

## Theoretical analysis of dielectric properties of polar liquids in the far-infrared spectral range

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The Zwanzig-Mori theory is applied to the study of dielectric behavior of polar liquids in the far-infrared spectral range. The basic dynamical variables on which the calculation is based are the macroscopic dipole moment  $\vec{M}(t)$  of the liquid sample and its time derivatives. The return to transparency and the excess absorption are analyzed in detail. It is shown that the spectral behavior of pure liquids can be described by the same formulas as those applicable to analyze diluted solutions provided microscopic time parameters of the latter theories are replaced by new macroscopic time parameters chosen in an appropriate way.

### I. INTRODUCTION

A considerable interest has been manifested in the study of dielectric behavior of polar liquids, or liquid solutions of polar molecules, in the far-infrared spectral range. Two essential facts have been discovered: the return to the transparency of molecular liquids in this region<sup>1</sup> and the existence of strong excess absorption at the high-frequency edge of the absorption area.<sup>2,3</sup> The first of these phenomena, predicted many years ago<sup>4,5</sup> is a consequence of the finite value of molecular moments of inertia and the second is a manifestation of libration-type motions in the liquid.

The simple Debye theory was rapidly seen to be inadequate in treating this problem and three groups of theories have been proposed to study the dielectric behavior of diluted solutions of polar molecules. In stochastic-type theories either molecular motions are considered to be similar to free rotations and to be weakly perturbed by a random force,<sup>6</sup> or they are thought to follow the  $M$  or  $J$  extended diffusion model,<sup>7</sup> or else they are assumed to be libration-type at short times and diffusion-type at longtimes and are described by the cumulant expansion technique<sup>8-12</sup> (see also work by Birnbaum and Cohen<sup>13</sup>). In quasi-crystal-line theories, a molecule of a liquid solution is believed to be trapped into a potential well of a given symmetry and its motion to be weakly perturbed by a random force.<sup>14-16</sup> Finally, in the memory function type theories, the memory kernel is constructed in the way to describe different kinds of molecular rotations going from the free rotation to the rotational diffusion.<sup>17-21</sup> The results of these theories strongly support the interpretation sketched above and allow a quantitative reproduction of different sorts of diagrams the experimentalists use to express the experimental data.

The purpose of the present paper is to extend above theories to the case of pure liquids. The

method applied is the Zwanzig-Mori theory<sup>22-27</sup> in the version used by Kivelson-Keyes.<sup>28</sup> The theory is given a form which makes appear a series of successive approximations; all modelist assumptions are carefully avoided. A good agreement is found between theory and experiment.

### II. BASIC APPROACH AND METHODOLOGY

#### A. Relation between dielectric constant and macroscopic dipole moment correlation function

The system  $S$  undergoing the investigation is a sample of liquid dielectric material of spherical form. This choice of the reference volume is a matter of convenience and, by no means, a question of principle. Then, the dielectric constant  $\epsilon$  is obtained by submitting  $S$  to the action of a variable electric field and by analyzing its response to it;  $\epsilon$  is expressed in terms of the macroscopic dipole moment correlation function  $G(t) = \langle \vec{M}(t)\vec{M}(0) \rangle / \langle \vec{M}(0)\vec{M}(0) \rangle$ . Practically, the problem is treated by (i) applying the linear-response theory in its classical version, (ii) developing the Born-Oppenheimer expression for  $\vec{M}$  into a power series of vibrational coordinates of individual molecules, and (iii) introducing the conventional high-frequency dielectric constant  $\epsilon_\infty$  as well as its static value  $\epsilon_0$ . Then, choosing the  $Z$  axis in an arbitrary direction, e.g., in the direction of the applied electric field, the following well-known formula is easily obtained:

$$\frac{(\epsilon - \epsilon_\infty)(\epsilon_0 + 2)}{(\epsilon_0 - \epsilon_\infty)(\epsilon + 2)} = - \int_0^\infty dt e^{-i\omega t} \frac{d}{dt} \frac{\langle M_z(0)M_z(t) \rangle}{\langle M_z(0)M_z(0) \rangle} \quad (1)$$

This relation is the basic relation used in the present theory. The Hamiltonian  $H$ , or the Liouvillian  $L$ , determining the natural motion of  $\vec{M}(t)$  is that of the complete macroscopic sample  $S$  placed into an empty, force-free space and the statistical average designated by angular brackets

is over a canonical ensemble in absence of an electric field. No reduction of the macroscopic sphere  $S$  into smaller units is needed in this work; thus problems associated with this reduction, and difficulties related to it, do not arise here.

