)}\,d\mathbf{r}'\,d\mathbf{u}_3, \tag{24}$$

and

$$\mathbf{I}_2(\mathbf{R},\mathbf{r},\mathbf{u}_1,\mathbf{u}_2,t)=\int\nabla_{\mathbf{r}'}U_{\mathrm{int}}(\mathbf{r}',\mathbf{u}_2,\mathbf{u}_3)n_1\left(\mathbf{R}-\frac{\mathbf{r}}{2}-\mathbf{r}',\mathbf{u}_3,t\right)\frac{G_3\left(\mathbf{R}+\frac{\mathbf{r}}{2},\mathbf{u}_1,\mathbf{R}-\frac{\mathbf{r}}{2},\mathbf{u}_2,\mathbf{R}-\frac{\mathbf{r}}{2}-\mathbf{r}',\mathbf{u}_3,t\right)}{G_2\left(\mathbf{R}+\frac{\mathbf{r}}{2},\mathbf{u}_1,\mathbf{R}-\frac{\mathbf{r}}{2},\mathbf{u}_2,t\right)}\,d\mathbf{r}'\,d\mathbf{u}_3. \tag{25}$$

As it stands, ϕ_2 is an effective pair interaction potential and therefore should not depend on the center of mass coordinate of a pair. This means that we must have $\nabla_{\mathbf{R}}\phi_2=\mathbf{0}$, so that Eq. (22) reads

$$\mathbf{I}_2(\mathbf{R},\mathbf{r},\mathbf{u}_1,\mathbf{u}_2,t)=-\frac{3}{5}\mathbf{I}_1(\mathbf{R},\mathbf{r},\mathbf{u}_1,\mathbf{u}_2,t). \tag{26}$$

Next, since we consider a single-component polar fluid (i.e., with identical molecules), we have

$$G_3(\mathbf{r}_1,\mathbf{u}_1,\mathbf{r}_2,\mathbf{u}_2,\mathbf{r}_3,\mathbf{u}_3,t)=G_3(\mathbf{r}_2,\mathbf{u}_2,\mathbf{r}_1,\mathbf{u}_1,\mathbf{r}_3,\mathbf{u}_3,t),\quad G_2(\mathbf{r}_1,\mathbf{u}_1,\mathbf{r}_2,\mathbf{u}_2,t)=G_2(\mathbf{r}_2,\mathbf{u}_2,\mathbf{r}_1,\mathbf{u}_1,t),$$

so that for arbitrary vectors $(\mathbf{R},\mathbf{r},\mathbf{u}_1,\mathbf{u}_2)$ we have

$$\mathbf{I}_1(\mathbf{R},-\mathbf{r},\mathbf{u}_1,\mathbf{u}_2,t)=\mathbf{I}_2(\mathbf{R},\mathbf{r},\mathbf{u}_2,\mathbf{u}_1,t). \tag{27}$$

Finally, because $\nabla_{\mathbf{R}}\phi_2=\mathbf{0}$, we also have

$$\nabla_{\mathbf{R}}\phi_2(\mathbf{R},\mathbf{r},\mathbf{u}_1,\mathbf{u}_2,t)=\nabla_{\mathbf{R}}\phi_2(\mathbf{R},-\mathbf{r},\mathbf{u}_2,\mathbf{u}_1,t),$$

which, using Eqs. (22), (26), and (27), leads to

$$\mathbf{I}_1=\mathbf{I}_2=\mathbf{0}. \tag{28}$$

It follows that Eq. (23) becomes the remarkably simple result

$$\nabla_{\mathbf{r}}\phi_2(\mathbf{r},\mathbf{u}_1,\mathbf{u}_2,t)=\nabla_{\mathbf{r}}U_{\mathrm{int}}(\mathbf{r},\mathbf{u}_1,\mathbf{u}_2). \tag{29}$$

Finally, by integrating Eq. (21) with respect to $\mathbf{R}$ and accounting for the fact that $\nabla_{\mathbf{R}}\phi_2=\mathbf{0}$ and for Eqs. (17) and (29), we finally arrive at the sought equation, *viz.*,

$$\begin{aligned}\frac{\partial n_2}{\partial t}(\mathbf{r},\mathbf{u}_1,\mathbf{u}_2,t|N,\upsilon)={}&\frac{D_T}{2}\nabla_{\mathbf{r}}\cdot[\nabla_{\mathbf{r}}n_2(\mathbf{r},\mathbf{u}_1,\mathbf{u}_2,t|N,\upsilon)+\beta n_2(\mathbf{r},\mathbf{u}_1,\mathbf{u}_2,t|N,\upsilon)\nabla_{\mathbf{r}}U_{\mathrm{int}}(\mathbf{r},\mathbf{u}_1,\mathbf{u}_2)]\\&+D_R\sum_{i=1}^{2}\nabla_{\mathbf{u}_i}\cdot[\nabla_{\mathbf{u}_i}n_2(\mathbf{r},\mathbf{u}_1,\mathbf{u}_2,t|N,\upsilon)+\beta n_2(\mathbf{r},\mathbf{u}_1,\mathbf{u}_2,t|N,\upsilon)\nabla_{\mathbf{u}_i}V_2(\mathbf{r},\mathbf{u}_1,\mathbf{u}_2,t)]\\&+\beta D_R\sum_{i=1}^{2}\nabla_{\mathbf{u}_i}\cdot\int\nabla_{\mathbf{u}_i}U_{\mathrm{int}}(\mathbf{r}',\mathbf{u}_i,\mathbf{u}_3)n_3(\mathbf{r},\mathbf{r}',\mathbf{u}_1,\mathbf{u}_2,\mathbf{u}_3,t|N,\upsilon)\,d\mathbf{r}'\,d\mathbf{u}_3,\end{aligned} \tag{30}$$

where

$$n_3(\mathbf{r},\mathbf{r}',\mathbf{u}_1,\mathbf{u}_2,\mathbf{u}_3,t|N,\upsilon)=\frac{1}{\upsilon}\int_{\upsilon}n_3\left(\mathbf{R}+\frac{\mathbf{r}}{2},\mathbf{u}_1,\mathbf{R}-\frac{\mathbf{r}}{2},\mathbf{u}_2,\mathbf{R}\pm\frac{\mathbf{r}}{2}-\mathbf{r}',\mathbf{u}_3,t\right)d\mathbf{R} \tag{31}$$

defines the three-body density that any three molecules are distant of $(\mathbf{r},\mathbf{r}')$ with orientations $(\mathbf{u}_1,\mathbf{u}_2,\mathbf{u}_3)$ at time t given N molecules are in υ. Finally, by inspection of Eq. (12), it can be readily seen that the ± sign in the right-hand side of Eq. (31) is of no importance since in Eq. (12), the summation indices are dummy. Hence, it follows that choosing either sign defines *one and the same function*, *viz.*, $n_3(\mathbf{r},\mathbf{r}',\mathbf{u}_1,\mathbf{u}_2,\mathbf{u}_3,t|N,\upsilon)$. Equation (30) is the main result of this subsection. As it seems, Eqs. (16) and (30) should suffice in order to calculate the linear complex permittivity of polar fluids. In the next subsection we eliminate the rotational degrees of freedom from Eq. (30) to single out the translational part of the relaxation process, and provide relation of this translational part with the distinct part of the Van Hove function [36].

B. Elimination of rotational degrees of freedom from Eq. (30) and relation to the Van Hove function

In Appendix A, it is demonstrated that without any approximation, one can factorize $n_2(\mathbf{r},\mathbf{u}_1,\mathbf{u}_2,t|N,\upsilon)$ as follows:

$$n_2(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t|N, \upsilon) = \rho_0 W_2(\mathbf{u}_1, \mathbf{u}_2, t) G(\mathbf{r}, t|N, \upsilon), \tag{32}$$

where $W_2(\mathbf{u}_1, \mathbf{u}_2, t)$ is the orientational pair probability density (depending on N and υ only through ρ_0) and the meaning of $G(\mathbf{r}, t|N, \upsilon)$ will be given when we have derived a kinetic equation for this function. Actually, this equation is easily obtained by integrating Eq. (30) over $(\mathbf{u}_1, \mathbf{u}_2)$ and using the split (32). This yields for G the *Fokker-Planck* equation

$$\begin{aligned}&\frac{\partial G}{\partial t}(\mathbf{r}, t|N, \upsilon)\\ &= \frac{D_T}{2}\nabla_{\mathbf{r}} \cdot [\nabla_{\mathbf{r}} G(\mathbf{r}, t|N, \upsilon) + \beta G(\mathbf{r}, t|N, \upsilon)\nabla_{\mathbf{r}} \bar{U}_{\text{int}}(\mathbf{r}, t)],\end{aligned} \tag{33}$$

where

$$\bar{U}_{\text{int}}(\mathbf{r}, t) = \int U_{\text{int}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2) W_2(\mathbf{u}_1, \mathbf{u}_2, t)\, d\mathbf{u}_1\, d\mathbf{u}_2. \tag{34}$$

The meaning of $G(\mathbf{r}, t|N, \upsilon)$ can now be given. First, we can easily obtain $n_2(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t|N, \upsilon)$ in terms of δ functions by using Eqs. (9) and (17) to obtain

$$\begin{aligned}&n_2(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t|N, \upsilon)\\ &= \frac{1}{\upsilon}\sum_{i=1}^{N}\sum_{j\neq i}\overline{\delta(\mathbf{r} + \mathbf{r}_j(t) - \mathbf{r}_i(t))\delta(\mathbf{u}_1 - \mathbf{u}_i(t))\delta(\mathbf{u}_2 - \mathbf{u}_j(t))}.\end{aligned} \tag{35}$$

We can replace the left-hand side of Eq. (35) with the factorization (32), integrate over $\mathbf{u}_1$ and $\mathbf{u}_2$ and account that W_2 is a probability density to obtain

$$G(\mathbf{r}, t|N, \upsilon) = \frac{1}{N}\sum_{i=1}^{N}\sum_{j\neq i}\overline{\delta(\mathbf{r} + \mathbf{r}_j(t) - \mathbf{r}_i(t))}. \tag{36}$$

This has to be compared with the definition of the distinct part of the Van Hove function $G^{(d)}_{VH}(\mathbf{r}, t, t')$ given by [36]

$$G^{(d)}_{VH}(\mathbf{r}, t, t') = \frac{1}{N}\sum_{i=1}^{N}\sum_{j\neq i}\overline{\delta(\mathbf{r} + \mathbf{r}_j(t) - \mathbf{r}_i(t'))}, \tag{37}$$

so that it is easily seen that $G(\mathbf{r}, t|N, \upsilon) = G^{(d)}_{VH}(\mathbf{r}, t, t)$, i.e., $G(\mathbf{r}, t|N, \upsilon)$ serves as an "initial condition" for $G^{(d)}_{VH}(\mathbf{r}, t, t')$. Since the Van Hove function for $t = t' = 0$ is the number density times the spatial pair distribution function $\mathfrak{g}(\mathbf{r})$ [19,36], we have

$$G(\mathbf{r}, 0|N, \upsilon) = \rho_0 \mathfrak{g}(\mathbf{r}). \tag{38}$$

However, when thermal equilibrium is attained $t \to \infty$ so that the solution of Eq. (33) is time independent and given by the "virial formula," *viz.*,

$$G(\mathbf{r}, \infty|N, \upsilon) = A_N e^{-\beta \bar{U}_{\text{int}}(\mathbf{r}, \infty)}, \tag{39}$$

where A_N is a nonzero integration constant. This is in contrast with the value $G^{(d)}_{VH}(\mathbf{r}, 0, \infty) = \rho_0$ of the Van Hove function. Therefore, the two functions *are different* and $G(\mathbf{r}, t|N, \upsilon)$ relaxes from the value specified by Eq. (38) to Eq. (39), while the relaxation of the Van Hove function $G^{(d)}_{VH}$ is much more complicated. Physically, this can be understood as follows: the liquid has no stable molecular order, so that such order changes from time to time. From the point of view of the Van Hove function, this change is "initially" given by by the time-dependent solution of Eq. (33). If the timescale of the experiment measuring the structure is larger than the translational timescale, then the value Eq. (38) is observed. If thermal equilibrium is attained, then indeed the result of the measurement will be Eq. (39) since the structure of the liquid will have relaxed to its equilibrium value. In other words, Van Hove [36] assumed that $G^{(d)}_{VH}(\mathbf{r}, t, t')$ is stationary in all phases of matter, i.e., $G^{(d)}_{VH}(\mathbf{r}, t, t') = G^{(d)}_{VH}(\mathbf{r}, 0, |t - t'|)$. This is certainly true in crystalline solids, but this might not be so in liquids since the local order in molecular liquids changes from time to time according to the Langevin equation (3) where thermal agitation drives the molecular motion. To illustrate our above arguments, let us assume that translational timescales prescribed by the Fokker-Planck equation (33) (i.e., their negative inverse nonzero eigenvalues) and rotational timescales involved in the dynamics of W_2 are separated in such a way that a structural measurement does not noticeably disturb the orientations of the molecules in the absence of externally applied fields (very much like in an x-ray scattering experiment). Then, in Eq. (34) we can replace W_2 by its equilibrium value $W_2^{(0)}$. By Eq. (34) this gives rise to the potential $\bar{U}^{\infty}_{\text{int}}(\mathbf{r})$ given by

$$\bar{U}^{\infty}_{\text{int}}(\mathbf{r}) = \int U_{\text{int}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2) W_2^{(0)}(\mathbf{u}_1, \mathbf{u}_2)\, d\mathbf{u}_1\, d\mathbf{u}_2. \tag{40}$$

