ANL-7381

ANL-7381

MASTER

Argonne National Laboratory

STATISTICAL THEORY OF
ELECTRIC POLARIZATION

by

A. Bellemans

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

The facilities of Argonne National Laboratory are owned by the United States Government. Under the terms of a contract (W-31-109-Eng-38) between the U. S. Atomic Energy Commission, Argonne Universities Association and The University of Chicago, the University employs the staff and operates the Laboratory in accordance with policies and programs formulated, approved and reviewed by the Association.

MEMBERS OF ARGONNE UNIVERSITIES ASSOCIATION

The University of Arizona	The University of Iowa	Northwestern University
Carnegie Institute of Technology	Kansas State University	University of Notre Dame
Case Institute of Technology	The University of Kansas	The Ohio State University
The University of Chicago	Loyola University	Purdue University
University of Cincinnati	Marquette University	Saint Louis University
Illinois Institute of Technology	Michigan State University	Washington University
University of Illinois	The University of Michigan	Wayne State University
Indiana University	University of Minnesota	The University of Wisconsin
Iowa State University	University of Missouri	

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Printed in the United States of America
Available from

Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U. S. Department of Commerce
Springfield, Virginia 22151

Price: Printed Copy \$3.00; Microfiche \$0.65

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

STATISTICAL THEORY OF
ELECTRIC POLARIZATION

Based on a series of six lectures by

A. Bellemans

University of Brussels

Solid State Science Division

August 1967

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

TABLE OF CONTENTS

	<u>Page</u>
FOREWORD	5
General References	6
PART I. STATIC DIELECTRIC CONSTANT	7
1. Electric polarization of matter.	7
2. The dielectric constant.	8
3. Relations between $\vec{E}$ and $\vec{E}_0$ in special cases.	9
4. Classical problems of electrostatics.	10
5. The theory of Onsager.	11
6. Assembly of dipolar molecules in an external field.	13
7. General statistical formulation of ϵ .	15
8. Non-polar substances.	17
9. Polar substances.	19
10. High temperature expansions.	21
REFERENCES TO PART I.	22
APPENDIX I. THE DEBYE EQUATION.	23
PART II. THE DYNAMIC DIELECTRIC FUNCTION	24
11. The behavior of a dielectric body in a time-dependent field.	24
12. The dynamic dielectric function.	25
13. Relations between $\vec{E}$ and $\vec{E}_0$ in special cases.	28
14. A macroscopic formulation of $\epsilon(\omega)$.	28
15. Brownian motion and dielectric relaxation.	30
16. The description of a system in phase space.	37
17. The response of a system to an electric field.	39
18. General formulation of $\epsilon(\omega)$.	42

TABLE OF CONTENTS (Cont.)

	<u>Page</u>
PART II. THE DYNAMIC DIELECTRIC FUNCTION (Cont.)	
19. Generalization of the static theory of Kirkwood (polar substances).	43
20. Discussion of the correlation function $\Psi(s)$.	43
21. Some results of molecular dynamics.	45
22. Perturbation methods of statistical mechanics of irreversible processes.	46
REFERENCES TO PART II.	47

FOREWORD

This report corresponds to a series of six lectures given to the members of the Solid State Science Division of Argonne National Laboratory in August 1967. The material presented herein gives a review of the present situation in the statistical theory of dielectrics, as far as linear effects in the field are concerned: theory of the static dielectric constant and of the dynamic (frequency dependent) dielectric function.

The author wishes to express here his sincere thanks to Dr. O. C. Simpson and to the members of the Division, for their kind hospitality and for making his stay most profitable and enjoyable.

General References

1. H. Fröhlich, Theory of Dielectrics, Oxford Clarendon Press (1958).
2. C. F. J. Böttcher, Theory of Electric Polarization, Elsevier, New York (1952).
3. P. Debye, Polar Molecules, Dover Publications, Inc., New York (1945).
4. J. C. Anderson, Dielectrics, Chapman and Hall, London (1958).
5. C. P. Smyth, Dielectric Behavior and Structure, McGraw-Hill Book Co., Inc., New York (1955).

STATISTICAL THEORY OF ELECTRIC POLARIZATION

by

A. Bellemans

I. THE STATIC DIELECTRIC CONSTANT

1. Electric polarization of matter.

From the microscopic point of view, a piece of matter is an ensemble of interacting point charges (nuclei and electrons) in vacuo, and the resulting electric field $\underline{e}(\underline{r})$ is determined by Maxwell's equations

$$\underline{\nabla} \times \underline{e} = 0, \quad \underline{\nabla} \cdot \underline{e} = 4\pi \rho_{\text{mic}}$$

(neglecting all magnetic effects); ρ_{mic} is the local density of charges

$$\rho_{\text{mic}}(\underline{r}) = \sum_{\alpha} \sum_{j_{\alpha}} q_{j_{\alpha}} \delta(\underline{R}_{j_{\alpha}} - \underline{r})$$

where α represents some stable entity (atom, ion, molecule) and j_{α} is the j -th particle of α (nucleus or electron) with position $\underline{R}_{j_{\alpha}}$. A detailed description like this involves a characteristic time and length of $\sim 10^{-20}$ sec and 10^{-13} cm respectively, which goes far beyond the experimental possibilities. What we do actually observe is the local average $\underline{E} = \langle \underline{e} \rangle$ over time and space, which obeys the equations

$$\underline{\nabla} \times \underline{E} = 0, \quad \underline{\nabla} \cdot \underline{E} = 4\pi \langle \rho_{\text{mic}} \rangle.$$

We shall describe the entity α by a positional vector $\underline{R}_{\alpha}$ defining its center, plus a set of internal coordinates $\underline{r}_{j_{\alpha}} = \underline{R}_{j_{\alpha}} - \underline{R}_{\alpha}$. Expanding $\rho_{\text{mic}}(\underline{r})$ in terms of these internal coordinates, we have

$$\begin{aligned} \rho_{\text{mic}}(\underline{r}) &= \sum_{\alpha} \sum_{j_{\alpha}} q_{j_{\alpha}} \left\{ \delta(\underline{R}_{\alpha} - \underline{r}) - \underline{r}_{j_{\alpha}} \cdot \underline{\nabla} \delta(\underline{R}_{\alpha} - \underline{r}) \right. \\ &\quad \left. + \frac{1}{2} (\underline{r}_{j_{\alpha}} \cdot \underline{\nabla})^2 \delta(\underline{R}_{\alpha} - \underline{r}) - \dots \right\} \\ &= \sum_{\alpha} \left\{ q_{\alpha} - \underline{m}_{\alpha} \cdot \underline{\nabla} + \frac{Q_{\alpha}}{2} \underline{\nabla} \cdot \underline{\nabla} - \dots \right\} \delta(\underline{R}_{\alpha} - \underline{r}) \end{aligned}$$

where q_α , m_α , Q_α are respectively the charge, the dipole and the quadrupole moments of α . The average of this expression may be written as

$$\langle \rho_{\text{mic}}(\underline{r}) \rangle = \rho(\underline{r}) - \underline{\nabla} \cdot \underline{P}$$

where $\rho(\underline{r})$ is the local macroscopic charge per unit volume, and $\underline{P}$ is the polarization vector which takes care of the multipole expansion:

$$\rho(\underline{r}) = \left\langle \sum_{\alpha} q_{\alpha} \delta(\underline{R}_{\alpha} - \underline{r}) \right\rangle$$

$$\underline{P}(\underline{r}) = \left\langle \sum_{\alpha} m_{\alpha} \delta(\underline{R}_{\alpha} - \underline{r}) \right\rangle - \underline{\nabla} \cdot \left\langle \sum_{\alpha} Q_{\alpha} \delta(\underline{R}_{\alpha} - \underline{r}) \right\rangle + \dots$$

This gives

$$\underline{\nabla} \cdot \underline{E} = 4\pi\rho - 4\pi\underline{\nabla} \cdot \underline{P}$$

and by defining the electric displacement $\underline{D} = \underline{E} + 4\pi \underline{P}$, one recovers the classical equations

$$\underline{\nabla} \times \underline{E} = 0, \quad \underline{\nabla} \cdot \underline{D} = 4\pi\rho.$$

The introduction of $\underline{P}$ (or $\underline{D}$) eliminates all references to the particular structure of the medium and permits one to establish a macroscopic theory of electrostatics, but obviously, any relationship between $\underline{E}$ and $\underline{P}$ (or $\underline{D}$) can only be obtained by reconsidering the molecular nature of the system.

2. The dielectric constant.

Any material body becomes polarized when submitted to an external field, because of a relative displacement of its interior positive and negative charges. Generally speaking these charges are either bound or free. In a perfect insulator no free charges exist and $\underline{P}$ results from small displacements of bound charges all over the specimen. For fields slowly varying with respect to molecular dimensions, $\underline{P}(\underline{r})$ is essentially the mean dipole moment per unit volume. The response of the body to a weak applied field $\underline{E}_0(\underline{r})$ will be linear, i.e., both $\underline{P}$ and $\underline{E}$ will be proportional to $\underline{E}_0$, and in a phenomenological way one writes

$$\underline{P} = \chi \underline{E} \quad \text{or} \quad \underline{D} = \epsilon \underline{E}.$$

Both the electric susceptibility χ and permittivity ϵ are tensors but we shall limit ourselves to homogeneous and isotropic materials so that they behave as scalars. (Note that a cubic crystal behaves as an isotropic dielectric material.)

Relating the dielectric constant ϵ of a given specimen with its molecular structure is typically a problem of statistical mechanics. The obvious way to proceed is to compute both $\vec{E}$ and $\vec{P}$, given the Hamiltonian of the system in an applied field $\vec{E}_0$, and to deduce ϵ from the macroscopic equation

$$\vec{P} = \chi \vec{E} = \frac{\epsilon - 1}{4\pi} \vec{E} \quad (2.1)$$

To make it as simple as possible, we assume $\vec{E}_0$ homogeneous. Even so, because of the long range of the dipolar field ($\sim r^{-3}$), $\vec{P}$ and $\vec{E}$ vary from point to point within the specimen, unless particular assumptions are made, concerning its external shape.

3. Relations between $\vec{E}$ and $\vec{E}_0$ in special cases.

The electric field $\vec{E}$ inside a specimen polarized by an external field $\vec{E}_0$ is the sum of $\vec{E}_0$ and a depolarization field $\vec{E}_{\text{dep}}$. If $\vec{E}_0$ is homogeneous and if the body has an ellipsoidal shape, $\vec{E}$ and $\vec{P}$ are uniform through its whole volume; further $\vec{E}$ and $\vec{P}$ are parallel to $\vec{E}_0$ if one of the principal axes of the ellipsoid is itself parallel to $\vec{E}_0$. (Theorem of Poisson¹). When these conditions are met, one has

$$\vec{E} = \vec{E}_0 - N\vec{P}$$

where N is the depolarization coefficient, depending on the ratios of the principal axes a, b, c of the ellipsoid, in such a way that $N_a + N_b + N_c = 4\pi$. Combining with Eq. (2.1), one obtains

$$\vec{E} = \left(1 + N \frac{\epsilon - 1}{4\pi}\right)^{-1} \vec{E}_0 \quad (\leq E_0)$$

The following cases are of interest:

(a) Spherical specimen:

$$N = 4\pi/3, \quad \vec{E} = \frac{3}{\epsilon + 2} \vec{E}_0 \quad (3.1)$$

- (b) Plate condenser (= infinitely flat ellipsoid normal to $\vec{E}_0$):

$$N = 4\pi, \quad E = \frac{1}{\epsilon} E_0. \quad (3.2)$$

- (c) Infinitely long cylinder perpendicular to $\vec{E}_0$ (limiting case):

$$N = 2\pi, \quad E = \frac{2}{\epsilon + 1} E_0. \quad (3.3)$$

There is a definite advantage in doing statistical calculations on such body-shaped specimens: E is known from the start in terms of E_0 and ϵ , so that P alone has to be computed. For a sphere, the combination of Eqs. (2.1) and (3.1) gives

$$\frac{\epsilon - 1}{\epsilon + 2} E_0 = \frac{4\pi}{3} P \quad (3.4)$$

4. Classical problems of electrostatics.²

(a) Cavity field

Consider a spherical cavity of dielectric constant ϵ_c inside an otherwise uniformly polarized medium of dielectric constant ϵ . The electric field inside the cavity is homogeneous and equal to

$$\vec{G} = \frac{3\epsilon}{2\epsilon + \epsilon_c} \vec{E} \quad (4.1)$$

where $\vec{E}$ is the homogeneous field in the surrounding medium at large distances.

