Zeitschrift: Archives des sciences [1948-1980]
Herausgeber: Société de Physique et d'Histoire Naturelle de Genève
Band: 12 (1959)
Heft: 8: Colloque Ampère : Maxwell-Ampère conference

Artikel: Theory of dielectric relaxation in molecular crystals
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DOI: https://doi.org/10.5169/seals-739093

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Theory of Dielectric Relaxation in Molecular Crystals

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Résumé.

Le travail présenté ici est une vue d'ensemble basée sur un certain nombre de publications relatives à la théorie de la relaxation diélectrique dans les cristaux moléculaires. Dans toutes ces publications, l'idée de base est que l'anisotropie du champ cristallin au sein duquel les dipôles se réorientent en surmontant le système des barrières de potentiel de l'état solide, peut faire apparaître un ensemble de temps de relaxation diélectrique. Cet ensemble de temps de relaxation entraîne à son tour un élargissement marqué des courbes de pertes diélectriques (diagrammes de ε'' en fonction de log f).

On a établi un système d'équations différentielles linéaires et homogènes pour décrire la vitesse avec laquelle les dipôles prennent et abandonnent une orientation donnée. Chaque équation met en jeu à la fois les valeurs du temps de séjour et les probabilités de transition. Les valeurs propres de la matrice de ces équations sont les valeurs inverses, changées de signe, des temps de relaxation. La théorie rend compte aisément d'une courbe d'absorption très large, même de type « bimodal ». Un certain nombre de prédictions théoriques générales concernant l'allure des courbes d'absorption avec la fréquence et la température sont indiquées.

Lauritzen a vérifié dans le détail les conséquences de cette théorie en utilisant les mesures diélectriques de Meakins sur certains composés d'occlusion de l'urée contenant des molécules dipolaires. Les valeurs du système de barrières de potentiel des dipôles orientables ont été calculées par deux méthodes: le potentiel 6-12 et le recouvrement en volume (« volume overlap »). Il a alors été possible d'établir le système convenable d'équations différentielles et de calculer les temps de relaxation et les polarisabilités. Les courbes de pertes prédites sont fortement bimodales aux basses températures mais deviennent du type Debye, légèrement élargi, aux hautes températures.

La comparaison de la théorie et de l'expérience laisse subsister peu de doute que l'anisotropie du champ cristallin soit la principale source du système ou de la distribution des temps de relaxation dans ces substances.

1. Introduction.

Dielectric loss data on a number of systems consisting of polar molecules in a molecular lattice indicate the existence of a distribution (or set) of dielectric relaxation times. It has been suggested that the anisotropy of

the crystalline field in which the dipoles reorient is an important contributing factor in establishing such a set of relaxation times [1]. This point of view has been examined in some detail since it was first proposed. Much of this work has been of a purely theoretical nature aimed at uncovering generalizations, but detailed comparison of theory with experiment has been accomplished for one type of compound. The chief objectives of this paper are *(a)* to indicate the nature of the theory, *(b)* to summarize the general results of the theoretical studies, and *(c)* to mention some aspects of the comparision of theory with experiment for certain urea addition compounds with occluded long-chain ketone and secondary bromide molecules.

2. Origin of Relaxation Times.

If the polarization of a system of dipoles approaches equilibrium after the abrupt removal of a static electric field according to the polarization decay function

$$P(t) = P_0 e^{-t/\tau} , \tag{1}$$

the response of the same system in a sinusoidal field is described by the familiar Debye equation [2]

$$\varepsilon''(\omega) = \frac{(\varepsilon_s - \varepsilon_\infty)\,\omega\tau}{1 + \omega^2 \tau^2} . \tag{2}$$

This is the case of a single relaxation time, τ. (In the above expressions, the small difference between the macroscopic and microscopic relaxation time, which is a result of the difference between the internal field F and the applied field E, has been ignored for the sake of simplicity.) On the other hand, if the polarization decays according to

$$P(t) = \sum_{\beta=1}^{\Omega} P_\beta e^{-t/\tau_\beta} , \tag{3}$$

then for a sinusoidal field it follows from the principle of superposition that

$$\varepsilon''(\omega) = \sum_{\beta=1}^{\Omega} \frac{\Delta\varepsilon_\beta\,\omega\tau_\beta}{1 + \omega^2 \tau_\beta^2} . \tag{4}$$

Here τ_β represents a set of relaxation times where $\beta = 1, 2, \ldots \Omega$, and $\Delta\varepsilon_\beta$ is the increment of dielectric constant associated with the β-th mode of decay.