Replacing $\bar{U}_{\text{int}}$ by $\bar{U}^{\infty}_{\text{int}}$ in the Fokker-Planck equation (33) gives rise to the solution

$$\begin{aligned}G(\mathbf{r}, t|N, \upsilon) &= A_N \exp[-\beta \bar{U}^{\infty}_{\text{int}}(\mathbf{r})]\\ &\quad + \exp(-\lambda t)\exp\left[-\frac{\beta}{2}\bar{U}^{\infty}_{\text{int}}(\mathbf{r})\right]\mathfrak{f}_{\lambda}(\mathbf{r}),\end{aligned} \tag{41}$$

where $\lambda > 0$ is a relaxation rate [technically, an eigenvalue of Eq. (33)] and $\mathfrak{f}_{\lambda}(\mathbf{r})$ obeys the stationary Schrödinger equation

$$\nabla^2_{\mathbf{r}}\mathfrak{f}_{\lambda}(\mathbf{r}) + \left(\frac{2\lambda}{D_T} - V_S(\mathbf{r})\right)\mathfrak{f}_{\lambda}(\mathbf{r}) = 0, \tag{42}$$

where [29]

$$V_S(\mathbf{r}) = -\frac{\beta}{2}\left(\nabla^2_{\mathbf{r}}\bar{U}^{\infty}_{\text{int}}(\mathbf{r}) - \frac{\beta}{2}[\nabla_{\mathbf{r}} U^{\infty}_{\text{int}}(\mathbf{r})]^2\right). \tag{43}$$

This (dimensionless) potential is repulsive at short molecular separations, vanishes at large ones, and in a word behaves just as the molecular interaction potential U_{int} does, *viz.*,

$$\lim_{|\mathbf{r}|\to 0} V_S(\mathbf{r}) = +\infty,$$

$$\lim_{|\mathbf{r}|\to \infty} V_S(\mathbf{r}) = 0,$$

so that by inspection of Eq. (42) and the second of the two above equations, we easily deduce from asymptotic analysis [39] that

$$\lim_{|\mathbf{r}|\to \infty} \mathfrak{f}_{\lambda}(\mathbf{r}) = 0,$$

$$\lim_{|\mathbf{r}|\to 0} \mathfrak{f}_{\lambda}(\mathbf{r}) = 0.$$

Hence, in the large intermolecular separation situation and when translational and rotational timescales are well separated, the "virial formula" (39) for $G(\mathbf{r}, t|N, \upsilon)$ holds at all times, as it must be in dense gases. When the intermolecular separations are arbitrary, Eq. (41) interpolates between Eqs. (38) and (39). Finally, Eq. (41) is of the form of the closure of the Ornstein-Zernike (OZ) equation [19] at $t = 0$ for *constant* n_1, *viz.,* a statistical state where n_1 does not depend nor on translational, nor orientational degrees of freedom at all (a situation which is *never* assumed here). Therefore, Eq. (41) for $t = 0$ provides a family of exact closures of the OZ equation parametrized by the timescale $(\lambda)^{-1}$, and the latter equation can further be used to calculate the direct pair density correlation function if necessary. The main result of this subsection are Eqs. (33) and (42). Now we turn to the derivation of a kinetic equation for W_2.

IV. KINETIC EQUATION FOR THE ORIENTATIONAL PAIR PROBABILITY DENSITY

The derivation of a kinetic equation for the orientational pair probability density W_2 is subtler than that for G. Actually, this equation must be obtained before translational and rotational timescales are separated. Here we recall that (see Appendix A)

$$\int_{\upsilon} G(\mathbf{r}, t|N, \upsilon)\, d\mathbf{r} = \rho_0 \upsilon - 1. \tag{44}$$

This leaves some ambiguity regarding the volume υ which must be taken to calculate the integral. A way out of this difficulty is first to relate ρ_0 to the mass density of the fluid $M(T)$ via the following "macroscopic" relation, *viz.,*

$$N_A M(T) = M_{\mathrm{mol}} \rho_0(T), \tag{45}$$

where M_{mol} is the molar mass and N_A is Avogadro's number. Next, we introduce a minimal volume $\upsilon_{\min}$ in such a way that the right-hand side of Eq. (44) is equal to unity. This yields

$$\upsilon_{\min}(T) = \frac{2}{\rho_0(T)}. \tag{46}$$

For liquid water, this minimal volume represents 30 million molecules at room temperature, which is still a very large number. This volume in turn represents a maximal intermolecular separation of 300 water molecular radii, an intermolecular separation for which we can reasonably assume that $U_{\mathrm{int}} \approx \bar{U}_{\mathrm{int}}$ (our estimates are given for close molecular packing). Of course, naively inserting this value in Eq. (44) yields $N = 2$, which is *a priori* meaningless. In fact, in order to understand what $N = 2$ means, it is best to average Eq. (44) over a probability density of occurrence of υ, centered on $\upsilon_{\min}$. Since this probability density is unknown, we *choose* a sharp one, *viz.,* $\delta(\upsilon - \upsilon_{\min})$. It follows that the value $N = 2$ is to be interpreted as the *minimal size of the statistical representative of the ensemble onto which* W_2 *is defined*. Of course, this size is 2. Denoting by $G(\mathbf{r}, t)$ the value

$$G(\mathbf{r}, t) = G\left(\mathbf{r}, t|2, \frac{2}{\rho_0}\right)$$

we have

$$\int_{\frac{2}{\rho_0}} G(\mathbf{r}, t)\, d\mathbf{r} = 1. \tag{47}$$

This has the advantage that now $G(\mathbf{r}, t)$ can be analyzed as the probability density that two molecules are separated by vector $\mathbf{r}$ at time t, since it is normalized to unity and obeys the Fokker-Planck equation (33). Very little is known on the rototranslational three-body density $n_3(\mathbf{r}, \mathbf{r}', \mathbf{u}_1, \mathbf{u}_2, \mathbf{u}_3, t|N, \upsilon)$. Since we need only $n_3(\mathbf{r}, \mathbf{r}', \mathbf{u}_1, \mathbf{u}_2, \mathbf{u}_3, t|2, 2/\rho_0)$, we assume that, *for this specific value*, we can make the mean-field estimate

$$n_3\left(\mathbf{r}, \mathbf{r}', \mathbf{u}_1, \mathbf{u}_2, \mathbf{u}_3, t|2, \frac{2}{\rho_0}\right) \approx \rho_0 W_3(\mathbf{u}_1, \mathbf{u}_2, \mathbf{u}_3, t) G(\mathbf{r}, t) G(\mathbf{r}', t), \tag{48}$$

where W_3 is the three-body orientational probability density. Next, we make use of Eqs. (32), (33), (47), and (48) in conjunction with Eq. (30) with $N = 2$ and $\upsilon = 2/\rho_0$ which we integrate with respect to $\mathbf{r}$ over $\upsilon = 2/\rho_0$ to obtain finally the desired equation

$$\begin{aligned}\frac{\partial W_2}{\partial t}(\mathbf{u}_1, \mathbf{u}_2, t) = {}& D_R \sum_{i=1}^{2} \nabla_{\mathbf{u}_i} \cdot \{\nabla_{\mathbf{u}_i} W_2(\mathbf{u}_1, \mathbf{u}_2, t) + \beta W_2(\mathbf{u}_1, \mathbf{u}_2, t) \nabla_{\mathbf{u}_i} [V_1(\mathbf{u}_1, t) + V_1(\mathbf{u}_2, t)]\} \\ & + \beta D_R \sum_{i=1}^{2} \nabla_{\mathbf{u}_i} \cdot [W_2(\mathbf{u}_1, \mathbf{u}_2, t) \nabla_{\mathbf{u}_i} U_m(\mathbf{u}_1, \mathbf{u}_2, t)] + \beta D_R \sum_{i=1}^{2} \nabla_{\mathbf{u}_i} \cdot \left(\int \nabla_{\mathbf{u}_i} U_m(\mathbf{u}_i, \mathbf{u}_3, t) W_3(\mathbf{u}_1, \mathbf{u}_2, \mathbf{u}_3, t)\, d\mathbf{u}_3 \right),\end{aligned} \tag{49}$$

where we have introduced the mean-torque orientational pair potential U_m, *viz.,*

$$U_m(\mathbf{u}_1, \mathbf{u}_2, t) = \int_{\frac{2}{\rho_0}} U_{\mathrm{int}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2) G(\mathbf{r}, t) d\,\mathbf{r}. \tag{50}$$

Notice that Eq. (49) with time-independent U_m is the equation that would be obtained for the orientational probability pair density if the polar molecules were rotating at fixed sites randomly distributed in space. Using Eqs. (32) and (50) in Eq. (16) simply yields the exact equation

$$\begin{aligned}&\frac{\partial W_1}{\partial t}(\mathbf{u}_1, t) \\ &\quad = D_R \nabla_{\mathbf{u}_1} \cdot [\nabla_{\mathbf{u}_1} W_1(\mathbf{u}_1, t) + \beta W_1(\mathbf{u}_1, t) \nabla_{\mathbf{u}_1} V_1(\mathbf{u}_1, t)] \\ &\qquad + \beta D_R \nabla_{\mathbf{u}_1} \cdot \left(\int \nabla_{\mathbf{u}_1} U_m(\mathbf{u}_1, \mathbf{u}_2, t) W_2(\mathbf{u}_1, \mathbf{u}_2, t)\, d\mathbf{u}_2 \right).\end{aligned} \tag{51}$$

Equations (49) and (51) constitute the main statistical mechanical equations of this work. With Eqs. (33), (34), and (50), they form a set that must be solved for a specified pair interaction potential U_{int} and externally applied torque specified by V_1, and these equations cannot be solved analytically without making further approximations. Since the spatial part of $n_2(\mathbf{r},\mathbf{u}_1,\mathbf{u}_2,t|N,\upsilon)$ is governed by Eq. (33), which is a Fokker-Planck equation, it may be worthwhile investigating up to which extent Eq. (49) can be approximated by a Fokker-Planck equation too.