(b) Reaction field

Consider the same cavity with a point-dipole $\vec{m}$ in its center. The surrounding medium, which is assumed to extend to infinity, is polarized by the dipole and generates in return a reaction field in the cavity

$$\vec{R} = \frac{2}{a^3} \frac{\epsilon - \epsilon_c}{2\epsilon + \epsilon_c} \vec{m} = g \vec{m} \quad (4.2)$$

(a = radius of the cavity).

As we limit ourselves to linear effects (no saturation), the cavity and the reaction fields are simply additive when problems (a) and (b) are simultaneously considered.

5. The theory of Onsager.³

This theory is semi-macroscopic as it mixes molecular and microscopic concepts: the average dipole moment of a molecule embedded in a uniformly polarized body is computed by considering this one molecule explicitly, filling a spherical cavity of radius a , and treating the surroundings as a continuum of dielectric constant ϵ .

Calling E the electric field within the specimen and $\tilde{m}$ the instantaneous value of the electric moment of the molecule, we equate the local field F inside the cavity to the sum of the cavity and the reaction fields (4.1)-(4.2)

$$\tilde{F} = \tilde{G} + \tilde{R} = \frac{3\epsilon}{2\epsilon + 1} \tilde{E} + g\tilde{m}$$

with $g = (2/a^3)(\epsilon - 1)/(2\epsilon + 1)$; $\tilde{m}$ is generally the sum of a permanent term $\tilde{\mu}$ and an induced term $\alpha\tilde{F}$, where α is the molecular polarizability,

$$\tilde{m} = \tilde{\mu} + \alpha\tilde{F},$$

so that

$$\tilde{F} = \frac{1}{1 - g\alpha} \left\{ \frac{3\epsilon}{2\epsilon + 1} \tilde{E} + g\tilde{\mu} \right\},$$

$$\tilde{m} = \frac{1}{1 - g\alpha} \left\{ \tilde{\mu} + \alpha \frac{3\epsilon}{2\epsilon + 1} \tilde{E} \right\}.$$

Taking ρ as the number density in the system, we have

$$\tilde{P} = \rho \langle \tilde{m} \rangle = \frac{\rho}{1 - g\alpha} \left\{ \langle \tilde{\mu} \rangle + \alpha \frac{3\epsilon}{2\epsilon + 1} \tilde{E} \right\}$$

where $\langle \dots \rangle$ denotes a canonical average. Now the torque acting on the molecule is $\tilde{\mu} \times \tilde{F}$ and corresponds to the potential energy

$$U = - \frac{1}{1 - g\alpha} \frac{3\epsilon}{2\epsilon + 1} \tilde{\mu} \cdot \tilde{E}$$

(the part of the reaction field which is proportional to μ does not contribute to the torque). It follows that, in the linear approximation

$$\langle \tilde{\mu} \rangle = \int \tilde{\mu} e^{-\beta U} d\tilde{\omega} / \int e^{-\beta U} d\tilde{\omega} \quad (\beta = 1/kT)$$

$$= \frac{1}{1 - g\alpha} \frac{3\epsilon}{2\epsilon + 1} \left(\frac{\mu^2}{3kT} \right) \tilde{E}.$$

Hence the final expression

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{3\epsilon} = \frac{4\pi\rho}{1 - g\alpha} \left(\alpha + \frac{1}{1 - g\alpha} \frac{\mu^2}{3kT} \right). \quad (5.1)$$

There is some ambiguity here about the relation between ρ and a , which makes this formula somewhat difficult to apply to dilute systems. In dense media however, one expects that $4\pi a^3/3 = 1/\rho$ and we shall confine to this situation here.

(a) Non-polar substance ($\mu = 0$):

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{3\epsilon} = \frac{4\pi\rho\alpha}{1 - g\alpha}$$

Noting that

$$g\alpha = \frac{2}{a^3} \frac{\epsilon - 1}{2\epsilon + 1} \alpha = \frac{8\pi\rho\alpha}{3} \frac{\epsilon - 1}{2\epsilon + 1}$$

we finally find the well-known expression

$$\boxed{\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi\rho\alpha}{3}} \quad (5.2)$$

which agrees reasonably well with experiment. (Note that ϵ is here equivalent to the square of the refractive index n , extrapolated to infinite wavelength).

(b) Polar substances:

It is convenient here to eliminate α in terms of ϵ_∞ defined as

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} = \frac{4\pi\rho\alpha}{3} \quad (5.3)$$

($\epsilon_\infty = n_\infty^2$). We have

$$1 - g\alpha = 1 - 2 \frac{(\epsilon_\infty - 1)(\epsilon - 1)}{(\epsilon_\infty + 2)(2\epsilon + 1)} = 3 \frac{2\epsilon + \epsilon_\infty}{(\epsilon_\infty + 2)(2\epsilon + 1)}$$

and

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{3\epsilon} = \frac{(\epsilon_\infty - 1)(2\epsilon + 1)}{(2\epsilon + \epsilon_\infty)} + \frac{4\pi\rho\mu^2}{3kT} \left(\frac{\epsilon_\infty + 2}{3} \right)^2 \frac{(2\epsilon + 1)^2}{(2\epsilon + \epsilon_\infty)^2}$$

This gives finally

$$\epsilon - \epsilon_{\infty} = \frac{3\epsilon}{2\epsilon + \epsilon_{\infty}} \left(\frac{\epsilon_{\infty} + 2}{3} \right)^2 \frac{4\pi\rho\mu^2}{3kT} \quad (5.4)$$

This formula agrees roughly with experiments for normal liquids (10 to 20%). For associated ones, the deviations are larger: in the extreme case of water, (5.4) gives $\epsilon \approx 29$ instead of 78.5 at 25°C. At any rate, the Onsager's formula, given in 1936, constitutes an enormous improvement with respect to the Debye equation (cf. Appendix I).

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi\rho}{3} \left(\alpha + \frac{\mu^2}{3kT} \right) \quad (5.5)$$

which is strictly valid for dilute systems only and wrongly predicts spontaneous polarization when

$$\frac{4\pi\rho\mu^2}{9kT} \left(\frac{\epsilon_{\infty} + 2}{3} \right) > 1$$

("liquid" water would be ferroelectric up to $\sim 1200^\circ\text{C}$). A large effort has been made to improve Onsager's formula as well as to strengthen its physical basis by deriving it from molecular arguments. Actually Eq. (5.4) accounts correctly for long range polarization effects but neglects the discrete structure of the surrounding of a molecule, where

- (i) one cannot treat the polarization macroscopically,
- (ii) short range forces may be important.

6. Assembly of dipolar molecules in an external field.

Though it certainly is a drastic simplification, we consider here molecules with a point-dipole $\tilde{m}$ at their center. The dipolar field at a distance $\tilde{r}$ of such a molecule is

$$\tilde{T}(\tilde{r}) \cdot \tilde{m} \quad (6.1)$$

with

$$\tilde{T}(\tilde{r}) = -\nabla\nabla\left(\frac{1}{r}\right) = \frac{1}{r^3}(\tilde{U} - 3\tilde{r}\tilde{r}/r^2)$$

($\tilde{U}$ = unit tensor), and the interaction energy between a pair ($\tilde{j}, \tilde{k}$) is

$$\tilde{m}_{\tilde{j}} \cdot \tilde{T}_{\tilde{j}\tilde{k}} \cdot \tilde{m}_{\tilde{k}},$$

while the interaction of $\tilde{j}$ with an external field $\tilde{E}_0$ is

$$- \tilde{m}_j \cdot \tilde{E}_0$$

The dipole moment $\tilde{m}_j$ is generally the sum of a permanent part μ_j and an induced part $\alpha \tilde{F}_j$

$$\tilde{m}_j = \mu_j + \alpha \tilde{F}_j \quad (6.2)$$

where $\tilde{F}_j$ is the local field acting on j :

$$\tilde{F}_j = \tilde{E}_0 - \sum_{k(\neq j)} \frac{T_{jk}}{\tilde{r}_{jk}} \cdot \tilde{m}_k \quad (6.3)$$

The deformation energy required for inducing the dipole $\alpha \tilde{F}_j$ is

$$\frac{1}{2} \alpha \tilde{F}_j^2$$

Hence the total potential energy of a system of N molecules in an applied field $\tilde{E}_0$:

$$U = \frac{1}{2} \sum_{j \neq k} \tilde{m}_j \cdot \frac{T_{jk}}{\tilde{r}_{jk}} \cdot \tilde{m}_k - \tilde{E}_0 \cdot \sum_j \tilde{m}_j + \frac{1}{2} \alpha \sum_j \tilde{F}_j^2 + U_{\text{short}} \quad (6.4)$$

where the last term takes care of short range interactions. Note that instead of the quantum mechanical concept of polarizability, one may equivalently use the classical model of an oscillating charge q , with elongation u and potential energy $1/2 Ku^2$; one has then

$$\tilde{m} = \mu + qu$$

with the correspondence

$$\alpha \tilde{F} \equiv qu, \quad \frac{1}{2} \alpha \tilde{F}^2 \equiv \frac{1}{2} Ku^2,$$

so that $\alpha \equiv q^2/K$. The total electric moment of the system is related to U by

$$\tilde{M} = \sum_j \tilde{m}_j = - \frac{\partial U}{\partial \tilde{E}_0}, \quad (6.5)$$

irrelevant to the use of α or of the oscillator model.

It is useful to distinguish in U and M between these parts which are dependent on $\tilde{E}_0$ and those which are not.

Noticing from Eqs. (6.2) and (6.3) that the $\tilde{m}_j$'s are fixed by the set of linear equations

$$\tilde{m}_j + \alpha \sum_{k(\neq j)} T_{jk} \cdot \tilde{m}_k = \mu_j + \alpha \tilde{E}_0 \quad (j = 1, \dots, N)$$

(for a given molecular configuration), we split $\tilde{m}_j$ into

$$\tilde{m}_j = \tilde{m}_j^0 + \alpha \tilde{K}_j \quad (6.6)$$

where the first part corresponds to zero field

$$\tilde{m}_j^0 + \alpha \sum_{k(\neq j)} T_{jk} \cdot \tilde{m}_k^0 = \mu_j \quad (6.7)$$

which the second one is linear in $\tilde{E}_0$

$$\tilde{K}_j + \alpha \sum_{k(\neq j)} T_{jk} \cdot \tilde{K}_k = \tilde{E}_0 \quad (6.8)$$

($\tilde{K}$ is the part of the local field $\tilde{F}$ which arises from $\tilde{E}_0$). A skillful rearrangement of Eq. (6.4) gives

$$\begin{aligned} U &= U_{\text{short}} + \frac{1}{2} \sum_{j \neq k} \mu_j \cdot T_{jk} \cdot \tilde{m}_k^0 - \tilde{E}_0 \cdot \sum_j \tilde{m}_j^0 \\ &= \frac{1}{2} \alpha \tilde{E}_0 \cdot \sum_j \tilde{K}_j, \end{aligned} \quad (6.9)$$

where the first two terms are independent of $\tilde{E}_0$, while the third and fourth ones are respectively proportional to $\tilde{E}_0$ and $\tilde{E}_0^2$. (The last term may be dropped in a linear theory.)