Equation 4, with a suitable set of τ_β and $\Delta\varepsilon_\beta$, can often accurately reproduce the broadened loss curves characteristic of many well-defined systems. The task that confronts the theory is that of showing how a set of relaxation times τ_β (and " intensity factors ", $\Delta\varepsilon_\beta$) can arise in a natural way as a result of an anisotropy in the crystalline field that hinders reorientation of dipoles in a crystal.

Consider first the two-position model proposed by Debye [2]. The model (slightly generalized) is characterized by a potential well with two non-equivalent rotational positions 180° apart. Let the difference in potential energy between these two positions be V, and refer to the more stable position as " site 1 " and the less stable one as " site 2 ". Denote the barrier for a dipole jumping from site 2 to site 1 as W. Then the elementary process transition probabilities are

$$k_{12} \equiv k = \mathrm{A}\, e^{-(\mathrm{W}+\mathrm{V})/\mathrm{RT}} \tag{5a}$$

$$k_{21} \equiv k' = \mathrm{A}\, e^{-\mathrm{W}/\mathrm{RT}} . \tag{5b}$$

The transitions across the barrier are caused by thermal fluctuations in the system, and the barrier system itself is a result of the crystalline field. The net rate at which dipoles enter and leave each site is

$$\frac{d\mathrm{N}_1}{dt} = -2k\mathrm{N}_1 + 2k'\mathrm{N}_2 \tag{6a}$$

$$\frac{d\mathrm{N}_2}{dt} = -2k'\mathrm{N}_2 + 2k\mathrm{N}_1 . \tag{6b}$$

The factor 2 is inserted because each k is defined as the probability each dipole will turn in a specified direction, but this factor could be omitted if desired. We have employed it here, since a definition with an analogous meaning is used when models with more than two orientational sites are treated. The solutions of equations (6a) and (6b) will be obtained by a general mathematical method [1] useful for models with any number of sites, despite the fact that the solutions for the case at hand can be written down at once. The characteristic determinant of equations 6 is

$$\begin{vmatrix} (\mathrm{D} + 2k) & -2k' \\ -2k & (\mathrm{D} + 2k') \end{vmatrix} \tag{7}$$

where D is the operator d/dt. By setting this determinant equal to zero, the eigenvalues of the operator D are found to be zero and $-2(k+k')$. Hence the solutions of equations 6 are

$$N_1 = C_{11} + C_{12}\, e^{-2(k+k')t} \tag{8a}$$

$$N_2 = C_{21} - C_{12}\, e^{-2(k+k')t}\,. \tag{8b}$$

Here C_{11} and C_{21} are the equilibrium number of dipoles in sites 1 and 2, respectively. The polarization of the system is associated with the vector $\binom{+C^{12}}{-C^{12}}$. The system approaches equilibrium according to the decay function $\exp[-2(k+k')t]$, and a simple calculation [1] shows that the polarization decay function is

$$P(t) = P_2\, e^{-2(k+k')t} \tag{9}$$

where $P_2 = (4\, C_{11}\, C_{21}\, F/N)\,(\mu^2/3kT)$, corresponding to an orientational polarizability of $\alpha_2 = (4\, C_{11}\, C_{21}/N^2)\,(\mu^2/3kT)$. The quantity α_2 is directly related to the " intensity " factor $\varepsilon_s - \varepsilon_\infty$. (The polarizabilities cited refer to polycrystalline media).

Thus, the simple two-position model gives but one relaxation time

$$\tau_2 = \frac{1}{2\,(k+k')} \tag{10}$$

as Debye [2], and later Fröhlich [3], have indicated. It is clear that in order to explain the very broad—and even bimodal—loss curves commonly encountered in dielectric studies that something besides a two-position model must be invoked.

It should be realized that the assumption that a dipole can occupy but two orientational sites is certainly too simple to be physically realistic in many cases. For example, there is ample evidence for certain long-chain compounds that behave as single-axis hindered rotators [4, 5] that there must be more than two sites accessible to each orienting dipole. Further, Powles [6] has cited substantial reasons for believing that more than two orientational sites exist in certain of the low-temperature phases of the hydrogen halides, the latter being considered as three-dimensional hindered rotators. It is probably no accident that a number of the materials mentioned above often exhibit broadened, and in some cases bimodal, loss curves. (More will be said of this later.) In any event, the investigation

of the properties of models where the dipoles have more than two orientational positions seems amply justified.

A simple and fully illustrative example that brings out the origin of multiple dielectric relaxation times will be considered. Assume that a dipole, acting as a single-axis rotator, may occupy *four* orientational sites 90° apart. Let site 1 be the most stable one, and let sites 2, 3, and 4 each have a potential energy V above site 1.