### B. Principle of calculation

The calculation of  $G(t)$  is based on the Zwanzig-Mori theory of Brownian motion. According to this theory, the correlation matrix  $\theta(t) = \langle A(0)A(t) \rangle$  of a dynamical quantity  $A = (A_1, A_2, \dots, A_n)$  obeys the generalized Langevin equation:

$$\frac{d}{dt} \theta(t) = i\Omega \theta(t) - \int_0^t ds K(s) \theta(t-s), \quad (2)$$

where  $\Omega$  is the  $n \times n$  frequency matrix and  $K$  the corresponding  $n \times n$  memory matrix. This equation can be solved by successive approximations, either by truncating the continuous fraction formula established by Mori<sup>25</sup> or by applying the Kivelson-Keyes procedure.<sup>28</sup> The two methods are intimately related to each other and converge, in principle, to an exact solution.

The calculation involves the following steps. (i) The  $z$  component of  $\vec{M}(pq; t)$  should be expandable in a Taylor series in  $t$ :

$$M_z(pq; t) = \sum_{n=0}^{\infty} \frac{t^n}{n!} M_z^{(n)}(pq). \quad (3)$$

Equation (3) can be reinterpreted in terms of the Zwanzig-Mori theory by stating that  $M_z(pq; t)$  is contained in that part of the vector space of dynamical variables subtended by  $A = (M_z, M'_z, M''_z, \dots)$ . (ii) Successive approximations for  $G(t)$  are obtained by constructing  $\theta(t)$  on  $M_z$ , or on  $M_z, M'_z$ , or else on  $M_z, M'_z, M''_z$  and by treating the Eq. (2) according to the Kivelson-Keyes procedure. The approximations of this sequence are called the one-variable, the two-variable, and the three-variable theory, respectively. (iii) The parameters which appear in the theory after elimination of the projected Liouville operator are the time integral of  $G(t)$  and its time derivatives at  $t=0$ .

### C. Discussion

An approach similar to the present one has been proposed, in another context, by Levi.<sup>29</sup> It is based on the Doob theorem according to which the correlation matrix associated with a  $n$ -dimensional Markovian-Gaussian process is a  $n \times n$  exponential. Thus, a sequence of successive approximations can be constructed by supposing, in turn, that  $M_z(t)$ , or  $M_z(t), M'_z(t)$ , or else  $M_z(t), M'_z(t), M''_z(t)$ , etc. is a Markovian-Gaussian vector. This sequence of approximations can be easily shown

to converge to an exact solution when  $n \rightarrow \infty$ ; in fact, the correlation matrix associated with  $M_z(t), M'_z(t), M''_z(t), \dots$ , can be independently shown to be an exponential. It is very probable that the successive approximation scheme described in the present paper is based on a similar physical background although the techniques are very different.

### III. DILUTED SOLUTIONS OF POLAR MOLECULES IN NONPOLAR SOLVENTS

In this section, the present method is checked by applying it to the study of dielectric behavior of diluted solutions of polar molecules in nonpolar solvents, the systems for which the theory is already firmly established. For sake of simplicity, linear and symmetric-top molecules are only considered in this paper.

The calculation involves the following steps.

(i) The macroscopic dipole moment  $M$  is written as a sum of microscopic dipole moments  $\vec{m}_i$  associated with individual polar molecules; the solvent molecules are assumed to carry no measurable dipole moment. In the simplest description  $\vec{m}$  is the permanent (gas phase) dipole moment of the polar molecule; in a more accurate analysis it is an effective dipole moment including a component produced by the reaction field. (ii) The correlation function  $G(t)$  contains, both, self and distinct pair terms; the latter can safely be neglected if the dilution is sufficiently high. Thus, in applying the formulas of the Sec. II,  $G(t)$  can be assimilated either to the correlation function  $\langle \vec{u}(t)\vec{u}(0) \rangle$  of the unitary vector along the direction of  $\vec{m}$  if the molecule is nonpolarizable or to the correlation function  $\langle \vec{m}(t)\vec{m}(0) \rangle / \langle \vec{m}(0)\vec{m}(0) \rangle$  if it is polarizable. (iii) The inequalities  $\epsilon_0 - \epsilon_\infty \ll \epsilon_\infty$ ,  $\epsilon - \epsilon_\infty \ll \epsilon_\infty$  are expected to be valid and the Eq. (1) can be written as follows:

$$\frac{\epsilon - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = - \int_0^\infty dt e^{-i\omega t} \frac{d}{dt} \langle \vec{u}(t)\vec{u}(0) \rangle, \quad (4)$$

$$\frac{\epsilon - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = - \int_0^\infty dt e^{-i\omega t} \frac{d}{dt} \frac{\langle \vec{m}(t)\vec{m}(0) \rangle}{\langle \vec{m}(0)\vec{m}(0) \rangle}. \quad (5)$$

Equation (4) applies to the nonpolarizable case and Eq. (5) to the case of polarizable systems.

#### A. Nonpolarizable molecules

The case of nonpolarizable molecules is treated first. Three sorts of dielectric diagrams are considered: (i) the absorption coefficient  $\alpha(\omega)$  as a function of  $\omega$ , (ii) the Cole-Cole diagram, and (iii)  $G(t) = \langle \vec{u}(t)\vec{u}(0) \rangle$  as a function of  $t$ . The parameters of this theory are  $\tau = \int_0^\infty dt G(t)$  for the one-variable theory,  $\tau$  and  $G''(0)$  for the two-variable

theory, and  $\tau, G''(0)$ , and  $G^{iv}$  for the three-variable theory. No simple way exists to estimate  $\tau$ ; on the contrary  $G''(0)$  and  $G^{iv}(0)$  can be related to either macroscopic or molecular quantities by the help of the following relations<sup>30-32</sup>:

$$-G''(0) = \frac{2c}{\pi} \frac{\sqrt{\epsilon_\infty}}{\epsilon_0 - \epsilon_\infty} \int_0^\infty d\omega \alpha(\omega), \quad (6a)$$

$$G^{iv}(0) = \frac{2c}{\pi} \frac{\sqrt{\epsilon_\infty}}{\epsilon_0 - \epsilon_\infty} \int_0^\infty d\omega \omega^2 \alpha(\omega), \quad (6b)$$

$$-G''(0) = \frac{2KT}{I} \quad (7a)$$

$$G^{iv}(0) = 2 \left( \frac{2KT}{I} \right)^2 \left( 1 + \frac{I'}{4I} \right) + \frac{1}{I^2} \langle (\nabla V)^2 \rangle. \quad (7b)$$

In these equations,  $I$  is the moment of inertia of the polar molecule about an axis perpendicular to the symmetry axis and  $I'$  that about an axis parallel to the symmetry axis,  $\langle (\nabla V)^2 \rangle$  is the mean square torque acting on the polar molecule in the

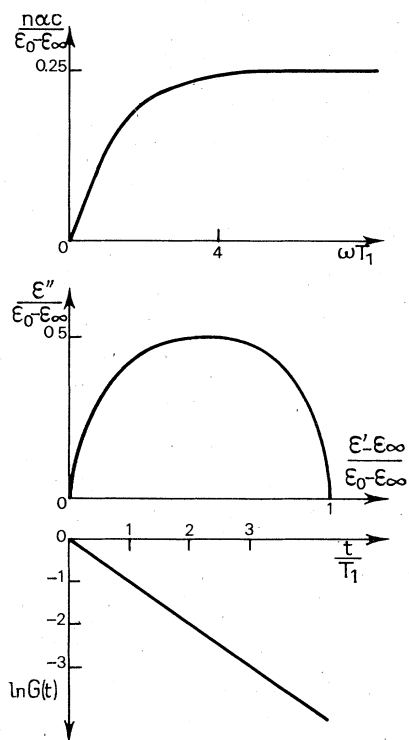


FIG. 1. Dielectric diagrams  $\alpha = \alpha(\omega)$ ,  $\epsilon'' = \epsilon''(\epsilon')$ , and  $\ln G(t)$  as given by the one-variable theory. According to the definition of the parameter  $T_1$ , these curves can be used to describe either diluted solutions or pure liquids. In the case of diluted solutions  $T_1 = \int_0^\infty dt G(t)$  is the microscopic time parameter, for pure liquids  $T_1 = [(\epsilon_0 + 2)/(\epsilon_\infty + 2)] \int_0^\infty dt G(t) = [3\epsilon_0/(\epsilon_\infty + 2\epsilon_0)] \int_0^\infty dt G_s(t)$  is the macroscopic time parameter ( $T_1 = 4t$  in arbitrary time units).

solution.