7. General statistical formulation of ϵ .

Consider a macroscopic body in vacuo, polarized by an applied field $\tilde{E}_0$. Its average total electric moment is

$$\langle \tilde{M} \rangle_{\tilde{E}_0} = \int \tilde{M} e^{-\beta U} d\tau / \int e^{-\beta U} d\tau$$

where we integrate over all coordinates. In the linear approximation, we have

$$\tilde{M} = \tilde{M}^0 + \tilde{E}_0 \cdot \left(\frac{\partial}{\partial \tilde{E}_0} \tilde{M} \right)^0, \quad U = U^0 + \left(\frac{\partial U}{\partial \tilde{E}_0} \right)^0 \cdot \tilde{E}_0,$$

and, assuming that there is no spontaneous polarization, we obtain

$$\begin{aligned}\langle \tilde{M} \rangle_{E_0} &= E_0 \cdot \left\langle \left(\frac{\partial}{\partial E_0} \tilde{M} \right)^0 \right\rangle - \beta \left(\frac{\partial U}{\partial E_0} \right)^0 \tilde{M}^0 \\ &= E_0 \cdot \left\langle \left(\frac{\partial}{\partial E_0} \tilde{M} \right)^0 \right\rangle + \beta \tilde{M}^0 \tilde{M}^0\end{aligned}$$

The quantities with a superscript "o" are taken at zero external field, as well as the canonical average of the r.h.s. For simplicity assume the specimen to be homogeneous, isotropic and of spherical shape: then $\tilde{P}$ is itself uniform and parallel to E_0 , and we have

$$\langle \tilde{M} \rangle_{E_0} = V \tilde{P} \quad (V = \text{volume})$$

$$\frac{4\pi}{3} P = \frac{\epsilon - 1}{\epsilon + 2} E_0 \quad (\text{cf. 3.4})$$

Moreover the averages of the type $\langle a \cdot b \rangle$ may be replaced by $1/3 \langle \tilde{a} \cdot \tilde{b} \rangle$ times the unit tensor. It follows that

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3V} \frac{1}{3} \left\langle \left(\frac{\partial}{\partial E_0} \cdot \tilde{M} \right)^0 + \beta \tilde{M}^0 \cdot \tilde{M}^0 \right\rangle_{\text{sphere}}$$

For a pure substance, all molecules being equivalent, we have, recalling that $\tilde{M} = \sum_j \tilde{m}_j$:

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi\rho}{3} \frac{1}{3} \left\langle \left(\frac{\partial}{\partial E_0} \cdot \tilde{m} \right)^0 + \beta \tilde{m}^0 \cdot \tilde{m}^0 \right\rangle_{\text{sphere}} \quad (7.1)$$

where ρ is the number density.

This expression is perfectly general (within the applicability of classical mechanics). One must however be cautious with respect to the physical interpretation of its two terms. For example, notwithstanding the equivalence of the polarizability α and the harmonic oscillator model, the separate contributions of the two terms of Eq. (7.1) are completely different in the two treatments.

If we describe the induced dipoles in terms of a polarizability α as in §6, we have following (6.6)-(6.8)

$$\left(\frac{\partial}{\partial E_0} \cdot \tilde{m} \right)^0 = \alpha \frac{\partial}{\partial E_0} \cdot \tilde{K}, \quad (7.2)$$

completely independent of the configuration of the permanent dipoles. Therefore the first term of (7.1) is exclusively

related to the induced dipoles. Its second term is due to the permanent dipoles (it drops to zero for $\mu = 0$), but it involves serious complications due to induced effects.

8. Non-polar substances.

For this particular case, Eq. (7.1) reduces to

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi\rho\alpha}{3} \left\langle \frac{1}{3} \left(\frac{\partial}{\partial \underline{E}_0} \cdot \underline{K} \right)^0 \right\rangle_{\text{sphere}}$$

on account of Eq. (7.2), and the local field $\underline{K}$ is determined by the set of equations (6.8)

$$\underline{K}_j + \alpha \sum_{k(\neq j)} T_{jk} \cdot \underline{K}_k = \underline{E}_0 \quad (j = 1, \dots, N) \quad (8.1)$$

The fact that T_{jk} is $\sim r_{jk}^{-3}$, implies that the second term of these equations is of the order of $\rho\alpha$ which is usually rather small (0.05 to 0.1 for liquids). This suggests the approximation

$$\underline{K}_j = \underline{E}_0, \quad \frac{1}{3} \frac{\partial}{\partial \underline{E}_0} \cdot \underline{K} = 1$$

which brings us back to (5.1)

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi\rho\alpha}{3}.$$

Although this expression follows here from the assumption $\rho\alpha \ll 1$, it is perfectly rigorous for a rigid cubic crystal. Indeed there are no fluctuations present in such a system, so that $\underline{K}$ is the same at all sites and parallel to $\underline{E}_0$ (spherical specimen). Putting $\underline{E}_0$ along z , we have from (8.1)

$$\left(1 + \alpha \sum_{k(\neq j)} T_{jk}^{zz} \right) K = E_0$$

The sum of the l.h.s. vanishes within a sphere, so that one rigorously finds $K = E_0$.

For a more realistic system with density fluctuations, one must first solve the set of equations (8.1). This leads to the following expansion in α

$$\underline{K}_j = \left\{ \underline{E}_0 - \alpha \sum_k T_{jk} \cdot \underline{K}_k + \alpha^2 \sum_k \sum_\ell T_{jk} \cdot T_{k\ell} \cdot \underline{K}_\ell - \alpha^3 \dots \right\} \cdot \underline{E}_0$$

(with the convention that $T_{jj} = 0$), so that

$$\frac{1}{3} \frac{\partial}{\partial E_0} \cdot K_j = 1 - \alpha \sum_k \frac{1}{3} \text{Trace } T_{jk} + \alpha^2 \sum_k \sum_l \frac{1}{3} \text{Trace } (T_{jk} \cdot T_{kl}) - \alpha^3 \dots$$

Actually the trace of T is zero, and up to terms in α^3 we have exactly

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi\rho\alpha}{3} \left\{ 1 + \alpha^2 \left\langle \sum_k \sum_l \frac{1}{3} \text{Trace}(T_{jk} \cdot T_{kl}) \right\rangle_{\text{sphere}} \right\} \quad (8.2)$$

For a harmonic solid the second term of Eq. (8.2) would be related to its thermal vibrations. For a liquid this term may be expressed by means of the pair and triplet-distribution functions g_2 and g_3 . A careful rearrangement gives

$$\begin{aligned} \left\langle \sum_k \sum_l \frac{1}{3} \text{Trace}(T_{jk} \cdot T_{kl}) \right\rangle_{\text{sphere}} &= 4\pi\rho \int_0^\infty \frac{2}{r^6} g_2(r) r^2 dr \\ &+ 8\pi^2 \rho^2 \int_0^\infty \int_0^\infty \int_0^\pi \frac{3 \cos^2 \theta - 1}{r^3 r'^3} [g_3(r, r', \theta) - g_2(r) g_2(r')] \\ &\quad r^2 dr r'^2 dr' \sin \theta d\theta \end{aligned} \quad (8.3)$$

where the integrations extend to infinity because each integrand is now short range. A rather crude estimate of Eq. (8.3) may be obtained from the following model:

$$g_2(r) \begin{cases} = 1 & \text{if } r > D \\ = 0 & \text{if } r < D \end{cases}$$

$$g_3(r, r', \theta) \begin{cases} = 1 & \text{if } r > D, r' > D \text{ and } r^2 + r'^2 - 2rr' \cos \theta > D^2 \\ = 0 & \text{otherwise} \end{cases}$$

The two terms involved in (8.3) give respectively $(8\pi\rho/3D^3)$ and $(15/16)(4\pi\rho/3)^2$. As in this picture, D stands for the diameter of a molecule, we may as well put $\pi D^3/6$ equal to $1/\rho$. This gives finally

$$\frac{\epsilon - 1}{\epsilon + 2} \simeq \frac{4\pi\rho\alpha}{3} \left\{ 1 - \frac{11}{16} \left(\frac{4\pi\rho\alpha}{3} \right)^2 \right\}.$$

For most liquids, $4\pi\rho\alpha/3$ is close to 0.4, so that the second term contributes roughly to $\sim 10\%$.

9. Polar substances.

Recalling that the first part of (7.1) results from induced effects alone, we may rewrite this expression as

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{\epsilon_{\infty} - 1}{\epsilon_{\infty} + 2} + \frac{4\pi\rho}{3} \frac{\langle \tilde{m}^0 \cdot \tilde{M}^0 \rangle_{\text{sphere}}}{3kT} \quad (9.1)$$

For simplicity, we first consider non-polarizable molecules ($\alpha = 0$, $\epsilon_{\infty} = 1$), so that

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi\rho}{3} \frac{\langle \tilde{\mu} \cdot \tilde{M} \rangle}{3kT} \quad (9.2)$$

with $\tilde{M} = \sum \mu_j$. This problem has been treated by Kirkwood⁶ as follows. Consider the average electric moment $\langle \tilde{M} \rangle_{\mu}$ of the whole specimen for one arbitrary molecule fixed in a given orientation μ , so that $\langle \tilde{M} \rangle_{\mu}$ is equal to μ itself, plus the polarization of the specimen by μ . In the close neighborhood of μ , it is certainly not allowed to treat the polarization on a macroscopic level. Therefore, let us divide the body into two regions by a small sphere of radius r_0 centered on μ , and split $\langle \tilde{M} \rangle_{\mu}$ accordingly into two parts. Let μ^* be that part of $\langle \tilde{M} \rangle_{\mu}$ corresponding to the inner region, and take r_0 just big enough so that the outer region of the specimen may be treated macroscopically. It is then a matter of classical electrostatics to show that

$$\langle \tilde{M} \rangle_{\mu} = \frac{9\epsilon}{(\epsilon + 2)(2\epsilon + 1)} \mu^* \quad (9.3)$$

provided that the external radius of the body is $\gg r_0$. The difference between $\langle \tilde{M} \rangle_{\mu}$ and μ^* arises from the polarization of the outer surface of the specimen. Actually we may now let this surface recede to infinity and consider μ^* as the average electric moment of a small macroscopic sphere centered upon μ , and embedded into its own medium; one can indeed show that μ^* is independent of the choice of r_0 (provided that it is macroscopic). For an isotropic homogeneous system, μ^* and μ will be parallel so that

$$\langle \tilde{\mu} \cdot \tilde{M} \rangle = \frac{9\epsilon}{(\epsilon + 2)(2\epsilon + 1)} \mu \mu^*$$

and finally

$$\epsilon - 1 = \frac{3\epsilon}{2\epsilon + 1} \frac{4\pi\rho\mu\mu^*}{3kT} \quad (9.4)$$

This expression is identical with Onsager's formula (5.4) in the case $\epsilon_{\infty} = 1$, apart from the introduction of μ^* which takes care of all kinds of short range effects which are not describable macroscopically. Putting r_0 equal to the radius of the cavity involved in Onsager's theory gives immediately $\mu^* = \mu$.

Expression (9.4) is general and rigorous. It must still be modified in order to include the induced effects. The simple and apparently obvious generalization of (9.3)

$$\langle \tilde{M}^O \rangle_{m^O} = \frac{9\epsilon}{(\epsilon + 2)(2\epsilon + 1)} m^*$$

turns out to be wrong: indeed, m^O is the total electric moment of a given molecule, and to keep it constant, we must freeze the local field acting on this molecule. This imposes restrictions on the configurations of the whole specimen and one cannot treat its outer part macroscopically.

As induced effects play a rather secondary role for strongly polar substances, we may approximately treat them in a macroscopic way, by substituting for the actual system an assembly of unpolarizable molecules with permanent dipole μ_O moving in a continuum of dielectric constant ϵ_∞ , corresponding to the smearing of the polarizability of the real molecules over all space.⁷ One has then

$$\frac{\epsilon - \epsilon_\infty}{4\pi} E = P_{\text{dip}} = \rho \frac{\langle \mu_O \cdot \tilde{M}_O \rangle}{3kT}$$

$$E = \frac{3}{\epsilon + 2} E_O$$

$$\langle \tilde{M}_O \rangle \mu_O = \frac{9\epsilon}{(\epsilon + 2)(2\epsilon + \epsilon_\infty)} \mu_O^*$$

where P_{dip} accounts for the permanent dipoles only. This gives

$$\epsilon - \epsilon_\infty = \frac{3\epsilon}{2\epsilon + \epsilon_\infty} \frac{4\pi\rho\mu_O\mu_O^*}{3kT} \quad (9.5)$$

where μ_O^* has the same meaning as previously. Each one of our fictitious molecules, when isolated in space, must behave as a small sphere of dielectric constant ϵ_∞ , containing a dipole μ_O , and as such, exerts a dipolar field

$$- \frac{3}{\epsilon_\infty + 2} \frac{T \cdot \mu_O}{\tilde{r}^3}$$

on its neighborhood. The corresponding expression for a real molecule is $-\frac{T \cdot \mu}{\tilde{r}^3}$, which implies the equivalence

$$\mu_O = \frac{\epsilon_\infty + 2}{3} \mu$$

It follows finally from Eq. (9.5)

$$\epsilon - \epsilon_{\infty} = \frac{3\epsilon}{2\epsilon + \epsilon_{\infty}} \left(\frac{\epsilon_{\infty} + 2}{3} \right)^2 \frac{4\pi\rho\mu\mu^*}{3kT} \quad (9.6)$$

which is the complete generalization of Onsager's formula (5.4).