The barrier for jumps between sites 2 and 3, 3 and 4, and the inverse jumps, and for jumps from 4 to 1 and 2 to 1 is W. (The proposed model is seen to be but a simple extension of the two-position model.) It is emphasized that this model may not correspond closely to the barrier system arising from crystalline field interactions in any real system—we are simply using it to show how a set of τ_β may arise. The transition probabilities in this system are

$$k_{12} = k_{14} \equiv k = A\, e^{-(W+V)RT} \tag{11a}$$

$$k_{41} = k_{21} = k_{23} = k_{32} = k_{34} = k_{43} \equiv k' = A\, e^{-W/RT}\,. \tag{11b}$$

The rate equations for this model are

$$\frac{dN_1}{dt} = -2kN_1 + k'N_2 + k'N_4 \tag{12a}$$

$$\frac{dN_2}{dt} = kN_1 - 2k'N_2 + k'N_3 \tag{12b}$$

$$\frac{dN_3}{dt} = k'N_2 - 2k'N_3 + k'N_4 \tag{12c}$$

$$\frac{dN_4}{dt} = kN_1 + k'N_3 - 2k'N_4\,. \tag{12d}$$

In writing these equations it was assumed that only a jump to an *adjacent* site is possible as an elementary process *(single-jump hypothesis, S-J)* [1]. The eigenvalues of the operator $D = d/dt$ in the characteristic determinant of equations (12) are $0, -2k', -(2k' + k - \sqrt{Q})$, and $-(2k' + k + \sqrt{Q})$, where Q is $2k'^2 - 2kk' + k^2$.

The relaxation times associated with this model are [1]

$$\tau_2 = \frac{1}{2k'} \tag{13a}$$

$$\tau_3 = \frac{1}{2k' + k - \sqrt{Q}} \tag{13b}$$

$$\tau_4 = \frac{1}{2k' + k + \sqrt{Q}} \cdot \tag{13c}$$

The model thus yields multiple relaxation times.

It is convenient to consider the limiting case where site 1 is deep. When site 1 is deep, so that $V > W$, and $k' >> k$, the relaxation times become

$$\tau_2 = \frac{1}{2k'} \tag{14a}$$

$$\tau_3 \cong \frac{1}{(2 - \sqrt{2})\, k'} = \frac{1}{0.586\, k'} \tag{14b}$$

$$\tau_4 \cong \frac{1}{(2 + \sqrt{2})\, k'} = \frac{1}{3.41\, k'}, \tag{14c}$$

and the solutions to equations 12 may be written

$$N_1 = C_{11} + 0 - (3\sqrt{2} + 4)\, C_{13}\, e^{-(2-\sqrt{2})k't} + (3\sqrt{2} - 4)\, C_{14}\, e^{-(2+\sqrt{2})k't} \tag{15a}$$

$$N_2 = C_{21} + C_{22}\, e^{-2k't} + (\sqrt{2} + 1)\, C_{13}\, e^{-(2-\sqrt{2})k't} + (1 - \sqrt{2})\, C_{14}\, e^{-(2+\sqrt{2})k't} \tag{15b}$$

$$N_3 = C_{21} + 0 + (\sqrt{2} + 2)\, C_{13}\, e^{-(2-\sqrt{2})k't} + (2 - \sqrt{2})\, C_{14}\, e^{-(2+\sqrt{2})k't} \tag{15c}$$

$$N_4 = C_{21} - C_{22}\, e^{-2k't} + (\sqrt{2} + 1)\, C_{13}\, e^{-(2-\sqrt{2})k't} + (1 - \sqrt{2})\, C_{14}\, e^{-(2+\sqrt{2})k't} \tag{15d}$$

In the above expressions, C_{11} is the equilibrium number of dipoles in site 1, and C_{21} is the equilibrium number in sites 2, 3 and 4. An examination of equations (15) shows that the *overall* process involved in mode 2, which relaxes according to exp $(-2k' t)$, involves a net transfer of dipoles from site 2 to 4, or the reverse. The polarization associated with this mode of decay may be obtained by evaluating the vector

$$\begin{pmatrix} 0 \\ +C_{22} \\ 0 \\ -C_{22} \end{pmatrix};$$

the corresponding orientational polarizability is found to be $\alpha_2 = (2\, C_{21}/N)\, (\mu^2/3kT)$. The other modes of decay are more complicated, but can be interpreted in a similar manner [1]. The orientational polarizability associated with modes 3 and 4 are $\alpha_3 = [C_{21}\, (3 + 2\sqrt{2})/N]\, (\mu^2/3kT)$ and $\alpha_4 = [C_{21}\, (3 - 2\sqrt{2})/N]\, (\mu^2/3kT)$. The polarizabilities cited are directly proportional to the $\Delta\varepsilon_\beta$ in equation (4).