V. FOKKER-PLANCK APPROXIMATION FOR EQ. (49)

In order to construct the Fokker-Planck approximation to Eq. (49), one must first start by assuming separation of rotational and translational timescales. This starts by replacing $\bar{U}_{\text{int}}(\mathbf{r},t)$ by $\bar{U}^{\infty}_{\text{int}}(\mathbf{r})$ given by Eq. (40), using $N=2$ and $\upsilon = 2/\rho_0$ in Eq. (33); this leads to Eq. (41) as a specific solution of Eq. (33). Now, assuming that the external field does not noticeably disturb the translational degrees of freedom of the system, we may replace U_m in Eqs. (49), (50), and (51) by U_m^{∞} defined by

$$U_m^{\infty}(\mathbf{u}_1,\mathbf{u}_2) = \int_{\frac{2}{\rho_0}} U_{\text{int}}(\mathbf{r},\mathbf{u}_1,\mathbf{u}_2)G_{\infty}(\mathbf{r})\,d\mathbf{r}, \tag{52}$$

where

$$G_{\infty}(\mathbf{r}) = G(\mathbf{r},\infty). \tag{53}$$

Next, we need to obtain a reasonable estimate of the integrals in Eq. (49) given that we use Eq. (52) in this equation. To this purpose, we introduce the two- and three-body *orientational* distribution functions g and g_3 defined by

$$g(\mathbf{u}_1,\mathbf{u}_2,t) = \frac{W_2(\mathbf{u}_1,\mathbf{u}_2,t)}{W_1(\mathbf{u}_1,t)W_1(\mathbf{u}_2,t)}, \tag{54}$$

$$g_3(\mathbf{u}_1,\mathbf{u}_2,\mathbf{u}_3,t) = \frac{W_3(\mathbf{u}_1,\mathbf{u}_2,\mathbf{u}_3,t)}{W_1(\mathbf{u}_1,t)W_1(\mathbf{u}_2,t)W_1(\mathbf{u}_3,t)}, \tag{55}$$

and the effective pair interaction potential $V_2^{\text{eff}}(\mathbf{u}_1,\mathbf{u}_2,t)$‘ defined by

$$V_2^{\text{eff}}(\mathbf{u}_1,\mathbf{u}_2,t) = U_m^{\infty}(\mathbf{u}_1,\mathbf{u}_2) + V_c(\mathbf{u}_1,\mathbf{u}_2,t), \tag{56}$$

where the complementary potential V_c is defined through the differential equations

$$\nabla_{\mathbf{u}_1}V_c(\mathbf{u}_1,\mathbf{u}_2,t) = \int \nabla_{\mathbf{u}_1}U_m^{\infty}(\mathbf{u}_1,\mathbf{u}_3)W_1(\mathbf{u}_3,t)\frac{g_3(\mathbf{u}_1,\mathbf{u}_2,\mathbf{u}_3,t)}{g(\mathbf{u}_1,\mathbf{u}_2,t)}\,d\mathbf{u}_3 \tag{57}$$

and

$$\nabla_{\mathbf{u}_2}V_c(\mathbf{u}_1,\mathbf{u}_2,t) = \int \nabla_{\mathbf{u}_2}U_m^{\infty}(\mathbf{u}_2,\mathbf{u}_3)W_1(\mathbf{u}_3,t)\frac{g_3(\mathbf{u}_1,\mathbf{u}_2,\mathbf{u}_3,t)}{g(\mathbf{u}_1,\mathbf{u}_2,t)}\,d\mathbf{u}_3. \tag{58}$$

Now, is was shown by Singer [40] that when thermal equilibrium holds, then the Kirkwood superposition approximation (KSA) may be used for g_3. Moreover, in standard DDFT [26], the integral terms are replaced in such a way that the true time evolution is replaced by a sequence of thermal equilibrium states. Following these ideas, we *assume* that g_3 is given by the *instantaneous* KSA, *viz.*,

$$g_3(\mathbf{u}_1,\mathbf{u}_2,\mathbf{u}_3,t) \approx g(\mathbf{u}_1,\mathbf{u}_2,t)g(\mathbf{u}_1,\mathbf{u}_3,t)g(\mathbf{u}_2,\mathbf{u}_3,t). \tag{59}$$

Algebraically, this is advantageous because this allows us to get rid of $g(\mathbf{u}_1,\mathbf{u}_2,t)$ in Eqs. (57) and (58) [however, information regarding $g(\mathbf{u}_1,\mathbf{u}_2,t)$ is not lost since it is contained in W_2 because of Eq. (54)]. Then we assume that the third body with orientation $\mathbf{u}_3$ is "subtracted" from the influence of the two others so that we also set $g(\mathbf{u}_1,\mathbf{u}_3,t) = g(\mathbf{u}_2,\mathbf{u}_3,t) = 1$ in the resulting equations. *With these approximations*, Eqs. (57) and (58) become

$$\nabla_{\mathbf{u}_1}V_c(\mathbf{u}_1,\mathbf{u}_2,t) = \int \nabla_{\mathbf{u}_1}U_m^{\infty}(\mathbf{u}_1,\mathbf{u}_3)W_1(\mathbf{u}_3,t)\,d\mathbf{u}_3 \tag{60}$$

and

$$\nabla_{\mathbf{u}_2}V_c(\mathbf{u}_1,\mathbf{u}_2,t) = \int \nabla_{\mathbf{u}_2}U_m^{\infty}(\mathbf{u}_2,\mathbf{u}_3)W_1(\mathbf{u}_3,t)\,d\mathbf{u}_3, \tag{61}$$

so that V_c can be written down as a sum of single-body potentials U_{an}, *viz.*,

$$V_c(\mathbf{u}_1,\mathbf{u}_2,t) = U_{an}(\mathbf{u}_1,t) + U_{an}(\mathbf{u}_2,t).$$

Next, since V_c is a pair interaction potential, it has global rotational invariance, meaning that $U_{an}(\mathbf{u},t)$ must be an even function of $\mathbf{u}$. Finally, the integrals in Eqs. (60) and (61) run over the orientational degrees of freedom of the third body, which, because of the approximations made, does no longer interact nor with the first, nor with the second, so that $W_1(\mathbf{u}_3,t)$ is actually arbitrary because we have used $g(\mathbf{u}_1,\mathbf{u}_3,t) = g(\mathbf{u}_2,\mathbf{u}_3,t) = 1$ [of course, nothing is stated for $g(\mathbf{u}_1,\mathbf{u}_2,t)$]. At this stage, this suggests that the orientations of the third body coincides either with those of the first or with those of the second and this at arbitrary times. Hence in Eq. (60) we set $W_1(\mathbf{u}_3,t) = \delta(\mathbf{u}_3 - \mathbf{u}_1)$, while in Eq. (61) we set $W_1(\mathbf{u}_3,t) = \delta(\mathbf{u}_3 - \mathbf{u}_2)$ instead. Hence Eqs. (60) and (61) become one and the same differential equation for the (now time-independent) U_{an}, *viz.*,

$$\nabla_{\mathbf{u}_1}U_{an}(\mathbf{u}_1) = \nabla_{\mathbf{u}_1}U_m^{\infty}(\mathbf{u}_1,\mathbf{u}_3)|_{\mathbf{u}_3=\mathbf{u}_1}. \tag{62}$$

entailing in turn that V_c is time independent, *viz.*,

$$V_c(\mathbf{u}_1,\mathbf{u}_2) = U_{an}(\mathbf{u}_1) + U_{an}(\mathbf{u}_2), \tag{63}$$

so that V_2^{eff} is also time independent. Hence,

$$V_2^{\text{eff}}(\mathbf{u}_1,\mathbf{u}_2) = U_m^{\infty}(\mathbf{u}_1,\mathbf{u}_2) + U_{an}(\mathbf{u}_1) + U_{an}(\mathbf{u}_2). \tag{64}$$

Yet Eq. (62) does not account for the fact that the reverse torque must also be included in the solution of the potential theory problem generated by Eqs. (57) and (58). We can make use of the properties of the Dirac delta function and of Newton's third law to demonstrate that we equally well have

$$\nabla_{\mathbf{u}_1}U_{an}(\mathbf{u}_1) = -\nabla_{\mathbf{u}_1}U_m^{\infty}(\mathbf{u}_1,\mathbf{u}_3)|_{\mathbf{u}_3=\mathbf{u}_1},$$

so that Eq. (62) really means

$$\nabla_{\mathbf{u}_1}U_{an}(\mathbf{u}_1) = \pm\nabla_{\mathbf{u}_1}U_m^{\infty}(\mathbf{u}_1,\mathbf{u}_3)|_{\mathbf{u}_3=\mathbf{u}_1}, \tag{65}$$

where the ± sign in this last equation reflects the lack of knowledge we have regarding the effect of the third body on the two others. This lack of knowledge arises from the approximations made, *viz.*, Eq. (48) and the KSA (59). Now, Eq. (65) generates *a priori* plethora of possibilities for fabricating V_2^{eff} from U_m^∞ as all combinations of signs are possible. However, some expressions arising for V_2^{eff} can be eliminated by using the criterion that the location of the stationary points of V_2^{eff} and U_m^∞ must be approximately (if not exactly) the same [examples of application of Eq. (65) are given in our companion paper]. Hence, it follows that Eq. (49) can be approximated by the *Fokker-Planck equation*

$$\frac{\partial W_2}{\partial t} \approx D_R \sum_{i=1}^{2} \nabla_{\mathbf{u}_i} \cdot \left(\nabla_{\mathbf{u}_i} W_2 + \beta W_2 \nabla_{\mathbf{u}_i} \Psi_2^{\text{eff}}\right), \tag{66}$$

where we omitted the arguments of the various functions in this equation for short, and where

$$\Psi_2^{\text{eff}}(\mathbf{u}_1, \mathbf{u}_2, t) = V_2^{\text{eff}}(\mathbf{u}_1, \mathbf{u}_2) + V_1(\mathbf{u}_1, t) + V_1(\mathbf{u}_2, t). \tag{67}$$

All the approximations we have made actually provide an initialization for solving Eqs. (16) and (30) by assuming a specific form for U_{int} and U_m^∞.

VI. KINETIC YBG FORMULATION OF THE DYNAMICAL KIRKWOOD-FRÖHLICH THEORY

As already mentioned in the Introduction, the calculation of the dielectric constant and complex permittivity is generally made of three parts, *viz.,* a macroscopic part, a microscopic statistical-mechanical part, and a calculation of the molecular field in terms of the Maxwell field which allows the relation between the two scales. If dielectric friction is neglected, then it is sufficient to relate the Maxwell field amplitude to that of the effective cavity field, which is the directing field [6]. At zero frequency, the Kirkwood-Fröhlich equation must result, yielding in particular in the zero frequency limit an expression of the Kirkwood correlation factor in terms of molecular parameters only. If spherical shapes for the sample and cavity are selected, the calculations are greatly simplified and should not affect the results for ε and $\varepsilon(\omega)$. Therefore, we recall that in the dielectric sample, the number of molecules N_T composing the substance is made of two subgroups: one, noted N_c, is treated by electrostatics in continuous media, while the other, N, are contained in a volume υ of spherical shape of size much smaller than that of the specimen and is treated by the methods of statistical mechanics. In this section we also assume that the rotational and translational timescales are well separated, so that Eq. (51) explicitly reads

$$\begin{aligned}\frac{\partial W_1}{\partial t}&(\mathbf{u}_1, t)\\ &= D_R \nabla_{\mathbf{u}_1} \cdot [\nabla_{\mathbf{u}_1} W_1(\mathbf{u}_1, t) + \beta W_1(\mathbf{u}_1, t) \nabla_{\mathbf{u}_1} V_1(\mathbf{u}_1, t)]\\ &\quad + \beta D_R \nabla_{\mathbf{u}_1} \cdot \left(\int \nabla_{\mathbf{u}_1} U_m^\infty(\mathbf{u}_1, \mathbf{u}_2) W_2(\mathbf{u}_1, \mathbf{u}_2, t)\, d\mathbf{u}_2\right)\end{aligned} \tag{68}$$

and is an *exact* equation in the time-independent, thermal equilibrium situation. This equation generalizes Eq. (12) of Ref. [41] established in another context.