Expression (9.6) is fairly general, notwithstanding some weakness due to the macroscopic treatment of induced effects. Much work has been spent on rederiving (9.6) in a better way or for somewhat particular models.^{8,9} In a sense the theory is complete as far as long range effects are concerned; on the other hand there remains to calculate μ^* . This, however, is a matter of short range interactions and local structure, which varies for each particular case.

Empirically, when (9.6) is applied to normal liquids, one finds that μ^*/μ varies usually between 0.8 and 1.2. For associated substances, larger deviation from unity are frequent. For water at 25°C, with $\epsilon = 78.5$, $\epsilon_{\infty} \simeq 1.8$, $\mu = 1.84$ D, one obtains $\mu^*/\mu \simeq 2.8$. This high value may be understood from the Bernal-Fowler model: the oxygen atoms are on the sites of a tetrahedral lattice and there is exactly one hydrogen atom between each pair of adjacent oxygens. Looking at nearest neighbors only, one has

$$\mu^*/\mu = 1 + 4\left(\frac{1}{3}\right) = 2.33$$

which gives $\epsilon \simeq 65$. A closer agreement is obtained when all neighbors are retained: $\mu^*/\mu = 3$ and $\epsilon \simeq 84$.

10. High temperature expansions.

Purely statistical calculations of the average $\langle \tilde{m}^0 \cdot \tilde{M}^0 \rangle$ involved in (9.1) have been attempted by considering perturbation expansions in powers of $(\rho\mu^2/3kT)$:

$$\langle \tilde{m}^0 \cdot \tilde{M}^0 \rangle = \int e^{-\beta U^0} \tilde{m}^0 \cdot \tilde{M}^0 d\tau \int e^{-\beta U^0} d\tau$$

with

$$U^0 = U_{\text{short}} + \frac{1}{2} \sum_j \sum_k \mu_j \cdot T_{jk} \cdot \tilde{m}_k^0$$

(cf. §6). A few first terms can be worked out, but the rate of convergence is so poor that the results are of little practical use. Up to μ^6 , one finds for a rigid cubic lattice of permanent dipoles ($\alpha = 0$)^{10,11}

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} \left(\frac{\rho\mu^2}{3kT} \right) \left\{ 1 - 2 \left(\frac{\rho\mu^2}{3kT} \right)^2 \sum_j \frac{1}{R_j^6} + \dots \right\} \quad (10.1)$$

(R_j is dimensionless and such that the mean volume per site is unity.) For a s.c. lattice, the sum in the r.h.s. is ~ 8.23 , so that the formula fails completely for $(\rho\mu^2/3kT) \simeq 0.2$.

Note that (10.1), when suitably rearranged in the form of (9.4), provides us with some information on μ^*/μ :

$$\mu^*/\mu \simeq 1 + 2 \left(\frac{\rho\mu^2}{3kT} \right)^2 \left\{ \left(\frac{4\pi}{3} \right)^2 - \sum_j \frac{1}{R_j^6} \right\} + \dots \quad (10.2)$$

For the s.c. lattice this gives

$$\mu^*/\mu \simeq 1 + 18.6 \left(\frac{\rho\mu^2}{3kT} \right)^2 + \dots$$

On the other hand, if we approximate the lattice sum of (10.2) by an integral (excluding a unit volume around the origin), we have an exact cancellation so that $\mu^*/\mu = 1$: this is just the continuous approximation of Onsager.

REFERENCES TO PART I

1. J. C. Maxwell, Treatise of Electricity and Magnetism, Oxford University Press (1904) p. 66.
2. H. Fröhlich, Theory of Dielectrics, Oxford Clarendon Press, (1958), p. 163.
3. L. Onsager, J. Am. Chem. Soc. 58, 1486 (1936).
4. M. Mandel and P. Mazur, Physica 24, 116 (1958).
5. J. G. Kirkwood, J. Chem. Phys. 4, 592 (1936).
6. J. G. Kirkwood, J. Chem. Phys. 7, 911 (1939).
7. H. Fröhlich, see Ref. 2, p. 49.
8. A. D. Buckingham, Proc. Roy. Soc. A238, 235 (1956).
9. R. H. Cole, J. Chem. Phys. 27, 33 (1957).
10. J. H. Van Vleck, J. Chem. Phys. 5, 556 (1937).
11. R. Rosenberg and M. Lax, J. Chem. Phys. 21, 424 (1953).

APPENDIX I. THE DEBYE EQUATION

Equation (5.5) may be obtained as follows: the polarization $\tilde{P}$ is given by

$$\tilde{P} = \rho \langle \tilde{m} \rangle = \rho \left\{ \langle \mu \rangle + \alpha \langle \tilde{F} \rangle \right\} = \frac{\epsilon - 1}{4\pi} \tilde{E}$$

with

$$\begin{aligned} \langle \tilde{F} \rangle &= \frac{3\epsilon}{2\epsilon + 1} \tilde{E} + \frac{2}{a^3} \frac{\epsilon - 1}{2\epsilon + 1} \langle \tilde{m} \rangle \\ &= \left\{ \frac{3\epsilon}{2\epsilon + 1} + \frac{2(\epsilon - 1)^2}{4\pi a^3 \rho (2\epsilon + 1)} \right\} \tilde{E} \\ &= \frac{\epsilon + 2}{3} \tilde{E} \quad , \quad (= \tilde{E} + \frac{4\pi}{3} \tilde{P} = \text{Lorentz field}) \end{aligned}$$

when $4\pi a^3/3 = 1/\rho$. If we now assume the potential energy of μ to be $-\mu \cdot \langle \tilde{F} \rangle$, then, in the linear approximation

$$\langle \mu \rangle = \frac{\mu^2}{3kT} \langle \tilde{F} \rangle$$

and (5.5) follows immediately

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi\rho}{3} \left(\alpha + \frac{\mu^2}{3kT} \right)$$

The wrong step is to calculate $\langle \mu \rangle$ from $\langle \tilde{F} \rangle$ instead of $\tilde{E}$, i.e., to perform two independent averages instead of a single one. As a consequence, the orienting force on μ is exaggerated by a factor $\sim \epsilon$, as it includes the mean value of the reaction field, whatever the orientation of μ may be. This is the origin of the spontaneous polarization predicted by (5.5).

II. THE DYNAMIC DIELECTRIC FUNCTION

11. The behavior of a dielectric body in a time-dependent field.

When a constant field E_0 is suddenly applied to a dielectric body, a certain time interval is required for the molecules to adjust their motions and their internal structure to this new situation (relaxation time). When the system eventually reaches equilibrium, its electric state is described by the polarization vector $\vec{P}$, and the electric field at each point is given by

$$\vec{E} = \vec{E}_0 + \vec{E}_{\text{dep}} = \frac{4\pi}{\epsilon - 1} \vec{P} ,$$

where E_{dep} is the depolarization field and ϵ is the static dielectric constant.

If we let E_0 vary with time, then E and P obviously become time-dependent. The important point is that, when $E_0(t)$ changes appreciably during a time interval comparable to the relaxation time of the system, then $P(t)$ can never approach the equilibrium value corresponding to a static field $\equiv E_0(t)$, and one has

$$\vec{E}(t) = \vec{E}_0(t) + \vec{E}_{\text{dep}}(t) \neq \frac{4\pi}{\epsilon - 1} \vec{P}(t) .$$

Of course there is not just one relaxation time in a molecular system: roughly speaking, each type of degree of freedom has its own characteristic time. In a simple system of polar molecules, the situation is as follows

- (a) The characteristic time for the reorientation of a dipole is at least $(I/kT)^{1/2} \sim 10^{-12}$ sec (I = mean moment of inertia of a molecule); for liquids with appreciable rotational hindrance, it is usually $\sim 10^{-10}$ sec, and it is even longer in solids.
- (b) The polarizability of a molecule is primarily related to electronic motions with characteristic times $\sim 10^{-16}$ sec, and secondarily to intramolecular vibrations with characteristic times $\sim 10^{-14}$ sec.

The deformation of the trajectories of the particles in the system is always very small ($\mu E_0/kT \sim 10^{-7}$ at room temperature for $\mu = 1$ Debye and $E_0 = 1$ Volt/cm). An oscillating field of frequency ω will systematically affect degrees of freedom with characteristic time τ as long as $\omega\tau \leq 1$; it will become ineffective for $\omega\tau \gg 1$, because the deformations of the trajectories average out to zero over periods of time smaller than τ . In this respect, permanent dipoles will contribute to the polarization of a liquid up to $\omega \sim 10^{10} - 10^{12}$ sec $^{-1}$, and polarizability effects up to $\omega \sim 10^{16}$ sec $^{-1}$. We here will mainly be concerned with the relaxation effects related to the permanent dipoles (rotational motion of the molecules).

12. The dynamic dielectric function.¹

The values of $\tilde{P}(t)$ and $\tilde{E}(t)$ are not simply related to $\tilde{E}_0(t)$, but depend upon all values that $\tilde{E}_0$ has assumed in the past. Therefore, in the linear approximation, we write in a purely phenomenological way

$$\tilde{E}(t) = \tilde{E}_0(t) + \int_{-\infty}^t \tilde{\epsilon}(t - t') \cdot \tilde{E}_0(t') dt' ,$$

$$\tilde{P}(t) = \int_{-\infty}^t \tilde{g}(t - t') \cdot \tilde{E}_0(t') dt' ,$$

where the tensors $\tilde{\epsilon}$ and $\tilde{g}$ determine how much the values $\tilde{E}(t)$ and $\tilde{P}(t)$ are influenced by $\tilde{E}_0(t')$ for $t' < t$. Defining $s = t - t'$, we have equivalently

$$\tilde{P}(t) = \int_0^{\infty} \tilde{h}(s) \cdot \tilde{E}(t - s) ds . \quad (12.1)$$

For isotropic media, $\tilde{h}(s) = h(s) \tilde{U}$, where $\tilde{U}$ is the unit tensor (note that $\tilde{\epsilon}(s)$ and $\tilde{g}(s)$ are both shape-dependent). Expression (12.1) generalizes the static expression

$$P = \frac{\epsilon - 1}{4\pi} E$$

and it follows, by considering a constant field E in (12.1), that

$$\int_0^{\infty} h(s) ds = \frac{\epsilon - 1}{4\pi} .$$

Actually the function $h(s)$ contains all the required information for defining the static and the dynamic dielectric properties of the system. The expected form of $h(s)$ is schematically represented on the opposite figure. Note that $h(s)$ may (and sometimes does) become negative. Because of the different types of degrees of freedom involved in actual systems, $h(s)$ will be a superposition of several curves of the form represented here, with different time scales.

The complete generalization of the static dielectric constant is obtained by decomposing $\tilde{P}(t)$ and $\tilde{E}(t)$ in Fourier series

$$P(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} P(t) e^{-i\omega t} dt, \quad E(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} E(t) e^{-i\omega t} dt,$$

and Fourier transforming (12.1). This leads to

$$P(\omega) = \left(\int_0^{\infty} h(s) e^{-i\omega s} ds \right) E(\omega)$$

which can be rewritten as

$$P(\omega) = \frac{\epsilon(\omega) - 1}{4\pi} E(\omega); \quad (12.2)$$

$\epsilon(\omega)$ is called the dynamic dielectric function:

$$\epsilon(\omega) = 1 + 4\pi \int_0^{\infty} h(s) e^{-i\omega s} ds. \quad (12.3)$$

As $h(s)$ is real, one has $\epsilon^*(\omega) = \epsilon(-\omega)$. Let us consider the real and imaginary parts of $\epsilon(\omega)$ separately:

$$\epsilon(\omega) = \epsilon'(\omega) - i\epsilon''(\omega).$$

The following relations are obvious

$$\begin{aligned} (a) \quad \epsilon'(\omega) &= \epsilon'(-\omega), & \epsilon''(\omega) &= -\epsilon''(-\omega); \\ (b) \quad \epsilon'(0) &= \epsilon, & \epsilon''(0) &= 0; \\ (c) \quad \epsilon'(\infty) &= 1, & \epsilon''(\infty) &= 0. \end{aligned}$$

Moreover one sees from (12.3) that $\epsilon'(\omega) - 1$ and $\epsilon''(\omega)$ are respectively the cosine and the sine Fourier transforms of $4\pi h(s)$, so that they are connected by the Kramers-Kronig relations

$$\epsilon'(\omega) - 1 = \frac{2}{\pi} \int_0^{\infty} \epsilon''(y) \frac{y}{y^2 - \omega^2} dy, \quad (12.4)$$

$$\epsilon''(\omega) = \frac{2}{\pi} \int_0^{\infty} [\epsilon'(y) - 1] \frac{\omega}{\omega^2 - y^2} dy. \quad (12.5)$$

As a by product of (12.4), we find, by letting ω go to zero,

$$\epsilon - 1 = \frac{2}{\pi} \int_0^{\infty} \epsilon''(y) \frac{dy}{y} \quad (12.6)$$

implying that $\epsilon''(\omega)$ is positive within some region of positive frequencies.