The results of the theory are as follows. The one-variable theory coincides with the Debye theory; neither the return to transparency nor the excess absorption are reproduced (Fig. 1). The functions  $\alpha(\omega)$ ,  $\epsilon'(\omega)$ ,  $\epsilon''(\omega)$ , and  $G(t)$  have simple Debye form and do not need to be reproduced here; the parameter  $T_1$  entering into these expressions is  $\tau = \int_0^\infty dt G(t)$ . The two-variable theory introduces the inertial effect, accounts for the return to the transparency but fails to explain the presence of the excess absorption (Fig. 2). The functions  $\alpha(\omega)$ ,  $\epsilon'(\omega)$ ,  $\epsilon''(\omega)$ , and  $G(t)$  remain simple enough to be expressible analytically. Putting  $T_1 = \tau = \int_0^\infty dt G(t)$  and  $T_2^{-2} = -G''(0)$  the following formulas are found:

$$n\alpha = \frac{\epsilon_0 - \epsilon_\infty}{c} \frac{\omega^2 T_1}{1 + \omega^2(T_1^2 - 2T_2^2) + \omega^4 T_2^4}, \quad (8a)$$

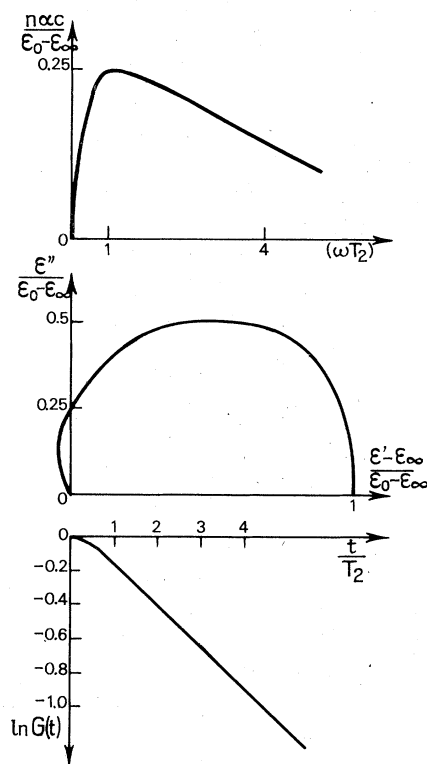


FIG. 2. Dielectric diagrams  $\alpha = \alpha(\omega)$ ,  $\epsilon'' = \epsilon''(\epsilon')$ , and  $\ln G(t)$  as given by the two-variable theory. These curves can be applied to describe either diluted solutions or pure liquids, provided the parameters  $T_1, T_2$  are defined in an appropriate way. In the case of diluted solutions  $T_1 = \int_0^\infty dt G(t)$ ,  $T_2^{-2} = -G''(0)$  are microscopic time parameters, for pure liquids  $T_1 = [(\epsilon_0 + 2)/(\epsilon_\infty + 2)] \int_0^\infty dt G(t) = [3\epsilon_0/(2\epsilon_0 + \epsilon_\infty)] \int_0^\infty dt G_s(t)$ ,  $T_2^{-2} = -[(\epsilon_\infty + 2)/(\epsilon_0 + 2)] G''(0) = -[(\epsilon_\infty + 2\epsilon_0)/3\epsilon_0] G_s''(0)$  represent macroscopic time parameters ( $T_1 = 4t$ ,  $T_2 = 1t$ ).

$$\frac{\epsilon' - \epsilon_\infty}{\epsilon_0 - \epsilon_\infty} = \frac{1 - \omega^2 T_2^2}{1 + \omega^2(T_1^2 - 2T_2^2) + \omega^4 T_2^4}, \quad (8b)$$

$$\frac{\epsilon''}{\epsilon_0 - \epsilon_\infty} = \frac{\omega T_1}{1 + \omega^2(T_1^2 - 2T_2^2) + \omega^4 T_2^4}. \quad (8c)$$