A. Macroscopic polarization

Let us consider a dielectric sample of spherical shape being subjected to a uniform external field $\mathbf{E}_0(t) = E_0 e^{i\omega t} \mathbf{e}$ arising from a charge distribution which is external to the dielectric. Then the electric field inside the sample (the Maxwell field) is uniform and lags behind the field. It is given by

$$\mathbf{E}(t) = \frac{3E_0\mathbf{e}}{\varepsilon(\omega) + 2} e^{i\omega t} = E(t)\mathbf{e} = \tilde{E}(\omega) e^{i\omega t} \mathbf{e}. \tag{69}$$

The total macroscopic polarization in the direction of the applied field $\mathbf{e}$ which we denote by $\Pi(t)$ is given by

$$\Pi(t) = \varepsilon_0(\varepsilon(\omega) - 1)E(t) = 3\varepsilon_0 \frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) + 2} E_0 e^{i\omega t}, \tag{70}$$

where ε_0 is the absolute permittivity of vacuum. According to the above formula, the "high frequency" polarization $\Pi_{\text{HF}}(t)$ reads ["high frequency" here means that $\varepsilon(\omega)$ is replaced by its value ε_∞ at visible optical frequencies]

$$\Pi_{\text{HF}}(t) = 3\varepsilon_0 \frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} E_0 e^{i\omega t} \tag{71}$$

where it is understood that $\varepsilon_\infty = \mathfrak{n}^2$ and $\mathfrak{n}$ is the Snell-Descartes refractive index. The difference between Eqs. (70) and (71) is

$$\Delta\Pi(t) = \frac{3\varepsilon_0[\varepsilon(\omega) - \varepsilon_\infty]}{\varepsilon_\infty + 2} E(t). \tag{72}$$

Felderhof has shown [42] that the total polarization may consist of a linear combination of partial polarization contributions, each partial contribution being associated with an elementary mechanism of polarization. Customarily, the macroscopic polarization is split into two contributions, one orientational mechanism and a distortional mechanism [22]. The distortional mechanism arises from the molecular polarizability and accounts for visible optical properties of the substance. Therefore, this polarization generally does not lag behind the Maxwell field except maybe in the visible optical absorption region, a region which is out of focus here. For the macroscopic distortional polarization, we have

$$\Pi_{\text{dst}}(t) = \varepsilon_0(\varepsilon_\infty - 1)E(t), \tag{73}$$

where, since we consider frequencies much below visible optical ones, we can take $\varepsilon_\infty = \mathfrak{n}^2$. The orientational polarization mechanism is obtained by subtracting Eq. (73) from (70), *viz.,*

$$\Pi_{\text{or}}(t) = \varepsilon_0[\varepsilon(\omega) - \varepsilon_\infty]E(t) = \frac{\varepsilon_\infty + 2}{3} \Delta\Pi(t), \tag{74}$$

so that

$$\Pi(t) = \Pi_{\text{dst}}(t) + \Pi_{\text{or}}(t). \tag{75}$$

In fact, Eq. (74) is the one to be equated with the microscopic calculation of the molecular polarization. This means that in accomplishing the microscopic polarization calculation, each molecular dipole μ must be affected in its magnitude by the factor $(\varepsilon_\infty + 2)/3$. Therefore, when accomplishing the microscopic calculation which follows, one must interpret μ in Eq. (15) by [6]

$$\mu = \frac{\varepsilon_\infty + 2}{3} \mu_g, \tag{76}$$

where μ_g is the individual dipole moment in the ideal gas phase, which can be found either in tables [8] or computed from quantum *ab initio* calculations. It follows that the cavity is assimilated to a medium in which the polarizability of the molecules is smeared out to form a continuum of dielectric constant $\varepsilon_\infty = \mathfrak{n}^2$ [6], in which case ε_∞ cannot depart too much from 1, e.g., $\varepsilon_\infty < 3$. Equally well, the cavity contains molecules separated by vacuum, nevertheless in which the individual molecular dipole moments are given by Eq. (76). Indeed, in such a physical cavity, the nonelectrostatic interactions are not affected [6], while those invoking the dipoles *are*.

B. Linear microscopic polarization

As mentioned, the microscopic polarization $P(t)$ is given by Eq. (15), but contains all powers of the field strength. It is therefore worthwhile defining a field parameter allowing one to evaluate Eq. (15) up to linear response in the field strength. This parameter is given by

$$\xi(t) = \Xi(\omega)e^{i\omega t} \tag{77}$$

with

$$\Xi(\omega) = \beta\mu E_c(\omega), \tag{78}$$

where $E_c(\omega)$, the amplitude of the field seen by the dipoles has to be related to $E(\omega)$ in some way. Since we are following here Nee and Zwanzig [11] we apply quasielectrostatics, both fields are collinear [4,6]. By expanding the probability density W_1 in perturbation series in the field strength, to linear order we have

$$W_1(\mathbf{u}_1, t) = W_1^{(0)}(\mathbf{u}_1) + \Xi(\omega)\tilde{W}_1^{(1)}(\mathbf{u}_1, \omega)e^{i\omega t} + \cdots, \tag{79}$$

where the superscript (i) denotes the perturbation order in the field strength. We can also write, for the microscopic polarization, the equation

$$P(t) = P^{(0)} + \tilde{P}^{(1)}(\omega)e^{i\omega t} \tag{80}$$

with

$$P^{(0)} = \rho_0\mu\int(\mathbf{u}_1\cdot\mathbf{e})W_1^{(0)}(\mathbf{u}_1)\,d\mathbf{u}_1 = 0 \tag{81}$$

because the equilibrium polarization is zero in zero applied field, and

$$\tilde{P}^{(1)}(\omega) = \rho_0\mu\,\Xi(\omega)\int(\mathbf{u}_1\cdot\mathbf{e})\tilde{W}_1^{(1)}(\mathbf{u}_1, \omega)\,d\mathbf{u}_1 \tag{82}$$

is proportional to the amplitude of the field seen by the dipoles.

C. A general equation for the complex permittivity

As well known [2,6], in the cavity the dipoles see the cavity field $\mathbf{E}_c(t)$ and the reaction field $\mathbf{R}(t)$. Following Evans *et al.* [23,24], we assume that $\mathbf{R}(t)$ is unable to orient the dipoles (i.e., we neglect dielectric friction). Thus, we assume the cavity adapts itself *instantaneously* to all polarization changes so that the total dipole in the cavity does not lag behind the reaction field. This allows us to account for the cavity field only in the statistical mechanical calculations and to apply quasielectrostatics. The resulting cavity field is the Fröhlich field [6] which, for a cavity of spherical shape, has amplitude given by

$$\tilde{E}_c(\omega) = \frac{3\varepsilon(\omega)\tilde{E}(\omega)}{2\varepsilon(\omega) + \varepsilon_\infty} \tag{83}$$

and which direction coincides with that of the Maxwell field and therefore, with that of the externally applied field. Equating now Eq. (82) with $\varepsilon_0(\varepsilon(\omega) - \varepsilon_\infty)\tilde{E}(\omega)$, we have

$$\begin{aligned}&\frac{[\varepsilon(\omega) - \varepsilon_\infty][2\varepsilon(\omega) + \varepsilon_\infty]}{3\varepsilon(\omega)}\\ &\quad= \frac{\beta\rho_0\mu^2}{\varepsilon_0}\int(\mathbf{u}_1\cdot\mathbf{e})\tilde{W}_1^{(1)}(\mathbf{u}_1, \omega)\,d\mathbf{u}_1.\end{aligned} \tag{84}$$

This equation is valid for *any* isotropic polar fluid since we have not specified as yet any specific mechanism by which the one-body density is affected. The Kirkwood correlation factor g_K is given by

$$g_\mathrm{K} = 3\int(\mathbf{u}_1\cdot\mathbf{e})\tilde{W}_1^{(1)}(\mathbf{u}_1, 0)\,d\mathbf{u}_1. \tag{85}$$

Unfortunately, Eqs. (84) and (85) are not very inspiring because correlations (had it been dipole correlations) do not seem to be apparent in these equations. Yet it is possible to relate g_K for simple polar fluids to $W_2(\mathbf{u}_1, \mathbf{u}_2, t)$ (i.e., density correlations) using Eq. (68) and therefore to pair density correlations using the split (32).

D. The complex permittivity in terms of the pair density for simple isotropic polar fluids

For simple isotropic polar fluids, $V_1(\mathbf{u}_1, t)$ is given by the simple expression

$$\beta V_1(\mathbf{u}_1, t) = -\Xi(\omega)(\mathbf{u}_1\cdot\mathbf{e})e^{i\omega t}. \tag{86}$$

We can use a perturbation expansion for $W_2(\mathbf{u}_1, \mathbf{u}_2, t)$ similar to Eq. (79), *viz.,*

$$W_2(\mathbf{u}_1, \mathbf{u}_2, t) = W_2^{(0)}(\mathbf{u}_1, \mathbf{u}_2) + \Xi(\omega)\tilde{W}_2^{(1)}(\mathbf{u}_1, \mathbf{u}_2, \omega)e^{i\omega t}. \tag{87}$$

Then by multiplying Eq. (16) by $(\mathbf{u}_1\cdot\mathbf{e})$, using perturbation theory and integrating we arrive at the following expression for the linear microscopic polarization response, *viz.,*

$$\tilde{P}_1^{(1)}(\omega) = \frac{\rho_0\mu\,\Xi(\omega)\tilde{g}_\mathrm{K}(\omega)}{3(1 + i\omega\tau_D)}, \tag{88}$$

where $\tau_D = (2D_R)^{-1}$ is the free rotational diffusion time, and the dynamical Kirkwood correlation factor $\tilde{g}_\mathrm{K}(\omega)$ is given by

$$\tilde{g}_\mathrm{K}(\omega) = 1 + \frac{\beta}{6}\int\nabla_{\mathbf{u}_1}U_m^\infty(\mathbf{u}_1, \mathbf{u}_2)\cdot\left(\nabla_{\mathbf{u}_1}P_2(\mathbf{u}_1\cdot\mathbf{e}) - 9\frac{\tilde{W}_2^{(1)}(\mathbf{u}_1, \mathbf{u}_2, \omega)}{W_2^{(0)}(\mathbf{u}_1, \mathbf{u}_2)}\nabla_{\mathbf{u}_1}(\mathbf{u}_1\cdot\mathbf{e})\right)W_2^{(0)}(\mathbf{u}_1, \mathbf{u}_2)\,d\mathbf{u}_1\,d\mathbf{u}_2, \tag{89}$$

where $P_2(z)$ is the second-order Legendre polynomial [43]. Equation (89) allows us to define the Kirkwood correlation factor as

$$g_{\mathrm{K}} = \tilde{g}_{\mathrm{K}}(0). \tag{90}$$

It follows that Eq. (84) can be written as follows:

$$\frac{[\varepsilon(\omega)-\varepsilon_\infty][2\varepsilon(\omega)+\varepsilon_\infty]}{3\varepsilon(\omega)} = \frac{\beta\rho_0\mu^2\tilde{g}_{\mathrm{K}}(\omega)}{3\varepsilon_0(1+i\omega\tau_D)}. \tag{91}$$