Actually $\epsilon''(\omega)$ is related to the delay of $P(t)$, or $D(t) = E(t) + 4\pi P(t)$, with respect to $E(t)$. For an oscillating field $E(t) = E \cos \omega t$, we have indeed

$$\begin{aligned} D(t) &= \frac{1}{2} E [\epsilon(\omega) e^{i\omega t} + \epsilon(-\omega) e^{-i\omega t}] \\ &= \epsilon'(\omega) E \cos \omega t + \epsilon''(\omega) E \sin \omega t, \end{aligned} \quad (12.7)$$

where that part of D proportional to $\epsilon'(\omega)$ is in phase with E , while the one proportional to $\epsilon''(\omega)$ has a phase different of $\pi/2$. Now, a dielectric body, kept in a thermostat and submitted to an oscillating field, performs a Carnot cycle in each period. Therefore the second law of thermodynamics requires the work W , spent by the external world on this system per unit time, to be positive or zero. By applying Joule's law to the displacement current $(\partial D/\partial t)/4\pi$, we find (per unit volume)

$$\begin{aligned} W &= \int_0^1 \left(\frac{1}{4\pi} \frac{\partial D}{\partial t} \right) E dt \\ &= (E^2/8\pi) \omega \epsilon''(\omega). \end{aligned}$$

Therefore $\epsilon''(\omega)$ corresponds to dissipation effects, and as W is ≥ 0 , one has

$$\epsilon''(\omega) > 0 \quad (12.8)$$

for all positive ω .

The final picture we obtain for $\epsilon'(\omega)$ and $\epsilon''(\omega)$ is shown on the opposite figure. Actual systems usually present more than one maximum in $\epsilon''(\omega)$ [and fall in $\epsilon'(\omega)$], each of these corresponding to the "freezing" of a particular kind of degree of freedom. Note that nothing prevents $\epsilon'(\omega)$ becoming negative.

13. Relations between $\tilde{E}$ and $\tilde{E}_0$ in special cases.

We discussed the relations between P , E and E_0 for the static case in § 3. All the formulas quoted there, as well as those of § 4, are immediately applicable to the Fourier components of P , E and E_0 in the dynamic case, when ϵ is replaced by $\epsilon(\omega)$. For example, the relations between $P(\omega)$, $E(\omega)$ and $E_0(\omega)$ for a spherical specimen, are

$$E(\omega) = \frac{3}{\epsilon(\omega) + 2} E_0(\omega) , \quad (13.1)$$

$$\frac{4\pi}{3} P(\omega) = \frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2} E_0(\omega) , \quad (13.2)$$

with

$$E_0(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} E_0(t) e^{-i\omega t} dt .$$

14. A macroscopic formulation of $\epsilon(\omega)$.

Consider the following intuitive model for the relaxation of $P(t)$: the change of P with time is proportional to the difference between $P(t)$ and its hypothetical equilibrium value in a static field equal to $E(t)$. This may be expressed as

$$\frac{dP}{dt} = - \frac{1}{\tau} \left\{ P - \frac{\epsilon - 1}{4\pi} E \right\}$$

where τ is a relaxation time. Actually in a polar substance, two different relaxation times (at least) are required for orientation and deformation effects respectively. We shall, however, assume that the variation of E with time is slow enough, so that the deformation effects may be treated by a static dielectric constant ϵ_∞ (= square of the refractive index). This corresponds to a splitting of P :

$$P = P_{\text{def}} + P_{\text{or}} , \quad P_{\text{def}} = \frac{\epsilon_\infty - 1}{4\pi} E ,$$

$$\frac{dP_{\text{or}}}{dt} = - \frac{1}{\tau} \left(P_{\text{or}} - \frac{\epsilon - \epsilon_\infty}{4\pi} E \right) .$$

This last equation can be solved in the form

$$P_{\text{or}}(t) = \frac{\epsilon - \epsilon_\infty}{4\pi\tau} \int_{-\infty}^t e^{-\frac{t-t'}{\tau}} E(t') dt'$$

$$= \frac{\epsilon - \epsilon_{\infty}}{4\pi\tau} \int_0^{\infty} e^{-s/\tau} E(t-s) ds.$$

Comparing with (12.1) shows that, within the present treatment, that part of $h(s)$ related to orientational effects takes the form

$$\frac{\epsilon - \epsilon_{\infty}}{4\pi\tau} e^{-s/\tau}$$

(incorrect for very short times as $h(0)$ should be zero). Adding orientation and deformation effects together, we obtain from (12.3)

$$\epsilon(\omega) = 1 + (\epsilon_{\infty} - 1) + \frac{\epsilon - \epsilon_{\infty}}{\tau} \int_0^{\infty} e^{-s/\tau} e^{-i\omega s} ds$$

i.e.

$$\boxed{\epsilon(\omega) - \epsilon_{\infty} = \frac{\epsilon - \epsilon_{\infty}}{1 + i\omega\tau}} \quad (14.1)$$

The real and imaginary parts of $\epsilon(\omega)$ take the simple form

$$\epsilon'(\omega) - \epsilon_{\infty} = (\epsilon - \epsilon_{\infty}) \frac{1}{1 + \omega^2\tau^2}$$

$$\epsilon''(\omega) = (\epsilon - \epsilon_{\infty}) \frac{\omega\tau}{1 + \omega^2\tau^2}$$

Their best representation is in terms of a logarithmic scale $\ln(\omega\tau)$ (see opposite figure).

An interesting representation due to Cole and Cole² is obtained by rewriting (14.1) in the equivalent form

$$\epsilon(\omega) - \frac{\epsilon + \epsilon_{\infty}}{2} = \frac{\epsilon - \epsilon_{\infty}}{2} \frac{1 - i\omega\tau}{1 + i\omega\tau} \quad (14.2)$$

The last factor has a modulus one, which means that in the superior complex half-plane (ϵ', ϵ'') , this expression corresponds to a semi-circle of radius $(\epsilon - \epsilon_{\infty})/2$ centered upon the point $[(\epsilon + \epsilon_{\infty})/2, 0]$.

Actual systems conform more or less to the preceeding picture. There is often a flattening and a broadening of $\epsilon'(\omega)$ and $\epsilon''(\omega)$ around $\omega \simeq 1$, with respect to Eq. (14.1). This is assumed to result from the fact that there is a whole spectrum of relaxation times, instead of a single one. Eq. (14.1) should then be replaced by

$$\epsilon(\omega) - \epsilon_{\infty} = (\epsilon - \epsilon_{\infty}) \int_0^{\infty} \frac{G(\tau) d\tau}{1 + i\omega\tau}$$

where $G(\tau)$ is a normalized distribution

$$\int_0^{\infty} G(\tau) d\tau = 1$$

The semi-circle diagram of Cole and Cole is obtained only in the case of a single relaxation time: a spectrum of relaxation times always corresponds to a contraction of the Cole and Cole plot inside this semi-circle.

For liquids like water or alcohols, τ is of the order of 10^{-10} sec. It usually increases considerably in the solid phase and when lowering T . No precise molecular meaning can yet be attributed to τ here, as it was introduced in a purely macroscopic way: it may therefore be preferable to call it a macroscopic decaying time, and reserve the term relaxation time for strictly molecular processes.

15. Brownian motion and dielectric relaxation.

The first attempt to account for the frequency dependence of the dynamic dielectric function of polar molecules was made by Debye in 1913. He considered the brownian motion of one molecule in its surroundings, in a time-dependent local electric field $F(t)$. This approach is semi-macroscopic (as is the model of Onsager for the static case), because the friction of the molecule in the medium is finally estimated from macroscopic data (i.e., viscosity).

We shall first rederive the Debye equation for the rotational motion of a polar molecule in two-dimensional space. Call $f(\varphi, t)$ $\delta\varphi$ the probability for finding its dipole oriented between φ and $\varphi + \delta\varphi$ at time t ; changes of $f(\varphi, t)$ with time will result from

(a) the torque $\mu \times F(t) = \Gamma(t)$

(b) the molecular interactions:

We now introduce the assumptions of brownian motion:⁴ the interaction of the molecule with the surrounding medium is described by a systematic frictional force $-\zeta\dot{\gamma}$, where γ is

its angular velocity, plus a rapidly fluctuating force $A(t)$ resulting from a large number of uncorrelated collisions between the molecule and its neighbors. Hence the stochastic equation of motion

$$I\ddot{\gamma} = -\zeta\dot{\gamma} + \Gamma(t) + A(t) \quad (15.1)$$

(I = moment of inertia)). We next focus on the variation of $f(\varphi, t) \delta\varphi$ during a time interval Δt sufficiently short so that γ , φ and $\Gamma(t)$ do not change much, but long enough so that $A(t)$ can appreciably fluctuate. We can then describe the change of $f(\varphi, t) \delta\varphi$ as the sum of two terms:

(a) A stream effect

$$- \frac{\partial}{\partial \varphi} (\gamma f) \delta\varphi \Delta t. \quad (15.2)$$

(b) A collision term corresponding to $A(t)$, expressed by means of transition probability $W(\varphi, \varphi')$ related to the time interval Δt , so that the change in $f(\varphi, t) \delta\varphi$ is

$$\begin{aligned} \delta\varphi \int \left\{ W(\varphi, \varphi') f(\varphi', t) - W(\varphi', \varphi) f(\varphi, t) \right\} d\varphi' \\ = \delta\varphi \int W(\varphi', \varphi) [f(\varphi', t) - f(\varphi, t)] \end{aligned}$$

[$W(\varphi, \varphi') = W(\varphi', \varphi)$ because of isotropy]. As small changes $\varphi' - \varphi$ are possible only, we expand $f(\varphi', t)$ around $f(\varphi, t)$ and find

$$\begin{aligned} \frac{1}{2} \delta\varphi \frac{\partial^2}{\partial \varphi^2} f(\varphi, t) \int W(\varphi', \varphi) (\varphi' - \varphi)^2 d\varphi' \\ = \frac{1}{2} a_2 \frac{\partial^2 f}{\partial \varphi^2} \delta\varphi \Delta t \end{aligned} \quad (15.3)$$

where we put $a_2 \Delta t$ equal to the second moment of $W(\varphi, \varphi')$.

Combining (15.2) and (15.3) we obtain

$$\frac{\partial f}{\partial t} = \frac{1}{2} a_2 \frac{\partial^2 f}{\partial \varphi^2} - \frac{\partial}{\partial \varphi} (\gamma f).$$

At this point we make the supplementary assumption that the friction is large enough so that the mean acceleration is always very small i.e., $\zeta\dot{\gamma} \simeq \Gamma(t)$. (This corresponds to neglecting inertial effects and treating very short times incorrectly). We then have

$$\frac{\partial f}{\partial t} = \frac{\partial}{\partial \varphi} \left(\frac{1}{2} a_2 \frac{\partial}{\partial \varphi} - \frac{\Gamma(t)}{\zeta} \right) f \quad (15.4)$$

The value of a_2 is obtained by considering a static field F oriented along $\varphi = 0$, so that $\Gamma = -\mu F \sin \varphi$. The equilibrium distribution

$$f_{eq} \sim \exp \frac{\mu F \cos \varphi}{kT}$$

must be a stationary solution of (15.4) and this implies $a_2 = 2kT/\zeta$. Hence the final result

$$\zeta \frac{\partial f}{\partial t} = \frac{\partial}{\partial \varphi} \left(kT \frac{\partial}{\partial \varphi} - \Gamma(t) \right) f \quad (15.5)$$

In three dimensions, the same kind of calculations for the brownian movement of the molecule around the z-axis gives for $f(\theta, t)$

$$\boxed{\zeta \frac{\partial f}{\partial t} = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \left(kT \frac{\partial}{\partial \theta} - \Gamma_\theta(t) \right) f} \quad (15.6)$$

where Γ_θ is the component of the torque $\mu \times F$ normal to the plane $(\hat{l}_z, \mu)$:

$$\Gamma_\theta = \frac{1}{\sin \theta} [\mu \cdot F \cos \theta - \mu \hat{l}_z \cdot F] \quad ; \quad (15.7)$$

if F is parallel to the z axis, then $\Gamma_\theta = -\mu F \sin \theta$.