In turn,  $G(t)$  appears as a sum of two exponentials; it can easily be cast to one or another form proposed in previous work.<sup>14</sup> The three-variable theory explains, both, return to transparency and excess absorption (Fig. 3); however, the description remains on a qualitative level. The occurrence of librations is associated, in this theory, with the existence of the complex roots of the transport matrix

$$\Gamma = i\Omega - \lim_{\omega \rightarrow 0} \int_0^\infty dt e^{-i\omega t} K(t);$$

they are only present if  $G^{iv}(0)$  is large enough, i.e., if intermolecular torques are sufficiently efficient. The analytical expressions for  $\alpha(\omega)$ ,  $\epsilon'(\omega)$ ,  $\epsilon''(\omega)$ , although relatively complex, are similar to (8a-c); the appropriate parameters are  $T_1 = \tau$ ,  $T_2^2 = -G''(0)^2 + G^{iv}(0)$ . It results from the above discussion that all qualitative features can be obtained from this three-variable theory; the quantitative agreement can only be obtained if the induced moments are explicitly introduced.

#### B. Polarizable molecules

The case of polarizable molecules can be treated in a way similar to that described above the only difference is that, here,  $G(t)$  is equal to  $\langle \vec{m}(t)\vec{m}(0) \rangle / \langle \vec{m}(0)\vec{m}(0) \rangle$  rather than to  $\langle \vec{u}(t)\vec{u}(0) \rangle$ ; the Eqs. (6a) and (6b) and (8a)-(8c) remain valid but not the Eqs. (7a) and (7b). Practically, the three quantities  $\tau$ ,  $G''(0)$ , and  $G^{iv}(0)$  are considered as adjustable parameters and are fitted to reproduce experimental curves; only two of them,  $\tau$  and  $G^{iv}(0)$ , need to be treated in this way in the case of nonpolarizable molecules since, there,  $G''(0) = -2KT/l$ . Detailed calculations have been made for  $\text{CHBr}_3$  dissolved in  $\text{CCl}_4$ , the system which has already been carefully examined in the previous work.<sup>20</sup> The results are reproduced in Fig. 3 and show an excellent agreement between the theory and the experiment; the fact that  $|G''(0)| > 2KT/l$  is indicative of the presence of induced moments.

#### IV. PURE LIQUIDS

After having checked the present method in the case of diluted solutions where the detailed analysis is available, the theory is now applied to the study of pure liquids. It seems important to point out that the theory can be presented in two different forms according to the choice of basic dynamical variables. Either these variables are the