The loss curve predicted using these polarizabilities and the relaxation times given by equations (14) in equation (4) is considerably broader than that predicted with a single relaxation time. This effect is particular noticeable on the high-frequency side of the loss curve. The asymmetry of the loss curve is a result of the fact that the shorter relaxation times are associated with the weaker polarizability or " line strength ".

Details of the methods used to calculate the orientational polarizabilities associated with the various relaxation times have been given for both single-axis and three-dimensional hindered rotators by Hoffman and Axilrod [7]. It is of interest to note that the differential equations describing a model may be written out including the time-dependent sinusoidal field $\vec{F} = \vec{F}_0 e^{i\omega t}$. The solution of such equations gives results identical to those obtained with the method cited, and is therefore not worth the additional mathematical complication.

If the case where the barriers due to the crystalline field for the four-position model are all equivalent is considered, the results are much different. For this case, $V = 0$, $k = k'$, and all the barriers have the value W. In this event it is found that mode 4, which has a relaxation time of $1/4k$, is inactive * in the dielectric relaxation spectrum, and $\tau_2 = \tau_3 = 1/2k$ is the only dielectric relaxation time exhibited by the system. This means that as the barrier system becomes more isotropic, the dielectric relaxation times will converge, and tend toward a Debye-type loss curve, i.e., one with a single relaxation time. The results mentioned above are of importance when the dependence of the shape of the loss curves on temperature is considered.

It will be observed from the definitions given for the transition probabilities k and k' in equations (11*a*) and (11*b*) that they will tend to converge with increasing temperature. Since it has been noted above that converging k leads also to convergence of the active relaxation times, it follows that the loss curves for the special four-position model under consideration should be broad (and somewhat asymmetric) at low temperatures, and

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* Mode 4 is inactive in the dielectric relaxation spectrum when $k = k'$ because the vector C_{i4} then takes the form

$$\begin{pmatrix} + C_{14} \\ - C_{14} \\ + C_{14} \\ - C_{14} \end{pmatrix}$$

It should be noted that this type of mode will contribute to the Kerr effect.

tend to become more narrow and more symmetrical at higher temperatures. It will be seen shortly that this holds for a wide variety of models. The narrowing of the loss curves with rising temperature will be more rapid if cooperative interaction tends to smooth out the barrier system; this effect should be particularly noticeable near cooperatively-induced rotational phase transitions.

3. General Theoretical Results and Predictions.

The properties of the general three- and four-position single-axis polar rotator have been discussed in considerable detail [8]. These models possess six and eight arbitrary transition probabilities, respectively. (It should be remarked that the set of transition probabilities in these cases is not completely arbitrary, but is subject to the restriction that Πk_{ij} (clockwise) $= \Pi k_{ij}$ (counterclockwise), as required by the principle of detailed balancing). These models were treated using the S-J hypothesis. Despite the fact that any real crystalline field would possess considerably higher symmetry than was assumed for these general models, certain results of a general nature were obtained. It was shown that there were always $\Omega - 1$ relaxation times, where Ω is the number of sites, and that the relaxation times were always real, the latter obviating oscillatory solutions. Actually all that is needed to show that the relaxation times are real and positive is to apply the principle of detailed balancing to the set of equations describing the rate at which dipoles leave and enter each site. General equations for the vectors $C_{i\beta}$ and for the τ_β were obtained. A number of specialized models derived from the general ones were considered. It was shown that bimodal loss curves could easily arise for the four-position single-axis polar rotator. For all the models, the active relaxation times converged as the k converged. Thus, a narrowing of the dielectric loss curves with increasing temperature was predicted quite generally. The fundamental reason for this is essentially the same as for the special four-position model discussed in section 2. In the case of bimodal loss curves, the two loss regions coalesce with increasing temperature. Data from the literature were discussed, and it was shown that the shape of the loss curves for materials that could reasonably be considered to be single-axis rotators behaved in the manner described above.

The single-jump hypothesis is not required to obtain more than one relaxation time, despite the fact that it is the most reasonable approxima-

tion to use on physical grounds. A general model with one deep site and $\Omega - 1$ high and equivalent sites has been treated under the restriction of a " random-jump " hypothesis (R-J) [9]. In this model only two transition probabilities appear. The probability of leaving the deep site is k, and the probability of leaving a high site is k': in each case the dipole is assumed to lose all memory of its previous orientation and settle down at random in some other site. This model always gives two relaxation times,

$$\tau_2 = \frac{\Omega - 1}{2[(\Omega - 1)k + k']} \tag{16a}$$

and

$$\tau_3 = \frac{\Omega - 1}{2k'} . \tag{16b}$$

This shows that more than one relaxation time can arise as a result of the anisotropy of the crystalline field even if the S-J hypothesis is relaxed. It is emphasized that the S-J hypothesis is certainly the correct approximation to use in most applications.