As a first application of this equation, we look for the time required by the molecule to revert to a random distribution, after the removal of a weak static field oriented along the z axis:

$$F(t) = F_0 \text{ for } t < 0, \quad F(t) = 0 \text{ for } t > 0.$$

For $t < 0$, one has the equilibrium distribution

$$f_{eq}(\theta) = A \left(1 + \frac{\mu F_0}{kT} \cos \theta \right).$$

For $t > 0$, the solution of (15.6) is

$$f(\theta, t) = A \left(1 + \frac{\mu F_0}{kT} \cos \theta e^{-t/\tau_0} \right)$$

where τ_0 is a molecular relaxation time defined as

$$\tau_0 = \zeta/2kT \quad (15.8)$$

(not to be confused with the empirical macroscopic relaxation time τ of §14). Assuming the molecule to rotate like a sphere of radius a in a medium of viscosity η , one has $\zeta = 8\pi a^3 \eta$ (Stokes) and

$$\tau_0 = 4\pi a^3 \eta / kT = 3v\eta / kT \quad (15.9)$$

(v = molecular volume). This expression gives surprisingly good estimates of τ_0 for liquids and accounts qualitatively for the rapid increase of the observed relaxation times when the temperature is lowered.

The representation of the molecule by a small sphere embedded in a continuous medium reminds us the static model of Onsager, and a correct definition of $\Gamma(t)$ should actually lead to a generalization of Onsager's formula (5.4) for $\epsilon(\omega)$. The formulation of $\tilde{F}(t)$ is, however, not straightforward and several approximate treatments have been given. As in the static case $\tilde{F}(t)$ is the sum of a cavity field $\tilde{G}(t)$ and a reaction field $\tilde{R}(t)$. However, in the dynamic case the part of $\tilde{R}(t)$ related to the permanent dipole of the molecule is not parallel to $\tilde{\mu}(t)$ but is lagging behind, because it results from the past orientations of $\tilde{\mu}$. One consequence of this lag is an additional frictional force on the molecule.

We now derive the expression of $\tilde{F}(t)$ for a system polarized along the z axis. Let us first recall that the static relationships (4.1) and (4.2) still hold in the time-dependent case for the Fourier transforms of $\tilde{G}(t)$, $\tilde{E}(t)$, $\tilde{R}(t)$ and $\tilde{m}(t)$. If we generally write

$$\tilde{A}(\eta) \equiv \frac{1}{2\pi} \int_{-\infty}^{\infty} \tilde{A}(t) e^{-i\eta t} dt ,$$

($\eta \equiv$ frequency), then we have the following relations

$$\tilde{G}(\eta) = \frac{3\epsilon(\eta)}{2\epsilon(\eta) + 1} \tilde{E}(\eta)$$

$$\tilde{R}(\eta) = g(\eta) \tilde{m}(\eta)$$

$$\tilde{m}(\eta) = \tilde{\mu}(\eta) + \alpha \tilde{F}(\eta)$$

$$\tilde{F}(\eta) = \tilde{G}(\eta) + \tilde{R}(\eta)$$

so that

$$\tilde{F}(\eta) = \frac{1}{1 - \alpha g(\eta)} \left\{ \tilde{G}(\eta) + g(\eta) \tilde{\mu}(\eta) \right\} .$$

The quantity $\mu(\eta)$ is related to $\mu(t)$ by

$$\mu(\eta) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \mu(t') e^{-i\eta t'} dt',$$

and reverting $\tilde{F}(\eta)$ to $\tilde{F}(t)$, we find

$$\begin{aligned} \tilde{F}(t) = & \int_{-\infty}^{\infty} \frac{1}{1 - \alpha g(\eta)} g(\eta) e^{i\eta t} d\eta \\ & + \int_{-\infty}^{\infty} \frac{g(\eta)}{1 - \alpha g(\eta)} d\eta \frac{1}{2\pi} \int_{-\infty}^{\infty} \mu(t') e^{i\eta(t-t')} dt'. \end{aligned}$$

The first term corresponds to the macroscopic field $E(t)$, while the second one is related to the reaction field due to μ . We now consider an oscillating field $E(\omega) e^{i\omega t}$ parallel to z and calculate the torque $\Gamma_\theta(t)$ defined by (15.7). Rewriting $g(\eta)$ in function of $\epsilon(\eta)$ and replacing α in terms of ϵ_∞ , we finally obtain

$$\begin{aligned} \Gamma_\theta(t) = & - \frac{3\epsilon(\omega)}{2\epsilon(\omega) + \epsilon_\infty} \left(\frac{\epsilon_\infty + 2}{3} \right) \mu E(\omega) \sin \theta e^{i\omega t} \\ & - \frac{8\pi\rho\mu^2}{3} \left(\frac{\epsilon_\infty + 2}{3} \right) \int_{-\infty}^{\infty} \frac{\epsilon(\eta) - 1}{2\epsilon(\eta) + \epsilon_\infty} d\eta \\ & \quad \frac{1}{2\pi} \int_{-\infty}^{\infty} \sin[\theta(t) - \theta(t')] e^{i\eta(t-t')} dt'. \end{aligned} \quad (15.10)$$

The last term corresponds to the lag of the reaction field and gives rise to a frictional effect. Indeed, if θ was changing at a constant speed γ , this term would take the following value

$$\begin{aligned} & - \frac{8\pi\rho\mu^2}{3} \frac{\epsilon_\infty + 2}{3} \int_{-\infty}^{\infty} \frac{\epsilon(\eta) - 1}{2\epsilon(\eta) + \epsilon_\infty} d\eta \int_{-\infty}^{\infty} \sin \gamma(t - t') e^{i\eta(t-t')} dt' \\ & = - \frac{8\pi\rho\mu^2}{3} \frac{(\epsilon_\infty + 2)^2}{3} \frac{\epsilon''(\gamma)}{|2\epsilon(\gamma) + \epsilon_\infty|^2}. \end{aligned} \quad (15.11)$$

As $\epsilon''(\gamma)$ is odd in γ and positive for $\gamma > 0$, the sign of this expression is always opposite to the sign of γ .

No satisfactory treatment of this dielectric friction exists, although it has been considered by several authors.^{5,6,7}

In view of this situation one might argue that this effect might be formally absorbed into the frictional constant ζ (the weakness of the argument is that (15.11) is non-linear) and that one may only retain the first part of (15.10) in $\Gamma_\theta(t)$

$$\Gamma_\theta(t) = - \frac{3\epsilon(\omega)}{2\epsilon(\omega) + \epsilon_\infty} \left(\frac{\epsilon_\infty + 2}{3} \right) \mu E(\omega) \sin \theta e^{i\omega t} \quad (15.12)$$

It would of course be interesting to know the relative contributions to ζ of the viscous effects (short-range) and of the dielectric effects (long-range).⁸

If we accept Eq. (15.12) for $\Gamma_\theta(t)$, then the distribution function $f(\theta, t)$ has the following stationary periodic solution

$$f(\theta, t) = A \left\{ 1 + \frac{\mu \cdot E(\omega)}{kT} \frac{3\epsilon(\omega)}{2\epsilon(\omega) + \epsilon_\infty} \left(\frac{\epsilon_\infty + 2}{3} \right) \frac{e^{i\omega t}}{1 + i\omega\tau_0} \right\} \quad (15.13)$$

where τ_0 is still defined as $\zeta/2kT$ but is in principle different from (15.9) as it accounts as well for the dielectric friction.

The polarization of the system is given by $P(t) = \rho \langle \tilde{m}(t) \rangle$. Decomposing $P(t)$ in Fourier series, so that

$$4\pi P(\omega) = [\epsilon(\omega) - 1] E(\omega) \quad ,$$

we have

$$P(\omega) = \rho \langle \tilde{m}(\omega) \rangle = \rho \langle \tilde{\mu}(\omega) \rangle + \alpha \langle \tilde{F}(\omega) \rangle \quad ,$$

with

$$\langle \tilde{F}(\omega) \rangle = G(\omega) + g(\omega) \langle \tilde{m}(\omega) \rangle \quad .$$

As in the static case (cf. Appendix I), we find

$$\langle \tilde{F}(\omega) \rangle = \frac{\epsilon(\omega) + 2}{3} E(\omega) \quad (\text{Lorentz field}).$$

Further, the average value of $\mu(t)$ for an electric field of frequency ω is directly obtained from (15.13):

$$\langle \mu(t) \rangle = \int \mu f(\theta, t) \sin \theta \, d\theta \, d\phi / \int f(\theta, t) \sin \theta \, d\theta \, d\phi$$

$$\begin{aligned}
&= \frac{\mu^2}{3kT} \frac{3\epsilon(\omega)}{2\epsilon(\omega) + \epsilon_\infty} \frac{\epsilon_\infty + 2}{3} \tilde{E}(\omega) \frac{e^{i\omega t}}{1 + i\omega\tau_0} \\
&= \langle \mu(\omega) \rangle e^{i\omega t} .
\end{aligned}$$

Combining these various results together, we finally obtain

$$\epsilon(\omega) - 1 = 4\pi\rho\alpha \frac{\epsilon(\omega)+2}{3} + \frac{4\pi\rho\mu^2}{3kT} \frac{3\epsilon(\omega)}{2\epsilon(\omega) + \epsilon_\infty} \left(\frac{\epsilon_\infty + 2}{3} \right) \frac{1}{1 + i\omega\tau_0}$$

Substituting ϵ_∞ instead of α as before, we have the perfect analog of Onsager's expression (5.4)

$$\boxed{\epsilon(\omega) - \epsilon_\infty = \frac{3\epsilon(\omega)}{2\epsilon(\omega) + \epsilon_\infty} \left(\frac{\epsilon_\infty + 2}{3} \right)^2 \frac{4\pi\rho\mu^2}{3kT} \frac{1}{1 + i\omega\tau_0}} \quad (15.14)$$

The above formula was first proposed by Cole,⁹ as a substitute of the earliest Debye formula

$$\frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2} = \frac{4\pi\rho}{3} \left(\alpha + \frac{\mu^2}{3kT} \frac{1}{1 + i\omega\tau_0} \right) , \quad (15.15)$$

which follows immediately if one uses $\langle F(t) \rangle$ instead of $\tilde{F}(t)$ from the very beginning of the calculations of the torque $\tilde{\Gamma}_\theta(t)$ (cf. Appendix I for the static case).

A nice feature of the Debye expression is that it may be rewritten in the form (14.1)

$$\epsilon(\omega) - \epsilon_\infty = \frac{\epsilon - \epsilon_\infty}{1 + i\omega\tau_0 \left(\frac{\epsilon + 2}{\epsilon_\infty + 2} \right)}$$

so that the molecular relaxation time τ_0 gives rise to one macroscopic decaying time τ

$$\tau \equiv \tau_0 \frac{\epsilon + 2}{\epsilon_\infty + 2} \quad (15.16)$$

and the Cole-Cole plot is a semi-circle. As ϵ is usually much larger than ϵ_∞ , (15.16) implies τ_0 to be e.g., one order of magnitude smaller than τ , which seems to contradict the experimental results. Actually the peculiar form of (15.16) arises from the wrong use of the Lorentz field. Mandel¹⁰ and Powles¹¹ have considered more realistic forms of the local field, which lead to

$$\tau \approx \tau_0 \quad \text{or} \quad \frac{3}{2} \tau_0 \quad \text{for} \quad \epsilon \gg \epsilon_\infty.$$

Expression (15.14) is quadratic in $\epsilon(\omega)$ and gives a Cole-Cole plot which is not semi-circular. It cannot even be interpreted in terms of a spectrum of macroscopic decaying times corresponding to the one molecular relaxation time τ_0 , because its Cole-Cole plot lies outside the semi-circle corresponding to one macroscopic decaying time. Therefore this expression has always been considered with some distrust. However, in the limit $\epsilon \gg \epsilon_\infty$, and for frequencies such that $|\epsilon(\omega)| \gg \epsilon_\infty$, it still reproduces approximately the ideal Cole-Cole diagram: indeed, combining (5.4) with (15.14) we have

$$\begin{aligned} \epsilon(\omega) - \epsilon_\infty &= \frac{3\epsilon(\omega)}{2\epsilon(\omega) + \epsilon_\infty} \frac{2\epsilon + \epsilon_\infty}{3\epsilon} \frac{\epsilon - \epsilon_\infty}{1 + i\omega\tau_0} \\ &\approx \frac{\epsilon - \epsilon_\infty}{1 + i\omega\tau_0} \end{aligned}$$

and this implies that $\tau \approx \tau_0$.