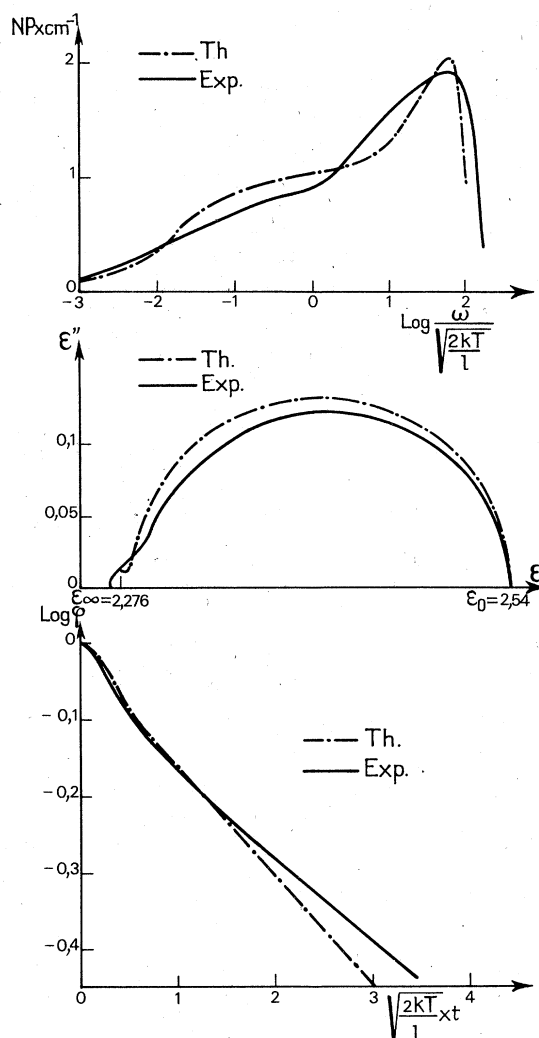


FIG. 3. Dielectric diagrams  $\alpha = \alpha(\omega)$ ,  $\epsilon'' = \epsilon''(\epsilon')$ , and  $\ln G(t)$  of diluted solutions as given by the three-variable theory; these curves describe, both, non polarizable and polarizable solute molecules. The parameters are  $T_1 = \int_0^\infty dt G(t)$ ,  $T_2^2 = -\ddot{G}(0)$ ,  $T_3^4 = -\ddot{G}(0)^2 + G^{iv}(0)$ ; one has  $G(t) = \langle \vec{u}(t)\vec{u}(0) \rangle$  in the former and  $G(t) = \langle \vec{m}(t)\vec{m}(0) \rangle / \langle \vec{m}(0)\vec{m}(0) \rangle$  in the latter case. These parameters have been chosen in the way to reproduce the experimental values for  $\text{CHBr}_3 + \text{CCl}_4$  (20%) at  $T = 25^\circ\text{C}$  ( $T_1 = 6.19 \times 10^{-12}$  sec,  $T_2 = 0.83 \times 10^{-12}$  sec,  $T_3 = 0.35 \times 10^{-12}$  sec).

macroscopic dipole moment vector and its time derivatives  $M_z^{(0)}(0)$ ,  $M_z^{(1)}(0)$ ,  $M_z^{(2)}(0)$ ..., or the Hilbert space is subtended by the microscopic dipole moments  $\vec{m}_1(0)$ ,  $\vec{m}_2(0)$ ... $\vec{m}_N(0)$  of the  $N$  molecules forming  $S$  and by their time derivatives. One concludes that the theory is a one, two, etc. variable theory in the former case and an  $N$ ,  $2N$ , etc., variable theory in the latter case. Surprisingly enough, the theory can be elaborated in both versions, at least in the one-variable macroscopic and the  $N$ -variable microscopic cases,

in spite of the very high order of the transport matrix  $\Gamma$  in the second method; this is due to the isotropy of the liquid conferring to  $\Gamma$  a very symmetrical structure. The results of both treatments turn out to be equivalent, thus the simple choice of dynamical variables  $M_z^{(0)}(0)$ ,  $M_z^{(1)}(0)$ ,  $M_z^{(2)}(0)$ , etc., is confirmed.<sup>33,34</sup>

The calculation implies the following steps. (i) The macroscopic dipole moment  $\vec{M}$  is written as a sum of microscopic dipole moment  $\vec{m}$ , of individual molecules of the liquid sample  $S$ ; for sake of generality, they are supposed to be effective dipole moments and to include a component due to reaction field. Then the correlation function  $G(t)$  is a multimolecular correlation function describing the effect of collective molecular rotations. (ii) No attempt is made to reduce the macroscopic sphere  $S$  to smaller units. If the basic variables are  $M_z^{(0)}(0)$ ,  $M_z^{(1)}(0)$ , and  $M_z^{(2)}(0)$ , the effort necessary to solve their equation of motion does not depend on the number of molecules contained in the sphere and there is no advantage to introduce the embedded sphere. Then, the relation between  $\epsilon$  and  $G(t)$  is that given by Eq. (1). (iii) The parameters of this theory are  $\tau = \int_0^\infty dt G(t)$  for the one-variable theory,  $\tau$  and  $G''(0)$  for the two-variable theory, and  $\tau$ ,  $G''(0)$ , and  $G^{iv}(0)$  for the three-variable theory. These parameters can be related either to macroscopic quantities  $\int_0^\infty d\omega \alpha(\omega)$ ,  $\int_0^\infty d\omega \omega^2 \alpha(\omega)$  or, if the comparison with the results of previous work is desired, to the parameters  $\tau_s$ ,  $G_s''(0)$ , and  $G_s^{iv}(0)$  associated with the microscopic sphere  $s$  embedded in  $S$ . One has, approximately<sup>35</sup>:

$$-G''(0) = \frac{2c}{\pi} \frac{(\epsilon_0 + 2)\sqrt{\epsilon_\infty}}{(\epsilon_0 - \epsilon_\infty)(\epsilon_\infty + 2)} \int_0^\infty d\omega \alpha(\omega), \quad (9a)$$