This equation reduces to the Kirkwood-Fröhlich one for $\omega = 0$, as it must. When intermolecular interactions are completely neglected, Eq. (89) yields $\tilde{g}_{\mathrm{K}}(\omega) = 1$ for arbitrary frequencies. It follows immediately that in this situation, Eq. (91) reduces to the so-called Onsager-Cole equation [37], *viz.*,

$$\frac{[\varepsilon(\omega)-\varepsilon_\infty][2\varepsilon(\omega)+\varepsilon_\infty]}{3\varepsilon(\omega)} = \frac{\beta\rho_0\mu^2}{3\varepsilon_0(1+i\omega\tau_D)}, \tag{92}$$

which was first proposed by Cole [37] on an empirical basis. This shows that the Onsager-Cole equation is valid in very dilute situations, i.e., for $\beta\rho_0\mu^2/\varepsilon_0 \ll 1$, and as such, is equivalent with the Debye equation [1]. Of course, Eq. (92) cannot hold at liquid densities, because in this situation the contribution of interaction torques is significant. If we assume that Eq. (66) is valid, then it is not difficult to realize that $\tilde{g}_{\mathrm{K}}(\omega)$ as given by Eq. (89) can formally be written as the superposition of a constant term and a dynamical term consisting of an infinite sum of Lorentzians, the characteristic times of which, noted τ_i, are the inverse (nonvanishing) eigenvalues of this equation with $V_1 = 0$. Then the permittivity spectrum consists of a microscopic set of relaxation times. We can therefore write Eq. (91) in a formal manner as follows:

$$\frac{[\varepsilon(\omega)-\varepsilon_\infty][2\varepsilon(\omega)+\varepsilon_\infty]}{3\varepsilon(\omega)} = \frac{\beta\rho_0\mu^2 g_{\mathrm{K}}}{3\varepsilon_0(1+i\omega\tau_D)}\left(\Delta_0 + \sum_{i=1}^{\infty}\frac{\delta_i}{1+i\omega\tau_i}\right), \tag{93}$$

where

$$g_{\mathrm{K}}\Delta_0 = 1 + \frac{\beta}{6}\int \nabla_{\mathbf{u}_1}U_m^\infty(\mathbf{u}_1,\mathbf{u}_2) \cdot \nabla_{\mathbf{u}_1}P_2(\mathbf{u}_1\cdot\mathbf{e})W_2^{(0)}(\mathbf{u}_1,\mathbf{u}_2)\,d\mathbf{u}_1\,d\mathbf{u}_2$$

and δ_i is the amplitude of relaxation mode τ_i defined in such a way that

$$\Delta_0 + \sum_{i=1}^{\infty}\delta_i = 1.$$

Equation (93) is reminiscent with Zwanzig's earlier result [9], with the difference nevertheless that one or several of these microscopic timescales may have Arrhenius behavior as a result of including pair intermolecular interactions in a *nonperturbative* manner. For example, it was recently found [34] that for pure dipole-dipole interactions and preferred parallel alignment of dipole pairs, an Arrhenius-Kramers [44] timescale occurs, and the only significant dynamical contribution to Eq. (89) is due to only one eigenvalue for any preferred dipole alignment. The latter result does hold for pure dipole-dipole interactions only, and at this stage of development of the theory, it is not possible to account for g_{K} values ranging between 0.5 and 1 at liquid densities. This is the outermost reason why in some occasions, the explicit calculations presented in Ref. [34] may be found inadequate. Nevertheless, as we show in Ref. [35], it is possible to include more terms in U_m^∞ so that all possible values of g_{K} appear as a function of temperature, even at liquid densities. To conclude with this paragraph, it is possible to obtain an approximate integral formula for g_{K} when Eq. (66) holds. In effect, since this equation is linear, we have, in the static limit, the linear response formula

$$\frac{\tilde{W}_2^{(1)}(\mathbf{u}_1,\mathbf{u}_2,0)}{W_2^{(0)}(\mathbf{u}_1,\mathbf{u}_2)} = (\mathbf{u}_1+\mathbf{u}_2)\cdot\mathbf{e}. \tag{94}$$

By using Eq. (94) together with Eq. (89), we obtain the following equation for g_{K}, *viz.*:

$$g_{\mathrm{K}} = 1 - \frac{2\beta}{3}\int \nabla_{\mathbf{u}_1}U_m^\infty(\mathbf{u}_1,\mathbf{u}_2)\cdot\Big(\nabla_{\mathbf{u}_1}P_2(\mathbf{u}_1\cdot\mathbf{e}) + \frac{9}{4}\nabla_{\mathbf{u}_1}[(\mathbf{u}_1\cdot\mathbf{e})(\mathbf{u}_2\cdot\mathbf{e})]\Big)W_2^{(0)}(\mathbf{u}_1,\mathbf{u}_2)\,d\mathbf{u}_1\,d\mathbf{u}_2. \tag{95}$$

This is the formula which we use in Ref. [35] to compute the Kirkwood correlation factor for some model potentials U_m^∞. Interestingly, the sign of the integral in Eq. (95) depends on the dot product in the integrand, so that comparing g_{K} with 1 to deduce dipolar alignment is more a *ad hoc* procedure and therefore, *is not justified at all* in reality.

E. Relation with previously derived results for g_{K}

Given Eqs. (89) and (95), one may not really see the relation with previously derived results in the area [12,14,15,17]. Nevertheless, it is clear that in Refs. [12,14,15], three-body correlations are neglected while in the work of Bagchi and Chandra [17], many-body interactions are included in a formal manner by functionally expanding the excess free energy in Taylor series about the completely uniform one-body density state, but explicit calculations are made in the mean spherical approximation (MSA) where three-body correlations are certainly neglected. We note that expanding the excess free energy functional is customary in equilibrium classical DFT [19,26]. We can obtain this already derived formula by also stating a reference $n_1^{(0)}$ which is a constant and given by

$$n_{1,\mathrm{ref}}^{(0)}(\mathbf{r}_1,\mathbf{u}_1) = \frac{\rho_0}{4\pi}.$$

In the context of the present theory, this is tantamount to use the replacements

$$W_2^{(0)}(\mathbf{u}_1,\mathbf{u}_2)G_\infty(\mathbf{r}) \to \frac{\rho_0}{(4\pi)^2}G_{2,\mathrm{ref}}(\mathbf{r},\mathbf{u}_1,\mathbf{u}_2),$$
$$U_{\mathrm{int}}(\mathbf{r},\mathbf{u}_1,\mathbf{u}_2) \to U_{\mathrm{int,ref}}(\mathbf{r},\mathbf{u}_1,\mathbf{u}_2)$$

in Eq. (95). For this reference state, the time-independent Eq. (7) in zero V_1 becomes

$$\nabla_{\mathbf{u}_1}\cdot\int \nabla_{\mathbf{u}_1}U_{\mathrm{int,ref}}(\mathbf{r},\mathbf{u}_1,\mathbf{u}_2)G_{2,\mathrm{ref}}(\mathbf{r},\mathbf{u}_1,\mathbf{u}_2)\,d\mathbf{r}\,d\mathbf{u}_2 = 0,$$

which, on using

$$G_{2,\mathrm{ref}}(\mathbf{r},\mathbf{u}_1,\mathbf{u}_2) = e^{-\beta U_{\mathrm{int,ref}}(\mathbf{r},\mathbf{u}_1,\mathbf{u}_2)},$$

can be rewritten

$$\int \nabla^2_{\mathbf{u}_1} G_{2,\mathrm{ref}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2)\, d\mathbf{r}\, d\mathbf{u}_2 = 0. \tag{96}$$

Multiplying the above equation by $P_2(\mathbf{u}_1 \cdot \mathbf{e})$ and integrating with respect to $\mathbf{u}_1$ leads after some algebra to

$$\int P_2(\mathbf{u}_1 \cdot \mathbf{e}) G_{2,\mathrm{ref}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2)\, d\mathbf{r}\, d\mathbf{u}_1\, d\mathbf{u}_2 = 0,$$

so that the term involving $P_2(\mathbf{u}_1 \cdot \mathbf{e})$ in Eq. (95) disappears. Using the aforementioned substitutions in Eq. (95) yields, after some algebra, any of the equivalent g_K expressions

$$\begin{aligned} g_K &= 1 + \frac{3\rho_0}{(4\pi)^2} \int (\mathbf{u}_1 \cdot \mathbf{e})(\mathbf{u}_2 \cdot \mathbf{e}) G_{2,\mathrm{ref}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2)\, d\mathbf{r}\, d\mathbf{u}_1\, d\mathbf{u}_2 \\ &= 1 + \frac{\rho_0}{(4\pi)^2} \int (\mathbf{u}_1 \cdot \mathbf{u}_2) G_{2,\mathrm{ref}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2)\, d\mathbf{r}\, d\mathbf{u}_1\, d\mathbf{u}_2 \\ &= 1 + \frac{\rho_0}{(4\pi)^2} \int (\mathbf{u}_1 \cdot \mathbf{u}_2) H_{2,\mathrm{ref}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2)\, d\mathbf{r}\, d\mathbf{u}_1\, d\mathbf{u}_2 \\ &= 1 + \frac{3\rho_0}{(4\pi)^2} \int (\mathbf{u}_1 \cdot \mathbf{e})(\mathbf{u}_2 \cdot \mathbf{e}) H_{2,\mathrm{ref}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2)\, d\mathbf{r}\, d\mathbf{u}_1\, d\mathbf{u}_2, \end{aligned} \tag{97}$$

where $H_{2,\mathrm{ref}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2) = G_{2,\mathrm{ref}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2) - 1$ is the pair density correlation function for this *completely uniform* one-body density reference state. Since now Eq. (10) yields Eq. (96), it cannot be used for calculating $G_{2,\mathrm{ref}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2)$ explicitly because $U_{\mathrm{int,ref}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2)$ is unknown. Therefore, one has recourse to the constant density Ornstein-Zernike (OZ) relation [14,15,19]

$$\begin{aligned} H_{2,\mathrm{ref}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2) = c_{2,\mathrm{ref}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2) + \frac{\rho_0}{4\pi} \int c_{2,\mathrm{ref}}(\mathbf{r} \\ - \mathbf{r}', \mathbf{u}_1, \mathbf{u}_3) H_{2,\mathrm{ref}}(\mathbf{r}', \mathbf{u}_3, \mathbf{u}_2)\, d\mathbf{r}'\, d\mathbf{u}_3, \end{aligned} \tag{98}$$

where $c_{2,\mathrm{ref}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2)$ is the direct pair density correlation function for this reference state. Then, the OZ relation (98) has to be supplemented by another equation linking $H_{2,\mathrm{ref}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2)$ [or $G_{2,\mathrm{ref}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2)$] and $c_{2,\mathrm{ref}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2)$. A first closure is the virial approximation $U_{\mathrm{int,ref}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2) = U_{\mathrm{int}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2)$, yielding

$$G_{2,\mathrm{ref}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2) = e^{-\beta U_{\mathrm{int}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2)}. \tag{99}$$