Our opinion is that the form of (15.14) is substantially correct; the improvements that this expression require, are a more correct treatment of both the short-range effects and the dielectric friction. This would probably lead to a spectrum of molecular relaxation times.

One should also be aware of the fact that the Debye model corresponds to the limit of highly hindered rotation (high friction). If this is not so, initial effects ought to be considered.

Finally let us point out another limitation: the theory of brownian motion strictly applies to heavy particles or molecules immersed in a medium of light molecules, and its validity in the present case is certainly questionable.

16. The description of a system in phase space.

The evolution of a classical system with time is determined by the equations

$$\dot{q}_j = \frac{\partial H}{\partial p_j}, \quad p_j = - \frac{\partial H}{\partial q_j} \quad (16.1)$$

where $H(p, q, t)$ is the Hamiltonian function and p_j, q_j are the conjugated variables associated to the j -th degree of freedom. The instantaneous state of the system may be described by a point in the phase space (p, q) , and as t changes, this point moves along a definite trajectory determined by the differential equations (16.1). Actually our information about

the state of the system is only a macroscopic one (e.g. total energy, volume, temperature, . . .) and does not permit us to locate it on a particular trajectory. In view of this, we describe the real system by an ensemble of identical copies, distributed in phase space following a normalized density $\rho(p, q, t)$, which exactly matches our limited knowledge (Gibbs ensemble). The value of a macroscopic quantity associated with the mechanical function $A(p, q)$ is then given by the phase average

$$\langle A(t) \rangle = \int A(p, q) \rho(p, q, t) dp dq .$$

Because of the structure of Eq. (16.1), the extension in phase space is conserved and the density $\rho(p, q, t)$ itself is conserved along a trajectory

$$\frac{d\rho}{dt} = 0 \quad (\text{theorem of Liouville}) .$$

This means that its local rate of change is given by

$$\frac{\partial \rho}{\partial t} = \{H, \rho\} \quad \text{or} \quad i \frac{\partial \rho}{\partial t} = L_{\text{op}} \rho \quad (16.2)$$

where $\{A, B\}$ is the Poisson bracket defined as

$$\sum_j \left(\frac{\partial A}{\partial q_j} \frac{\partial B}{\partial p_j} - \frac{\partial A}{\partial p_j} \frac{\partial B}{\partial q_j} \right)$$

and L_{op} is the (hermitian) Liouville operator

$$i \sum_j \left(\frac{\partial H}{\partial q_j} \frac{\partial}{\partial p_j} - \frac{\partial H}{\partial p_j} \frac{\partial}{\partial q_j} \right) .$$

The time evolution of a dynamical function $A(p, q)$ is given by

$$\frac{dA}{dt} = \{A, H\} \quad \text{or} \quad i \frac{dA}{dt} = - L_{\text{op}} A \quad (16.3)$$

and may formally integrated as

$$A(p_t, q_t) = e^{itL_{\text{op}}} A(p_0, q_0) \quad (16.4)$$

where $\exp(itL_{\text{op}})$ is an operator of finite displacement acting upon (p, q) .

17. The response of a system to an electric field.

Consider a perfect dielectric body perturbed by a time-dependent external field $\tilde{E}_0(t)$ homogeneous in space. Its linearized hamiltonian function is

$$H(p, q, t) = H_0(p, q) - \tilde{M}^0(q) \cdot \tilde{E}_0(t) \quad (17.1)$$

where M^0 is the total electric moment at $E_0 = 0$. The response of this system to $\tilde{E}_0(t)$ may be studied following Kubo's method.¹¹

Assuming $\tilde{E}_0(t)$ to be weak, we split $\rho(p, q, t)$ into

$$\rho(t) = \rho_{eq} + \rho_1(t) \quad (17.2)$$

where ρ_{eq} is the equilibrium density in phase space and $\rho_1(t)$ is a linear perturbation $\sim \tilde{E}_0$. Inserting (17.1) and (17.2) into the Liouville equation (16.2), and neglecting non-linear terms in $\tilde{E}_0$, we find

$$i \frac{\partial \rho_1}{\partial t} = L_{op}^0 \rho_1 + i \left\{ \rho_{eq}, \tilde{M}^0 \right\} \cdot \tilde{E}_0(t)$$

by noticing that $L_{op}^0 \rho_{eq} = 0$ (L_{op}^0 = Liouville operator of the unperturbed system). For the conditions $\tilde{E}_0(-\infty) = 0$ and $\rho_1(-\infty) = 0$, the formal solution of this equation is

$$\rho_1(t) = \int_{-\infty}^t e^{-i(t-t')} L_{op}^0 \left\{ \rho_{eq}, \tilde{M}^0 \right\} \cdot \tilde{E}_0(t') dt'$$

or alternatively, by putting $s = t - t'$,

$$\rho_1(t) = \int_0^\infty e^{-is} L_{op}^0 \left\{ \rho_{eq}, \tilde{M}^0 \right\} \cdot \tilde{E}_0(t - s) ds$$

This already shows that the state of the system at time t does not depend solely on $\tilde{E}_0(t)$ but results from past values of $\tilde{E}_0$ in general.

If (as usually) the energy is the sole analytic invariant of the system, ρ_{eq} is a function of H_0 alone and

$$\left\{ \rho_{eq}, \tilde{M}^0 \right\} = \frac{\partial \rho_{eq}}{\partial H_0} \left\{ H_0, \tilde{M}^0 \right\} = - \dot{\tilde{M}}^0 \frac{\partial \rho_{eq}}{\partial H_0}$$

by means of (17.3), where $\dot{\tilde{M}}^0$ denotes the time derivative of $\tilde{M}^0$. We notice next that, if we represent $\tilde{M}^0(q)$ at time t by

$\tilde{M}^0(t)$, we have on account of (16.4)

$$e^{-isL_{op}^0} \tilde{M}^0(t) = \tilde{M}^0(t - s) \quad .$$

Further, whatever the Gibbs ensemble we use, we may write

$$\frac{\partial \rho_{eq}}{\partial H_0} = -\beta \rho_{eq} \quad , \quad (\beta = 1/kT) \quad .$$

Hence the final expression for $\rho_1(t)$:

$$\rho_1(t) = \beta \rho_{eq} \int_0^\infty \tilde{M}^0(t - s) \cdot \tilde{E}_0(t - s) ds$$

We are actually interested in the response of the system to E_0 , i.e., its polarization or the average value of its total electric moment, which is obtained from the phase average

$$\langle \tilde{M}(t) \rangle_{E_0} = \int \tilde{M}(q) \rho(p, q, t) dp dq \quad .$$

We assume that E_0 varies sufficiently slowly with time in order to describe the induced dipoles in terms of the static polarizability α . This means that, as in the static case, $\tilde{M}$ consists of two parts which may be written as

$$\tilde{M} = \tilde{M}^0 + \tilde{E}_0(t) \cdot \left(\frac{\partial}{\partial \tilde{E}_0} \tilde{M} \right)^0 \quad .$$

This gives

$$\begin{aligned} \langle \tilde{M}(t) \rangle_{E_0} &= \tilde{E}_0(t) \cdot \int \left(\frac{\partial}{\partial \tilde{E}_0} \tilde{M} \right)^0 \rho_{eq} dp dq \\ &\quad + \int \tilde{M}^0 \rho_1(t) dp dq \end{aligned}$$

as the equilibrium average of $\tilde{M}^0$ vanishes in the absence of spontaneous polarization. Substituting the expression for $\rho_1(t)$, we find finally

$$\langle \tilde{M}(t) \rangle_{E_0} = \tilde{E}_0(t) \cdot \left\langle \left(\frac{\partial}{\partial \tilde{E}_0} \tilde{M} \right)^0 \right\rangle$$

$$+ \beta \int_0^{\infty} \langle \tilde{M}^{\circ}(t) \dot{\tilde{M}}^{\circ}(t-s) \rangle \cdot \tilde{E}_0(t-s) ds .$$

Actually $\langle \tilde{M}^{\circ}(t) \dot{\tilde{M}}^{\circ}(t-s) \rangle$ depends on s only, so that it may be replaced by any of the equivalent expressions

$$\langle \tilde{M}^{\circ}(t+s) \dot{\tilde{M}}^{\circ}(t) \rangle , \quad \langle - \dot{\tilde{M}}^{\circ}(t+s) \tilde{M}^{\circ}(t) \rangle , \quad \langle \tilde{M}^{\circ}(s) \dot{\tilde{M}}^{\circ}(0) \rangle$$

or $\langle - \dot{\tilde{M}}^{\circ}(s) \tilde{M}^{\circ}(0) \rangle$. This gives e.g.

$$\langle \tilde{M}(t) \rangle_{E_0} = \tilde{E}_0(t) \cdot \left\langle \left(\frac{\partial}{\partial \tilde{E}_0} \tilde{M} \right)^{\circ} \right\rangle + \beta \int_0^{\infty} \langle - \dot{\tilde{M}}^{\circ}(s) \tilde{M}^{\circ}(0) \rangle \cdot \tilde{E}_0(t-s) ds$$

The quantity $\langle - \dot{\tilde{M}}^{\circ}(s) \tilde{M}^{\circ}(0) \rangle$ determines the response of the permanent dipoles to the applied field. In the case of a static field $\tilde{E}_0$, we have

$$\int_0^{\infty} \langle - \dot{\tilde{M}}^{\circ}(s) \tilde{M}^{\circ}(0) \rangle ds = \langle \tilde{M}^{\circ}(0) \dot{\tilde{M}}^{\circ}(0) \rangle - \langle \tilde{M}^{\circ}(\infty) \dot{\tilde{M}}^{\circ}(0) \rangle .$$

As values of $\tilde{M}^{\circ}$ separated by a large interval of time are totally uncorrelated and as $\langle \tilde{M}^{\circ} \rangle = 0$, the last term vanishes and we recover the static expression derived in § 7:

$$\langle \tilde{M} \rangle_{E_0} = \tilde{E}_0 \cdot \left\langle \left(\frac{\partial}{\partial \tilde{E}_0} \tilde{M} \right)^{\circ} \right\rangle + \beta \langle \tilde{M}^{\circ} \tilde{M}^{\circ} \rangle .$$

We notice finally that $\langle \dot{\tilde{M}}^{\circ}(s) \tilde{M}^{\circ}(0) \rangle$ is the time derivative of the autocorrelation function of the total electric moment $\tilde{M}^{\circ}$, i.e.

$$\langle \tilde{M}^{\circ}(0) \tilde{M}^{\circ}(s) \rangle ,$$

which is an even function of s because $\tilde{M}^{\circ}$ does not involve the angular velocities of the molecules explicitly, and the hamiltonian function is even in these velocities. We therefore obtain the schematic picture represented on the opposite figures.

18. General formulation of $\epsilon(\omega)$.

The various average quantities involved in (17.3) are shape dependent. For reasons of simplicity, consider a spherical specimen, so that P is uniform, equal to $\langle \tilde{M}^0 \rangle / V$ and parallel to E_0 . All averages of the type $\langle \tilde{a} \cdot \tilde{b} \rangle$ may now be replaced by $1/3 \langle \tilde{a} \cdot \tilde{b} \rangle_U$. Expanding $P(t)$ and $E_0(t)$ in Fourier space, we have (cf. § 14)

$$(4\pi/3) P(\omega) = \frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2} E_0(\omega) .$$

Finally all molecules being equivalent, we focus our attention upon the dipole moment $\tilde{m}$ of a particular one. This leads to the following expression

$$\begin{aligned} \frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2} &= \frac{4\pi\rho}{3} \left\{ \frac{1}{3} \left\langle \left(\frac{\partial}{\partial E_0} \cdot \tilde{m} \right)^0 \right\rangle_{\text{sphere}} \right. \\ &\quad \left. + \frac{1}{3} \beta \int_0^\infty \langle -\tilde{m}^0(o) \cdot \dot{\tilde{M}}^0(s) \rangle_{\text{sphere}} e^{-i\omega s} ds \right\} . \end{aligned}$$

The first term of the r.h.s. corresponds to the polarization at optical frequencies and may be replaced by $(\epsilon_\infty - 1)/(\epsilon_\infty + 2)$. Let us also introduce the correlation function

$$\Psi(s) = \frac{\langle \tilde{m}^0(o) \cdot \tilde{M}^0(s) \rangle}{\langle \tilde{m}^0(o) \cdot \tilde{M}^0(o) \rangle} \quad \text{for a sphere}$$

(note that $\Psi(s)$ is actually the autocorrelation function. $\langle \tilde{M}^0(o) \cdot \tilde{M}^0(s) \rangle$ in a spherical specimen, with the normalization $\Psi(o) = 1$). We then have

$$\frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2} = \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} + \frac{4\pi\rho}{3} \frac{\langle \tilde{m}^0 \cdot \tilde{M}^0 \rangle_{\text{sphere}}}{3kT} \int_0^\infty \left(-\frac{d}{ds} \Psi(s) \right) e^{-i\omega s} ds .$$

Combining with (9.1), we finally obtain

$$\frac{\epsilon(\omega) - \epsilon_\infty}{\epsilon(\omega) + 2} = \frac{\epsilon - \epsilon_\infty}{\epsilon + 2} \int_0^\infty \left(-\frac{d}{ds} \Psi(s) \right) e^{-i\omega s} ds$$

(18.1)

19. Generalization of the static theory of Kirkwood (polar substances).

In the static case (cf. §9), Kirkwood devised a method involving the subdivision of the specimen into two parts: (i) a small sphere surrounding a molecule with its permanent dipole moment in a fixed orientation, and (ii) the remaining part of the specimen. The basic point was that the average electric moment of the whole specimen $\langle \tilde{M} \rangle$ may be related to the average electric moment of the small sphere μ^* by using macroscopic electrostatics only.