$$G^{iv}(0) = \frac{2c}{\pi} \frac{(\epsilon_0 + 2)\sqrt{\epsilon_\infty}}{(\epsilon_0 - \epsilon_\infty)(\epsilon_\infty + 2)} \int_0^\infty d\omega \omega^2 \alpha(\omega), \quad (9b)$$

$$\frac{\tau}{\tau_s} = \frac{3\epsilon_0(\epsilon_\infty + 2)}{(2\epsilon_0 + \epsilon_\infty)(\epsilon_0 + 2)}, \quad (10a)$$

$$\frac{G''(0)}{G_s''(0)} = \frac{G^{iv}(0)}{G_s^{iv}(0)} = \frac{(2\epsilon_0 + \epsilon_\infty)(\epsilon_0 + 2)}{3\epsilon_0(\epsilon_\infty + 2)}. \quad (10b)$$

Equation (10a) applies to a Glarum-Cole type cavity and Eq. (10b) to both, Glarum-Cole and Fatuzzo-Mason type spheres,<sup>36-38</sup> see also Neuzwanzig.<sup>39</sup> The relation between  $\tau$  and  $\tau_s$  for a Fatuzzo-Mason cavity is ambiguous due to the presence of several relaxation times. (iv) The dependence between  $\epsilon$  and  $G(t)$  is linear in  $\epsilon$ ; this is a consequence of the Eq. (1). Thus, nonlinearities appearing in the Fatuzzo-Mason theory are not due to some physical process creating them, but to the individual decision of a theoretician to evaluate  $\tau$ ,  $G''(0)$ ,  $G^{iv}(0)$  by the help of the semi-

macroscopic embedded sphere approximation.

The results of the theory are as follows. The one-variable theory coincides with the Debye theory; neither the return to the transparency nor the excess absorption are reproduced. The function  $\alpha(\omega)$ ,  $\epsilon(\omega)$ , and  $G(t)$  have the simple Debye form and do not need to be reproduced here. However, the time parameter involved is

$$T_1 = \frac{\epsilon_0 + 2}{\epsilon_\infty + 2} \tau = \frac{3\epsilon_0}{\epsilon_\infty + 2\epsilon_0} \tau_s$$

rather than  $\tau$  or  $\tau_s$ . Curiously enough, the relation  $T_1 = T_1(\tau)$  coincides with that proposed by Lorentz-Debye<sup>40</sup> and the relation  $T_1 = T_1(\tau_s)$  with that suggested by Powles<sup>41</sup> (Fig. 1). The two-variable theory introduces the inertial effect, accounts for the return to the transparency but fails to explain the presence of the excess absorption. The functions  $\alpha(\omega)$ ,  $\epsilon'(\omega)$ , and  $\epsilon''(\omega)$  are still given by Eqs. (8a)–(8c) but the definition of  $T_1$ ,  $T_2$  is different:

$$T_1 = \frac{\epsilon_0 + 2}{\epsilon_\infty + 2} \tau = \frac{3\epsilon_0}{\epsilon_\infty + 2\epsilon_0} \tau_s, \quad (11a)$$

$$T_2^{-2} = -\frac{\epsilon_\infty + 2}{\epsilon_0 + 2} G''(0) = -\frac{\epsilon_\infty + 2\epsilon_0}{3\epsilon_0} G_s''(0). \quad (11b)$$