This was used by Madden and Kivelson [12], who further treated the dipole-dipole interaction perturbatively, and used also g_K given by the first of Eqs. (97), therefore bypassing Eq. (98) entirely. This, in effect, causes their static theory to be valid at weak densities only. Other standard closures include the hypernetted chain (HNC) approximation

$$\begin{aligned} \beta U_{\mathrm{int,HNC}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2) = \beta U_{\mathrm{int}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2) + c_{2,\mathrm{HNC}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2) \\ - H_{2,\mathrm{HNC}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2), \end{aligned} \tag{100}$$

the Percus-Yevick (PY) approximation

$$\begin{aligned} \beta U_{\mathrm{int,PY}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2) = \beta U_{\mathrm{int}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2) - \ln[1 + H_{2,\mathrm{PY}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2) \\ - c_{2,\mathrm{PY}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2)], \end{aligned} \tag{101}$$

and the MSA already alluded to above, for which $U_{\mathrm{int,MSA}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2) = U_{\mathrm{int}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2)$ but which must be supplemented by extra conditions, *viz.*,

$$\begin{aligned} G_{2,\mathrm{MSA}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2) &= 0, \quad |\mathbf{r}| < r_H, \\ c_{2,\mathrm{MSA}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2) &= -\beta U_{\mathrm{int}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2), \quad |\mathbf{r}| > r_H, \end{aligned} \tag{102}$$

where r_H is a hard sphere radius. Analytical results have been obtained by Wertheim [14] in the MSA. In all other situations, numerical calculations have to be performed. Tani, Henderson, Barker, and Hecht [45] have used the second of Eqs. (97) (the third is the same as the second) and simulated g_K using a density perturbation theory. These authors find ultimately that the Debye equation with a density perturbed Kirkwood correlation factor seems to provide a good starting point for calculating the dielectric constant of polar fluids; however, it is evident that their proposition cannot work for liquid densities. Carnie and Patey [46] use a special version of HNC quoted as linear HNC (LHNC) and quadratic HNC (QHNC) detailed in Ref. [15]. Their calculations of the dielectric constant are always performed for $\varepsilon_\infty = 1$, but include induced moments in the statistical part. Comparing their results with the temperature dependence of the static dielectric constant of water, agreement is found between theory and experiment regarding the temperature dependence of ε. However, the agreement is not overemphasized, because the HNC equation is again an approximation to the closure of the OZ equation (98), the range of validity of which is unknown (since it results from a truncated functional Taylor expansion [19]). Moreover, within their calculations they find $\varepsilon \approx 25$ at 25 °C when the effect of molecular polarizability is neglected, while in the same situation, Onsager's theory renders $\varepsilon \approx 18$ when $\varepsilon_\infty = 1$. When the polarizability of the molecules is included in the calculation, Onsager's theory yields $\varepsilon = 29$ when $\varepsilon_\infty = \mathrm{n}^2$, i.e., when the polarizability of the molecules is included, while in this situation Carnie and Patey find $\varepsilon = 80$, and when the quadrupolar contribution is included in the calculation of their effective dipole, the water dielectric constant is further increased by 50%. *Therefore, the Carnie-Patey result neglecting the polarizability of the molecules coincides with Onsager's result when the polarizability of the molecules are included.* Since they use an effective dipole moment $\mu_e = 2.56$ D, this renders, if the induced molecular dipole is included in their calculation $g = 2.37$ at 25°C, $g = 2.33$ at 0° and $g = 2.19$ at 100 °C. Therefore, their g factor seems to oscillate between the freezing and the boiling point, and varies by 8% between 25 °C and the boiling point, while experimentally it is found that g_K is almost constant for water between the freezing and the boiling point (the experimental temperature variation of g_K is about 0.7% across the whole temperature range, and is monotonic, with an experimental uncertainty of less than 5%). Therefore, we believe that in spite of the fact that their theory was undeniably a progress at the time of writing and that it agrees with the temperature variation of the dielectric constant of liquid water, their g factor *is not the Kirkwood correlation factor as usually deduced from experimental data* [6], so that their theory is not amenable to comparison with experiment *at all.*

Actually, it is very difficult to compute the proper $H_{2,\mathrm{ref}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2)$ because there is no definite simple way to close Eq. (98) *exactly* when the reference one-body density is $n_1 = \rho_0/(4\pi)$, *viz.,* the uniform one-body density because in a polar fluid, the true one-body density may strongly deviate from this constant value. In other words, it is well possible that the standard functional Taylor expansion of the excess free energy functional about the constant one-body density as a reference state needs higher order terms than the second. How many terms should be included in this expansion is difficult to state, because one has to solve higher many-body OZ equations and also to find the adequate closures. We refer the reader to Lee's paper for more on OZn equations [47], particularly on OZ2 equations.

VII. DISCUSSION

After a long statistical mechanical treatment of the kinetic YBG hierarchy generated by the Langevin equations (3) and (4), we have derived an equation for the complex permittivity of any isotropic polar fluid, Eq. (84). This equation shows that there is no real need to explicitly involve equilibrium dipole correlations in the theory. However, it is not very inspiring because it remains formal. Nevertheless, for simple polar fluids, the expression for the one-body potential V_1 is relatively simple, and this allows one to make explicit further Eq. (84), leading to Eq. (91), which trivially reduces to the Kirkwood-Fröhlich equation at zero frequency and involves the equilibrium and linear response of the orientational probability density W_2. Moreover, the Kirkwood correlation factor is the zero frequency limit of Eq. (89), which clearly shows that g_{K} may be less or larger than 1, and also that pair dipole order has little to do with comparing g_{K} with unity. Rather, Eq. (95) shows, using steepest descents arguments, that dipolar order can be traced from the minima of the effective orientational interaction potential V_2^{eff}, therefore from those of U_m^∞. As shown in Ref. [35], for a specific U_m^∞, the outcomes of the static theory is successfully compared with the temperature dependence of the dielectric constant of not less than 14 polar liquids with various dipolar order and of very different nature (in reality, the static version of the present theory has been tested for a much larger number of polar fluids with the same success, and more importantly, with the *same* potential). The failure of the theory for glycerol (and probably for propylene glycol, propylene carbonate and other glass formers) is not to seek on a specific H-bonding mechanism, because otherwise the theory would also fail for water and monohydroxy alcohols where clearly, H bonding is present. Nevertheless, the theory is sometimes able to interpret the temperature variation of the static dielectric constant of some glass formers such as tributyl phosphate (TBP), where the relative angle between pairs spreads across the range 0–97°, and a resulting Kirkwood correlation factor larger than 1, in spite of the absence of H bonding [35]. Now, we insist that Eq. (95) *does not work* for most glass formers. For example, glycerol is supercooled at room temperature and is a natural glass former. Moreover, the floppiness of the molecules makes this polar liquid rather special. Those specificities are not included in Ref. [35], and work on these glass-forming polar substances within the present theory is in progress.

Next, Eqs. (89) and (95) shows that contrarily to what is currently believed, g_{K} has little to do with the pair distribution function $\mathfrak{g}(\mathbf{r})$, because as we have demonstrated, $\mathfrak{g}(\mathbf{r})$ is not a thermal equilibrium quantity in liquids. Rather, the quantity to consider for g_{K} is $G_\infty(\mathbf{r})$, i.e., the probability density that two molecules are separated by vector $\mathbf{r}$ at thermal equilibrium. This is because at infinite times, $G_{VH}^{(d)}(\mathbf{r}, 0, \infty)$ is the number density ρ_0 [36] and does no longer depend on $\mathbf{r}$, while $G_\infty(\mathbf{r}) = G(\mathbf{r}, \infty) = G_{VH}^{(d)}(\mathbf{r}, \infty, \infty)$ *still depends* on $\mathbf{r}$. This subtlety does not seem to have been appreciated before in the area. Also, we have clearly shown that comparing g_{K} with 1 to deduce pair dipole alignment is an unjustified criterion which has, in fact, no established theoretical grounds.

Furthermore, we have shown that when the orientational pair probability density obeys the Fokker-Planck equation (66), then the complex permittivity spectrum consists of an infinite discrete set of relaxation times. This is reminiscent of Zwanzig's theory of dielectric relaxation where dipoles are located at sites of a simple cubic lattice [9]. The differences with Zwanzig's theory are that our dipoles are not located at lattice sites, that the present treatment is not perturbative and that intermolecular interactions may lead to thermally activated behavior of Arrhenius-Kramers type [44] for some of these relaxation timescales (an example where this occurs for one of these timescales is Ref. [34]). Again, this is demonstrated for the first time and is important, because in the context of fractional Brownian motion in a force field, the timescales occurring in the latter can be *analytically* related to those of *normal* Brownian motion in a force field [30]. This has explicitly been done for the Cole-Cole distribution, but remains still to be achieved for the more general (but extremely useful in practice) Havriliak-Negami one [10], and represents a major issue.

Our derivations strongly indicate that the Onsager-Cole [37] equation (92) is valid when the polar fluid under study is very dilute which was not rigorously explained before. This clearly follows because the sole microscopic timescale in this equation is the bare rotational diffusion time. Therefore, it also follows that its zero-frequency limit, i.e., Onsager's equation, is definitely valid when intermolecular interactions are neglected in the statistical mechanical calculation. The MSA dynamical equation adapted to our geometry gives

$$\frac{[\varepsilon(\omega) - \varepsilon_\infty][2\varepsilon(\omega) + \varepsilon_\infty]}{3\varepsilon(\omega)} = \frac{\beta\rho_0\mu^2 g_{\mathrm{K}}^{MSA}}{3\varepsilon_0(1 + i\omega\tau_D)}, \qquad (103)$$

where g_{K}^{MSA} is the value of the Kirkwood correlation factor computed with MSA [14]. This equation is also valid at weak densities, since no explicit thermally activated timescale emerges. Equation (103) is the Bagchi-Chandra result [17] at zero wave vectors, who found in this situation that the collective dipole correlation function decays with a single relaxation time τ_D. Nevertheless, in spite of their limited range of applicability, the Onsager-Cole and Bagchi-Chandra results are *benchmark ones* to which any theory of dielectric relaxation of interacting polar molecules must reduce in the weak density limit, and are therefore useful from both the theoretical and experimental points of view since they may help for dielectric specimens which are very diluted in nonpolar solvents.

The present results can be applied with minimal modifications to model the linear and nonlinear dynamic susceptibilities of isotropic dipolar suspensions. In the mean-field approximation valid at weak densities and for preferred antiparallel alignment, the nonlinear dielectric susceptibilities have been considered earlier [48], while the same was done by suitably adapting Berne's theory [38] to magnetic relaxation of randomly distributed magnetic nanoparticles in space [49]. Considering linear response and dipole dipole interactions beyond the mean-field approximation [34], the theory agrees very well with Ivanov's modified mean-field theory at weak densities [41,50,51], and provides a general framework to handle dipolar systems where density effects can become large.

A word should also be said about the solution of Eq. (42). An analytical solution is definitely possible for the hard sphere spherically symmetric interaction potential (which ignores dipole orientations), and in this situation $\rho_0\mathfrak{g}(\mathbf{r})$ definitely exhibits the characteristic spatial oscillations seen in the simulations of the same quantity for simple liquids [19]; this is therefore encouraging. Now, before solving it for the Stockmayer fluid (i.e., a fluid for which the interaction potential consists of a spherically symmetric Lennard-Jones potential plus dipole-dipole interactions, which would be of most interest here), one should consider the solution for the Lennard-Jones one, which is a purely spherically symmetric repulsive singular potential at short intermolecular separations and has one attractive potential well. To this aim, phase integral methods seem well indicated [39,52] and certainly promising. However, the potential in Eq. (42) is not U_{int}, rather it is V_S defined by Eq. (43). Partial wave analysis [39,53] shows that V_S plus the centrifugal potential unfortunately exhibits, for most "partial waves," three classical turning points, and we have not been able up to now to find a good uniform approximation [52] that would allow one to solve the problem (matching WKBJ-like solutions is possible when the three classical turning points are well separated). On the other hand, numerical solutions of Eq. (42) are difficult because the boundary conditions, being analogous with those of a stationary quantum-mechanical scattering problem, are known asymptotically only. Nevertheless, as all spatial integrals involved in the proposed dielectric theory converge due to their limited extension in space, we believe, especially because of the results presented in Ref. [35], that the theoretical developments given here will allow one to *quantitatively* model the temperature behavior of the static dielectric constant of quite a number of polar fluids, had these been complex ones.

A satellite (but important) comment must be made concerning the frequency range of validity of our results as in fact, they can be applied both to electric and spherical magnetic dipoles of fine magnetic particle assemblies without magnetocrystalline anisotropy. Regarding dielectrics, the result is evident: as molecular inertia has been ignored, the far-infrared region relevant to the THz frequency range is clearly excluded, and our results are valid in the nonresonant microwave absorption region (GHz range and below). Duncan and Camp have calculated natural (individual) resonance frequencies of interacting polar fluids by both molecular dynamics simulations and analytically [54]. Because of ignoring inertial effects in the theory, comparison with the work of Duncan and Camp cannot be achieved here. For magnetic dipoles of fine magnetic particles, resonance effects occur in the GHz range, however, our theory ignores gyroscopic effects, so that our results are restricted to an upper frequency of 10–100 MHz maximum.