Several authors have recently tried to extend this method to the dynamic case: besides the correlation function

$$\Psi(s) = \langle \mu(o) \cdot \tilde{M}(s) \rangle / \langle \mu(o) \cdot \tilde{M}(o) \rangle$$

for the whole specimen, they introduce the correlation function

$$\Phi(s) = \langle \mu(o) \cdot \mu^*(s) \rangle / \langle \mu(o) \cdot \mu^*(o) \rangle$$

for a small sphere surrounding some arbitrary molecule. (We consider here permanent dipoles only.) It is assumed that $\tilde{M}(s)$ results from the values that μ^* has assumed at times $s' < s$, plus some additional spontaneous fluctuations, and that $\Psi(s)$ may be related to $\Phi(s)$ on a macroscopic basis. At present two somewhat different treatments have been proposed by Glarum and Cole^{14,15} and by Fatuzzo and Mason¹⁶ respectively, with the alternative results^{14,16}

$$\epsilon(\omega) - \epsilon_\infty = [2\epsilon + \epsilon(\omega)] \frac{\epsilon - \epsilon_\infty}{3\epsilon} \int_0^\infty \left(-\frac{d}{ds} \Phi(s) \right) e^{-i\omega s} ds$$

$$\frac{[\epsilon(\omega) - \epsilon_\infty][2\epsilon(\omega) + \epsilon_\infty]}{3\epsilon(\omega)} = \frac{(\epsilon - \epsilon_\infty)(2\epsilon + \epsilon_\infty)}{3\epsilon} \int_0^\infty \left(-\frac{d}{ds} \Phi(s) \right) e^{-i\omega s} ds$$

The last of these two equations is the straightforward generalization of (9.6) to the dynamic case. Both of them lead to macroscopic relaxation times of the same order as the microscopic ones. There is, however, no doubt that some intermediate steps involved in the derivation of these equations require a careful investigation.

20. Discussion of the correlation function $\Psi(s)$.

We discuss here some features of $\Psi(s)$ or alternatively $\Phi(s)$, which appear to be the key-functions of the problems. For simplicity we first consider the autocorrelation function

of the permanent dipole moment of one molecule

$$\langle \mu(0) \cdot \mu(t) \rangle / \mu^2 = \gamma(t)$$

for two limiting cases: free rotation (inertial limit) and rotation in a highly viscous medium (Debye limit). We also carry the discussion out in two-dimensions so that the angle φ alone specifies the orientation of μ .

In the case of free rotation we have

$$\gamma(t) = \langle \cos[\varphi(t) - \varphi(0)] \rangle = \langle \cos(Jt/I) \rangle$$

(J = angular momentum, I = moment of inertia). The average is computed by considering the equilibrium distribution

$$\exp(-J^2/2IkT)$$

with the result

$$\gamma(t) = \exp[-\frac{1}{2}t^2(kT/I)] \quad (20.1)$$

In the Debye limit, we have to consider the solution of the diffusion equation (brownian motion in φ -space)

$$\frac{\partial f}{\partial t} = \frac{1}{\tau_0} \frac{\partial^2 f}{\partial \varphi^2} \quad (\tau_0 = \frac{\zeta}{kT})$$

i.e.

$$f(\varphi, t) = (4\pi t/\tau_0)^{-\frac{1}{2}} \exp - \frac{(\varphi - \varphi_0)^2}{(4t/\tau_0)}$$

where φ_0 is the orientation at time 0. This gives

$$\gamma(t) = \langle \cos(\varphi - \varphi_0) \rangle = e^{-t/\tau_0} \quad (20.2)$$

The behavior of (20.1) and (20.2) is totally different; nothing like a relaxation time appears in (20.1): the sole characteristic time is $(I/kT)^{\frac{1}{2}}$, i.e., the mean period of rotation of a molecule.

Experimentally it is observed that dense systems usually conform to the Debye scheme. Dilute systems on the contrary approach more or less the inertial limit and should therefore exhibit quite a different function $\epsilon(\omega)$ as well as Cole-Cole plot.¹⁷ See figure below.

Note that a more correct treatment of brownian motion combining inertial effects and viscous friction is easily developed along the same lines of the Langevin theory for the translational motion.¹⁸ One finds²⁵

$$\gamma(t) = \exp - \frac{1}{\tau_0} \left\{ t - (I/kT\tau_0) [1 - \exp(-t\tau_0 kT/I)] \right\} \quad (20.3)$$

This expression realizes the transition between the two limiting cases discussed above: the inertial limit and the Debye limit are recovered for $t(kT/I)\tau_0 \ll$ and $\gg 1$ respectively. The type of behavior which will predominate in $\gamma(t)$, depends upon the relative values of τ_0 and $(I/kT)^{1/2}$. The transition between them has been observed in gases on increasing the pressure.^{19,20}

Up to this point, we discussed the autocorrelation function of one dipole. Actually, what is required, is the correlation function $\Psi(s)$ relative to the whole specimen, or alternatively $\Phi(s)$, which refers to the dipole plus its neighborhood. These functions cannot reasonably be obtained from brownian motion theory. Another point to be clarified is: what type of intermolecular forces dominate dielectric relaxation processes? We briefly discuss this problem in the two following sections.

21. Some results from molecular dynamics studies.

The correlation functions $\Psi(t)$, $\Phi(t)$ and $\gamma(t)$ are very difficult to compute in general from statistical mechanics. We shall briefly discuss this problem in § 22. A more direct and, in some sense, experimental approach is to deduce them by the method of molecular dynamics. One considers an assembly of 100 particles or more, with definite properties and interactions, and one studies the evolution of this system with time (i.e., its trajectory in phase space) by integrating the equations of motions step by step. Assuming the equivalence of phase-averages and time-averages, one derives e.g., the correlation function between two quantities A and B as

$$\langle A(0) B(s) \rangle = \frac{1}{C} \int_0^C A(t) B(t+s) dt$$

where C is the time interval considered. As this method has been successfully applied to transport properties of gases and liquids, we thought it might be a valuable tool also in the case of dielectric relaxation. Actually as quite a number of different mechanisms seem possible, one should start from a not too sophisticated model and try to investigate each mechanism or type of force at a time.

We therefore have considered a two-dimensional rigid square lattice, from which we select a circular sample. On each site we place a two-dimensional rotator with moment of inertia I , angular momentum J and orientation ϕ . In the case of dipole-dipole interactions, the hamiltonian of this system is

$$H = \sum_j J_j^2 / 2I - 2\mu^2 \sum_j \sum_k \frac{1}{r_{jk}^2} \sin(\phi_j + \phi_k - 2\alpha_{jk}) \quad (21.1)$$

where r_{jk} , α_{jk} are the polar coordinates of site k relatively to site j . (Note that the dipole-dipole interaction is defined from $\sum \ln r$ and is long-range.) A first series of calculations were made with 421 rotators assuming first neighbor interaction only (because the computer-program was rather time consuming). We were essentially looking at $\Psi(s)$ in a circular sample. The outcoming result was that, even for a reasonable coupling between the rotators (i.e., |mean potential energy| $\sim$ mean kinetic energy), $\Psi(s)$ did not deviate very much from the expression corresponding to free rotators (20.1).²¹ The same kind of calculations with another type of angular potential corresponding to a strong tendency of the rotators to get parallel to each other, leads on the contrary to a behavior of the Debye type (apart from inertial effects always present for very short times).

These results have been carefully checked recently on the CDC 3600 computer of Argonne National Laboratory, by varying the size of the system, considering a much longer portion of trajectory in phase space and taking into account the long range character of dipolar forces. The essential conclusions are as follows:²²

(a) Dipole-dipole interactions only slightly modify the correlation function $\Psi(s)$ with respect to the case of free rotation. There seems to be no tendency towards a behavior of the Debye type: the only characteristic time of the system is the mean period of rotation of the molecules.

(b) The autocorrelation function of one dipole looks quite different from $\Psi(s)$, which means that correlations between different dipoles like

$$\langle \mu_j(0) \cdot \mu_k(t) \rangle / \mu^2$$

are important. This point is now being investigated.

22. Perturbation methods of statistical mechanics of irreversible processes.

Recent advances in the statistical theory of irreversible processes permits one to hope progress to be made soon in the field of dielectric relaxation, by using perturbational

techniques. The simplified two-dimensional assembly of rotators considered in the preceding section, has already been treated in the weak coupling approximation, following the formalism devised by Prigogine and coworkers.²³ The results obtained for the dielectric relaxation processes agree well with the molecular dynamics data.²⁴

REFERENCES TO PART II

1. H. Fröhlich, Theory of Dielectrics, Oxford Clarendon Press (1958), p. 4.
2. K. S. Cole and R. H. Cole, J. Chem. Phys. 9, 1484 (1941).
3. P. Debye, Polar Molecules, Dover Publications, Inc., New York (1945), p. 77.
4. An excellent analysis of the theory of brownian motion may be found in the review paper of S. Chandrasekhar, Rev. Mod. Phys. 15, 1 (1943).
5. R. Zwanzig, J. Chem. Phys. 38, 1605 (1963).
6. B. K. P. Scaife, Molecular Relaxation Processes, London, New York, Academic Press (1966), p. 15; Proc. Phys. Soc. 84, 616 (1964).
7. E. Fatuzzo and P. R. Mason, Proc. Phys. Soc. 90, 729 (1967).
8. It has been suggested (Ref. 5) that the dielectric friction is small, but the argument is not rigorous. See also Ref. 6 and 7.
9. R. H. Cole, J. Chem. Phys. 6, 385 (1938).
10. M. Mandel, Bull. Soc. Chim. Belges 60, 301 (1951); Physica 17, 799 (1951).
11. J. G. Powles, J. Chem. Phys. 21, 633 (1963).
12. R. Kubo, J. Phys. Soc. Japan 12, 570 (1957).
13. R. Zwanzig, J. Chem. Phys. 38, 2766 (1963).
14. S. H. Glarum, J. Chem. Phys. 33, 1371 (1960).
15. R. H. Cole, J. Chem. Phys. 42, 637 (1965).
16. E. Fatuzzo and P. R. Mason, Proc. Phys. Soc. 90, 741 (1967).

REFERENCES TO PART II (Cont.)

17. A discussion of inertial effects may be found in E. P. Gross, J. Chem. Phys. 23, 1415 (1955).
18. See Ref. 4, p. 21.
19. R. G. Gordon, J. Chem. Phys. 43, 1307 (1965); 44, 1830 (1966).
20. H. Shimizu, J. Chem. Phys. 43, 2453 (1965).
21. A. Bellemans, M. Gancberg and M. Köhler, Phys. Rev. Letters 18, 1192 (1967).
22. A. Bellemans, unpublished.
23. A. Bellemans and E. Kestemont, Physica 28, 1088 (1962); A. Bellemans, J. C. Bernard, M. Köhler and E. Kestemont, Physica 31, 1291 (1965).
24. E. Kestemont and A. Bellemans, unpublished.
25. W. A. Steele, J. Chem. Phys. 38, 2404 and 2411 (1967).