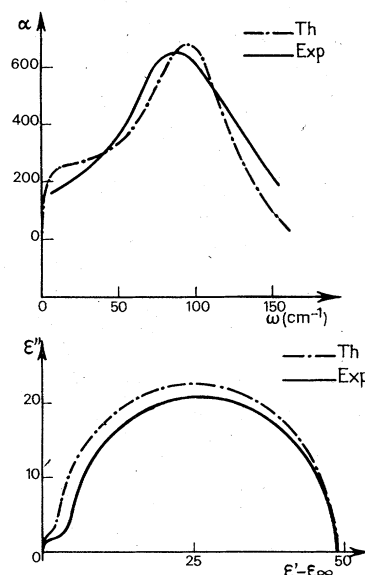


FIG. 4. Dielectric diagrams  $\alpha = \alpha(\omega)$ ,  $\epsilon'' = \epsilon''(\epsilon')$  of pure liquids as given by the tree-variable theory. The parameters are  $T_1 = [(\epsilon_0 + 2)/(\epsilon_\infty + 2)] \int_0^\infty dt G(t) = [3\epsilon_0/(\epsilon_\infty + 2\epsilon_0)] \int_0^\infty dt G_s(t)$ ,  $T_2^{-2} = -[(\epsilon_\infty + 2)/(\epsilon_0 + 2)] \ddot{G}(\omega) = -[(\epsilon_\infty + 2\epsilon_0)/3\epsilon_0] G_s(0)$ ,  $T_3^{-4} = [(\epsilon_\infty + 2)/(\epsilon_0 + 2)] [G^{iv}(0) - \ddot{G}(0)^2] = [(\epsilon_\infty + 2\epsilon_0)/3\epsilon_0] \{G_s^{iv}(0) - [(2\epsilon_0 + \epsilon_\infty)(\epsilon_0 + 2)/3\epsilon_0(\epsilon_\infty + 2)] \ddot{G}_s(0)^2\}$ . These curves refer to the liquid  $\text{CH}_3\text{F}$  at  $T = 133^\circ\text{K}$  ( $T_1 = 5.28 \times 10^{-12}$  sec,  $T_2 = 0.41 \times 10^{-12}$  sec,  $T_3 = 0.14 \times 10^{-12}$  sec).

Thus, after having changed the time parameters  $T_1, T_2$  according to this prescription, the Fig. 2 correctly reproduces the pure-liquid results. The three-variable theory explains, both, return to transparency and excess absorption; the discussion parallels word by word that given in the Sec. III A. The analytical expressions for  $\alpha(\omega)$ ,  $\epsilon'(\omega)$ , and  $\epsilon''(\omega)$  remain the same as for diluted solutions but the parameters are

$$T_1 = \frac{\epsilon_0 + 2}{\epsilon_\infty + 2} \tau = \frac{3\epsilon_0}{\epsilon_\infty + 2\epsilon_0} \tau_s, \quad (12a)$$

$$T_2^{-2} = -\frac{\epsilon_\infty + 2}{\epsilon_0 + 2} G''(0) = -\frac{\epsilon_\infty + 2\epsilon_0}{3\epsilon_0} G_s''(0), \quad (12b)$$

$$T_3^{-4} = \frac{\epsilon_\infty + 2}{\epsilon_0 + 2} [G^{iv}(0) - G''^2(0)] \\ = \frac{\epsilon_\infty + 2\epsilon_0}{3\epsilon_0} \left( G_s^{iv}(0) - \frac{(2\epsilon_0 + \epsilon_\infty)(\epsilon_0 + 2)}{3\epsilon_0(\epsilon_\infty + 2)} G_s''^2(0) \right). \quad (12c)$$

Detailed calculations have been made for liquid

$\text{CH}_3\text{F}$ , a system for which careful measurements have been made.<sup>42</sup> The results, obtained by considering  $\tau, G''(0), G^{iv}(0)$  as adjustable parameters, are reproduced in Fig. 4; there is a fair agreement between theory and experiment.

One concludes that the dielectric relaxation of polar liquids in the far-infrared range may be described by the help of the same formulas than those applicable to the analysis of diluted solutions; it is only necessary to redefine the time parameters  $T_1, T_2$ , and  $T_3$  in an appropriate way. Thus, the present theory can be viewed as generalization to the non-Debye case of the early theories discussing the relation between microscopic dielectric relaxation times.

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$$G^{(2K)}(0) = \frac{2C}{\pi} \frac{(\epsilon_0 + 2)(\epsilon_\infty + 2)}{(\epsilon_0 - \epsilon_\infty)} \int_0^\infty d\omega (-1)^K \frac{\omega^{2K-2} n(\omega) \alpha(\omega)}{(\epsilon' + 2)^2 + \epsilon''^2},$$

where  $K=1, 2, \dots$ , by putting  $\epsilon' \sim \epsilon_\infty$ ,  $\epsilon'' \ll \epsilon'$ . In fact,  $\alpha(\omega)$  is small at low frequencies for any relaxation process and the heavily weighted parts of the integral correspond to high frequencies. For liquids in this region  $\epsilon'$  is of the order of  $\epsilon_\infty$ ,  $n$  is of the order of  $\sqrt{\epsilon_\infty}$  and  $\epsilon''^2$  small with respect to  $\epsilon'^2$ . The same type of approximation is used in determining the Eq. (10b);

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