The thermodynamics of polar fluids is also an important question. It was investigated for example in Refs. [55–57] both in zero and nonzero externally applied fields, theoretically and with the help of Monte Carlo simulations, and where the theory is developed for low to moderate densities. Here it must be mentioned that our $G(\mathbf{r}, t)$ in general differs from the function which should be used to describe the thermodynamic state of the fluid, although at times related, and all this is explained in Appendix B. Briefly stated, when a thermodynamic phase transition (such as the gas-liquid phase transition) is completed, $G(\mathbf{r}, t)$ relaxes from the value $\rho_0\mathfrak{g}(\mathbf{r})$ it had during the phase transition to its equilibrium value $G_\infty(\mathbf{r})$ in the stabilized reached phase. Both functions are dependent on pair dipole order as shown in Appendix B. As long as the density is weak in the sense $\rho_0\mu^2/\varepsilon_0 \ll 3kT$, our results agree with those of Refs. [55–57] in all respects as the value of the density at which the phase transition occurs is not yet reached. Indeed, they may undoubtedly differ at larger ones, particularly at liquid densities where $\rho_0\mu^2/\varepsilon_0 > 3kT$ because $G_\infty(\mathbf{r})$ noticeably differs from $\rho_0\mathfrak{g}(\mathbf{r})$, and in this situation, the concerned phase is generally the liquid one [for liquid water at room temperature, $\beta\rho_0\mu^2/(3\varepsilon_0) \approx 10$ even if $\mu = 1.85$ D is not corrected by its refractive index, while in ferrofluids the situation is different as the analogous ratio is generally less than 1; see the works by Ivanov, Camp, and co-workers [55–57]]. In the situation $\rho_0\mu^2/\varepsilon_0 > 3kT$, thermodynamic virial expansions are irrelevant because, strictly speaking, they pertain to the dense gas approaching the gas-liquid phase transition, for which $\rho_0\mu^2/\varepsilon_0 < 3kT$. However, accomplishing a full discussion of the thermodynamics of polar fluids is out of scope here, and we hope to come back to this problem in future work. Indeed, in our view this specific topic still remains an open question.

The statistical-mechanical part of the theory also includes as special cases the Maier-Saupe theory of nematic liquid crystals, the Debye-Fröhlich model of dielectric relaxation, Brown's theory of superparamagnetism, etc. (see Ref. [30] for a clear and enlightening description of all these models) and is therefore *extremely versatile*.

VIII. SUMMARY AND CONCLUSIONS

In this work, we have given a complete and versatile theory of linear dielectric relaxation of polar fluids that reduces to known results in a tranparent manner. Our main theoretical results are Eqs. (32), (33), (49), (66), (84), (89), (93), and (95). In order to start legitimating the theory, the outcomes of its static version with Eq. (95) as a representation of the Kirkwood correlation factor is compared in a companion paper [35] with the temperature dependence of not less than 14 polar fluids which are of various nature (associated, nonassociated, glass-forming, non-glass-forming, etc). *Quantitative* agreement is found on what we may call simple polar fluids. Moreover, the present theory is also able to predict thermally activated microscopic timescales *analytically*, which was not possible before. Hence we may quote the present kinetic YBG theory as a largely successful approach to rototranslational relaxation when applied to dielectric relaxation of simple polar fluids and magnetic relaxation of fine ferromagnetic particles.

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APPENDIX A: DERIVATION OF EQ. (32)

Because we can introduce a one-body orientational probability density via Eq. (14) that does depend on (N, υ) only via the *constant* ratio $\rho_0 = N/\upsilon$ and because we can obtain an exact equation of motion for it involving $n_2(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t|N, \upsilon)$, Eq. (16) suggests in turn the introduction of a two-body orientational probability density $W_2(\mathbf{u}_1, \mathbf{u}_2, t)$ that also depends on (N, υ) only through the *constant* ratio ρ_0. We introduce the orientational pair probability density via the equation

$$g_\rho(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t|N, \upsilon) = \frac{n_2(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t|N, \upsilon)}{\rho_0 W_2(\mathbf{u}_1, \mathbf{u}_2, t)}, \tag{A1}$$

where the meaning of g_ρ will become clear later. It is evident that g_ρ may be written as a sum of an orientational-independent part G and an orientational-dependent part δg_ρ [this can be shown by expanding g_ρ in spherical harmonics $Y_{LM}(\mathbf{u}_1)Y_{JK}(\mathbf{u}_2)$ [58]]. Therefore,

$$g_\rho(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t|N, \upsilon) = G(\mathbf{r}, t|N, \upsilon) + \delta g_\rho(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t|N, \upsilon), \tag{A2}$$

where, *a priori*, δg_ρ is not small. Then, because we have

$$\int n_2(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t|N, \upsilon)\, d\mathbf{r}\, d\mathbf{u}_1\, d\mathbf{u}_2 = \rho_0(N-1), \tag{A3}$$

we use Eqs. (A1) and (A2) in conjunction with Eq. (A3) to obtain

$$\int G(\mathbf{r}, t|N, \upsilon)\, d\mathbf{r} + \int \delta g_\rho(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t|N, \upsilon) W_2(\mathbf{u}_1, \mathbf{u}_2, t)\, d\mathbf{r}\, d\mathbf{u}_1\, d\mathbf{u}_2 = N-1, \tag{A4}$$

where we have used $\int W_2\, d\mathbf{u}_1\, d\mathbf{u}_2 = 1$ since by its definition, W_2 is a probability density. This equation is valid for arbitrary times. Now, the contribution of each term in Eq. (A4) is a matter of choice since g_ρ is unknown. Therefore, without any loss of generality, we *make the choice* that for arbitrary times, we have

$$\int G(\mathbf{r}, t|N, \upsilon)\, d\mathbf{r} = N-1, \tag{A5}$$

$$\int \delta g_\rho(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t|N, \upsilon) W_2(\mathbf{u}_1, \mathbf{u}_2, t)\, d\mathbf{r}\, d\mathbf{u}_1\, d\mathbf{u}_2 = 0. \tag{A6}$$

Now, it is known from neutron scattering experiments [19] that the radial pair distribution function vanishes when $r = |\mathbf{r}|$ is beyond a certain value r_H (a hard sphere radius, which may vanish) and that its *slope* below r_H *and* above a certain *finite* value r_C (which may be infinite) is also zero. Physically, the same properties must hold for g_ρ since the properties of the radial pair distribution function is proportional to n_2. Therefore, since n_2 is positive, we must necessarily have the set of conditions (which include boundary conditions)

$$\nabla_{\mathbf{r}} G(\mathbf{r}, t|N, \upsilon)|_{r \leqslant r_H} = \mathbf{0}, \tag{A7a}$$

$$\nabla_{\mathbf{r}} G(\mathbf{r}, t|N, \upsilon)|_{r \geqslant r_C} = \mathbf{0}, \tag{A7b}$$

$$G(\mathbf{r}, t|N, \upsilon)|_{r \leqslant r_H} = 0, \tag{A7c}$$

$$\nabla_{\mathbf{r}} \delta g_\rho(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t|N, \upsilon)|_{r \leqslant r_H} = \mathbf{0}, \tag{A7d}$$

$$\nabla_{\mathbf{r}} \delta g_\rho(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t|N, \upsilon)|_{r \geqslant r_C} = \mathbf{0}, \tag{A7e}$$

$$\delta g_\rho(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t|N, \upsilon)|_{r \leqslant r_H} = 0. \tag{A7f}$$

Now, by accounting of Eqs. (A5)–(A7f), we use $n_2(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t|N, \upsilon)$ given by Eq. (A1), use the split (A2), insert this into Eq. (30), integrate the resulting equation over $(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2)$, and make use of Gauss's theorem on the $\mathbf{r}$ part to obtain

$$\int \{\nabla_{\mathbf{r}} \cdot [\nabla_{\mathbf{r}} \delta g_\rho(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t|N, \upsilon) + \beta \delta g_\rho(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t|N, \upsilon) \nabla_{\mathbf{r}} U_{\text{int}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2)]\} W_2(\mathbf{u}_1, \mathbf{u}_2, t)\, d\mathbf{r}\, d\mathbf{u}_1\, d\mathbf{u}_2 = 0.$$

Since W_2 is positive, the above equation can be satisfied at arbitrary times and for arbitrary υ only if we have

$$\nabla_{\mathbf{r}} \cdot [\nabla_{\mathbf{r}} \delta g_\rho(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t|N, \upsilon) + \beta \delta g_\rho(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t|N, \upsilon) \nabla_{\mathbf{r}} U_{\text{int}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2)] = 0. \tag{A8}$$

The solution of Eq. (A8) can be written

$$\delta g_\rho(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t|N, \upsilon) = K_0(\mathbf{u}_1, \mathbf{u}_2, t) \exp[-\beta U_{\text{int}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2)] + f_0(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t), \tag{A9}$$

where K_0 is a function of rotational degrees of freedom and time only, and f_0 is an arbitrary regular solution of Eq. (A8). Applying the boundary conditions Eqs. (A7d) and (A7e) yields an overdetermination of K_0, save if $K_0 = 0$ [which implies that f_0 also verifies Eqs. (A7a) and (A7b)]. Since f_0 is also a solution of Eq. (A8), we may write

$$f_0(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t) = K_1(\mathbf{u}_1, \mathbf{u}_2, t) \exp[-\beta U_{\text{int}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2)] + f_1(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t),$$

where K_1 and f_1 are of the same nature as K_0 and f_0 are. Since f_0 is an arbitrary solution of Eq. (A8) satisfying the boundary conditions Eqs. (A7a) and (A7b), K_1 is overdetermined save if $K_1 = 0$. We may iterate this process at infinity, finally leading to $f_0 = f_1 = \cdots = 0$. Hence,

$$\delta g_\rho(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t|N, \upsilon) = 0, \tag{A10}$$

which trivially verifies Eq. (A6) at arbitrary times. Therefore, we conclude that

$$n_2(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2, t|N, \upsilon) = \rho_0 W_2(\mathbf{u}_1, \mathbf{u}_2, t) G(\mathbf{r}, t|N, \upsilon),$$

which is Eq. (32).

APPENDIX B: MORE ON THE TIME-INDEPENDENT VALUES OF $G(\mathbf{r}, t)$

In this Appendix we briefly discuss the relation of the time-independent values of the function $G(\mathbf{r}, t)$ that is a solution of the Fokker-Planck equation (33) with the various quantities occurring in the thermodynamics of simple liquids, and evaluate its thermal equilibrium value $G_\infty(\mathbf{r})$ explicitly for a simple case.

1. Relation with previous formalisms

First, let us mention that the Fokker-Planck equation (33), although looking standard and simple, is in fact very difficult to solve, except at thermal equilibrium where its solution is $G_\infty(\mathbf{r})$ as provided by Eq. (39). Therefore we mostly focus on this function in this Appendix. As alluded to in the text, $G_\infty(\mathbf{r})$ is a probability density and has units of inverse volume. It is therefore *fundamentally* different from the pair distribution function averaged over its rotational degrees of freedom. In order to see this, we use the split (32), the standard expression (19) in its time-independent version, and Eq. (17). We write

$$\rho_0 G_\infty(\mathbf{r}) = \frac{1}{\upsilon} \int n_1\left(\mathbf{R} + \frac{\mathbf{r}}{2}, \mathbf{u}_1\right) n_1\left(\mathbf{R} - \frac{\mathbf{r}}{2}, \mathbf{u}_2\right) G_2\left(\mathbf{R} + \frac{\mathbf{r}}{2}, \mathbf{u}_1, \mathbf{R} - \frac{\mathbf{r}}{2}, \mathbf{u}_2\right) d\mathbf{R}\, d\mathbf{u}_1\, d\mathbf{u}_2, \tag{B1}$$

where in the right-hand side we deleted the time argument of the functions in order to state that the latter are thermal equilibrium quantities. The YBG partial density $n_1(\mathbf{r}_1, \mathbf{u}_1)$ is the time-independent thermal equilibrium solution of Eq. (7), which is exactly given by the solution of the self-consistent equation (using a time-independent V_1 for simplicity)

$$n_1(\mathbf{r}_1, \mathbf{u}_1) = \frac{N \exp\{-\beta[V_1(\mathbf{u}_1) + \Phi_1(\mathbf{r}_1, \mathbf{u}_1)]\}}{\int \exp\{-\beta[V_1(\mathbf{u}_1) + \Phi_1(\mathbf{r}_1, \mathbf{u}_1)]\}\, d\mathbf{r}_1\, d\mathbf{u}_1}, \tag{B2}$$

where Φ_1 is a one-body potential containing the effect of pair interactions and obeys the partial differential equations

$$\nabla_{\mathbf{r}_1} \Phi_1(\mathbf{r}_1, \mathbf{u}_1) = \int \nabla_{\mathbf{r}_1} U_{\text{int}}(\mathbf{r}_1 - \mathbf{r}_2, \mathbf{u}_1, \mathbf{u}_2) n_1(\mathbf{r}_2, \mathbf{u}_2) G_2(\mathbf{r}_1, \mathbf{u}_1, \mathbf{r}_2, \mathbf{u}_2)\, d\mathbf{r}_2\, d\mathbf{u}_2,$$

$$\nabla_{\mathbf{u}_1} \Phi_1(\mathbf{r}_1, \mathbf{u}_1) = \int \nabla_{\mathbf{u}_1} U_{\text{int}}(\mathbf{r}_1 - \mathbf{r}_2, \mathbf{u}_1, \mathbf{u}_2) n_1(\mathbf{r}_2, \mathbf{u}_2) G_2(\mathbf{r}_1, \mathbf{u}_1, \mathbf{r}_2, \mathbf{u}_2)\, d\mathbf{r}_2\, d\mathbf{u}_2.$$

As is apparent from Eq. (B2), n_1 is not $\rho_0/(4\pi)$ in general and its properties are absolutely nontrivial even in the absence of externally applied fields $V_1 = 0$, a situation which we consider in the following. Then if $\Phi_1 = 0$ (i.e., the purely noninteracting case), Eq. (B2) indeed yields

$$n_1(\mathbf{r}_1, \mathbf{u}_1) = \frac{\rho_0}{4\pi}. \tag{B3}$$

Then $G_2 = 1$ and Eq. (B1) renders, at thermal equilibrium

$$G_\infty(\mathbf{r}) = \rho_0, \tag{B4}$$

that is, the probability density that two noninteracting molecules are separated by $\mathbf{r}$ at thermal equilibrium is just the number density and is uniform, as it must. In this situation alone, $G_\infty(\mathbf{r}) = \rho_0 \mathfrak{g}(\mathbf{r})$ as $\mathfrak{g}(\mathbf{r}) = 1$ at all temperatures for the ideal gas.

Departing from the noninteracting situation slightly is difficult, however, it is customary to *assume* that in such a situation, Eq. (B3) holds, but $G_2 \neq 1$. This is the usual virial situation, and in this situation, we have

$$G_2(\mathbf{r}_1, \mathbf{u}_1, \mathbf{r}_2, \mathbf{u}_2) = \exp[-\beta U_{\text{int}}(\mathbf{r}_1 - \mathbf{r}_2, \mathbf{u}_1, \mathbf{u}_2)], \tag{B5}$$

which means that the integral terms are entirely neglected in the time-independent Eq. (10), and that G_2 is a function of the separation $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ and molecular orientational degrees of freedom only. In this situation, three-body effects are completely neglected, and we have

$$G_\infty(\mathbf{r}) = \rho_0 \bar{G}_2(\mathbf{r}), \tag{B6}$$

where

$$\bar{G}_2(\mathbf{r}) = \frac{1}{(4\pi)^2 \upsilon} \int G_2\left(\mathbf{R} + \frac{\mathbf{r}}{2}, \mathbf{u}_1, \mathbf{R} - \frac{\mathbf{r}}{2}, \mathbf{u}_2\right) d\mathbf{R}\, d\mathbf{u}_1\, d\mathbf{u}_2 = \frac{1}{(4\pi)^2} \int G_2(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2)\, d\mathbf{u}_1\, d\mathbf{u}_2 \tag{B7}$$

is the pair distribution function at equilibrium, and again coincides with $\mathfrak{g}(\mathbf{r})$. The virial coefficients can then be computed from the equilibrium density pair correlation function $\bar{H}_2$ defined by

$$\bar{H}_2(\mathbf{r}) = \bar{G}_2(\mathbf{r}) - 1 = \frac{G_\infty(\mathbf{r})}{\rho_0} - 1, \tag{B8}$$

where here again it is clear that $\mathfrak{g}(\mathbf{r})$ is a thermal equilibrium quantity. As commented in Sec. VI E, the situation becomes more difficult for higher densities, because Eq. (10) with n_1 given by Eq. (B3) is no longer explicitly exploitable. Nevertheless, the *forced* choice $n_1 = \rho_0/(4\pi)$ implies the following statement: for arbitrary densities, *given* $n_1 = \rho_0/(4\pi)$ we must have

$$G_2(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2) = \exp[-\beta \phi_2(\mathbf{r}, \mathbf{u}_1, \mathbf{u}_2)] \tag{B9}$$

and ϕ_2 obeys differential equations some of which are given in Sec. III, but as already stated in Sec. VI E, serves as a reference potential energy and can no longer coincide with the ϕ_2 alluded to in the main text of the present paper. Now, the point is that $\bar{G}_2$ may still be given by Eq. (B7) but its link to $G_\infty(\mathbf{r})$ is absolutely nontrivial. The reason for this is suggested in Secs. III B and VI E : it is not easy to compute G_2 nor it is easy to compute n_2 *because it is not easy to compute* n_1 (and G_2 is given by Eq. (19) where time arguments can be omitted). And in fact, the reason is that if we start with the virial approximation (B7), then matter is in a gaseous state where molecules interact weakly, $U_{\text{int}} \ll kT$. Increasing the density then G_2 is given by (B9) where it is evident that the density effects are yet small, because if they were not, n_1 would be given by solving Eq. (B2), which, in general, renders a nonconstant n_1. Now, $\mathfrak{g}(\mathbf{r}) = 1 + \mathfrak{h}(\mathbf{r})$ is, as we have seen, related to the initial value of the Van Hove function. This is the value of G/ρ_0 to be used as long as a thermodynamic phase transition is not completed. According to standard thermodynamics, for the gas-liquid transition one has to wait that all the gas volume is transformed into the liquid state in order for the thermodynamic phase transition to be complete. Then, when *it is completed*, $G(\mathbf{r}, t)$ *relaxes* from $\rho_0 \mathfrak{g}(\mathbf{r})$ to its equilibrium value $G_\infty(\mathbf{r})$ which for the liquid phase, is not so easily related to G_2 except by Eq. (B1). Furthermore, this argument suggests that $\mathfrak{g}(\mathbf{r})$ is *not* a thermal equilibrium quantity for the liquid phase. Hence we conclude from all this that the thermodynamics of polar fluids is still an open question that deserves further attention, more profound than what has been given earlier.

2. An explicit evaluation of $G_\infty(\mathbf{r})$ for pure dipole-dipole interactions

In Refs. [33–35], it is shown that for pure dipole-dipole interactions, $W_2^{(0)}(\mathbf{u_1}, \mathbf{u_2})$ is explicitly given by

$$W_2^{(0,\mp)}(\mathbf{u_1}, \mathbf{u_2}) = \frac{1}{Z_2} \exp\left(\frac{\lambda}{2}(\cos\vartheta_1 \pm \cos\vartheta_2)^2\right),\ Z_2 = \int_0^\pi \int_0^\pi \exp\left(\frac{\lambda}{2}(\cos\vartheta_1 \pm \cos\vartheta_2)^2\right) \sin\vartheta_1 \sin\vartheta_2\, d\vartheta_1\, d\vartheta_2, \tag{B10}$$

where ϑ_i is the angle that the vector $\mathbf{u}_i$ makes with the Z axis of the laboratory frame, $\lambda = \beta\rho_0\mu^2/(3\varepsilon_0)$, $W_2^{(0,-)}$ refers to preferred parallel alignment of dipole pairs and $W_2^{(0,+)}$ to preferred antiparallel alignment. By writing the pair interaction potential $U_{\text{int}}(\mathbf{r}, \mathbf{u}_1, \mathbf{u_2})$ in short- and long-range contributions (respectively indexed SR and LR) and if the long-range contribution consists of dipole-dipole interactions only, Eq. (40) yields (the dipole orientational average has no effect on the short-range term)

$$\bar{U}_{\text{int}}^{\infty(\mp)}(\mathbf{r}) = U_{SR}(\mathbf{r}) + \bar{U}_{LR}^{(\mp)}(\mathbf{r}), \tag{B11}$$

where

$$\bar{U}_{LR}^{(\mp)}(\mathbf{r}) = -\frac{\mu^2 f^{(\mp)}(\lambda)}{2\pi\varepsilon_0 r^3} P_2(\cos\vartheta_r) \tag{B12}$$

and where θ_r is the angle the separation vector $\mathbf{r}$ makes with the Z axis of the laboratory frame, P_2 is the second Legendre polynomial and

$$f^{(\mp)}(\lambda) = \int \cos\vartheta_1 \cos\vartheta_2 W_2^{(0,\mp)}(\mathbf{u}_1, \mathbf{u}_2)\, d\mathbf{u}_1\, d\mathbf{u}_2.$$

Explicit evaluation of this integral yields

$$f^{(-)}(\lambda) = -\frac{\sqrt{2\pi}\lambda^{3/2}\mathrm{erfi}\big(\sqrt{2\lambda}\big) + 3\lambda - e^{2\lambda}(\lambda+1) + 1}{3\lambda\big[\sqrt{2\pi\lambda}\,\mathrm{erfi}\big(\sqrt{2\lambda}\big) - e^{2\lambda} + 1\big]} = -f^{(+)}(\lambda), \tag{B13}$$

where $\mathrm{erfi}(z)$ is the error function of imaginary argument [43], *viz.*,

$$\mathrm{erfi}(z) = \frac{2}{\sqrt{\pi}}\int_0^z e^{t^2}\,dt.$$

It has to be mentioned that indeed, $0 \leqslant f^{(-)} \leqslant 1$ since dipoles have a trend to orient parallel, while $-1 \leqslant f^{(+)} \leqslant 0$ as a result of preferred antiparallel ordering. In effect, $f^{(\mp)}$ should not be confused with g_{K} which is always *positive*, even at the largest densities [33] and pertains to linear response of the dipolar system, as we have shown. Using Eq. (39) yields now the two possibilities for $G_\infty(\mathbf{r})$, *viz.* (A is an integration constant)

$$G_\infty^{(\mp)}(\mathbf{r}) = A\exp[-\beta U_{SR}(\mathbf{r})]\exp[-\beta\bar{U}_{LR}^{(\mp)}(\mathbf{r})], \tag{B14}$$

clearly demonstrating that pair dipolar ordering has an effect on $G(\mathbf{r}, t|N, \upsilon)$ in general, hence having an effect on the usual pair distribution function $\mathfrak{g}(\mathbf{r})$. Indeed, unlike $\mathfrak{g}(\mathbf{r})$, Eq. (B14) has no spatial oscillations at all. Hence the functional derivative

$$\frac{\delta G_\infty(\mathbf{r})}{\delta W_2^{(0)}(\mathbf{u}_1, \mathbf{u}_2)}$$

does not vanish, implying that $G(\mathbf{r}, t)$ always depends on preferred pair dipolar ordering at all times.

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