The general theory for the three-position single-axis rotator [8], as treated with the S-J hypothesis, has found use outside the field of dielectric relaxation. In certain saturated hydrocarbons and their derivatives, so-called " rotational " isomers can form by internal rotation of one part of a molecule with respect to the other. If the potential energy of any of the states formed by such a rotation is different, ultrasonic relaxation phenomena will appear in the liquid state. The barrier resisting internal rotation in these cases is of course not due to a crystalline field, but rather to interactions of one part of the molecule with the other.

Such cases have been uncovered in the studies of Young and Petrauskas [10], who treated their data using a theory based on reference 8. In ultrasonic relaxation, the calculation of the relaxation times is in every respect similar to the corresponding dielectric case, but the " intensity " factor is treated in a different way—transitions between energetically and sterically equivalent orientations do not lead to ultrasonic absorption. Krebs and Lamb [11] have treated the ultrasonic case with three non-equivalent sites in detail.

Theoretical studies have been carried out on the dielectric properties of a number of specialized three-dimensional rotators [7, 12]. In all of these cases, it was assumed that the orientational sites were arranged in an orthogonal manner, and the S-J hypothesis was used. A set of active

dielectric relaxation times always appeared when the sites were not energetically equivalent. The predicted loss curves were generally broad and asymmetrical at low temperatures, and narrow and much more symmetrical at high temperatures, just as in the case of the single-axis polar rotator.

The first attempt to relate dielectric relaxational behavior to lattice type and molecular shape was made in reference 12 for a three-dimensional polar rotator. In this paper, pear-shaped molecules in a body-centered orthorhombic and a body-centered tetragonal lattice were considered. In carrying out these calculations, we had in mind some of the ideas expressed by Powles [6] concerning possible orientational positions of the " protuberance " (hydrogen) in the hydrogen and deuterium halides, and the fact that in the low-temperature forms of some of these materials, strongly bimodal loss curves appear [13, 14, 15, 16, 17]. Powles' analysis suggests the number of accessible orientational sites, and their approximate orientation and energy with respect to the ground state. Any really detailed comparison of theory and experiment was defeated in this case by the fact that *(a)* the hydrogen and deuterium halides actually exist in the face-centered rather than the body-centered type of lattice for which the calculations were made and *(b)* at least some of the low-temperature forms evidently consist of zig-zag chains $H^{\diagup X \diagdown}H^{\diagup X}$ due to hydrogen bonding [18], so that simple repulsion of the protuberance (hydrogen) may not explain the orientation of the dipoles in the ground state, as was assumed in the calculations. Nevertheless, the orientation and energy of the metastable sites may have been surmised with sufficient accuracy. There is at present insufficient knowledge of the interactions in these halides to make more than guesses concerning the barrier system governing the transition probabilities between the various sites. Nevertheless, it was possible to show that the body-centered orthorhombic and body-centered tetragonal lattices consisting of pear-shaped polar molecules readily led in a plausible way to strongly bimodal loss curves with the general characteristics found in the low-temperature forms of HCl [13, 16], and HBr and DBr [13, 14, 15]. If the general approach used is valid at all for any of these halides, it is probably most nearly correct in the case of the chloride, which has a single first-order rotational transition where the dielectric constant abruptly rises to a liquid-like value. The bromides exhibit lambda transitions that are accompanied by strong dielectric cooperative effects leading to very high dielectric constants near the lowest transition [14, 15],

and this indicates that any " per molecule " approach, such as that employed in the present relaxation theory, would necessarily be highly oversimplified for such substances.

Theoretical studies have been carried out on the general (orthogonal) six-site three-dimensional rotator by Axilrod [19]. He was able to show that the eigenvalues of the characteristic determinant were always real and negative (or zero), showing that the relaxation times were all real and positive.

He was further able to derive a simple expression that placed a lower limit on the relaxation time. In carrying out this general analysis, some interesting theorems due to Goldberg [20] and Gerschgorin [21] were used. Axilrod's work, together with a paper mentioned earlier [8], has served to put the theory of the relaxational properties of the hindered rotator in a crystalline field on a firm mathematical footing.

A theoretical treatment of dielectric relaxation effects, based on a set of linear differential equations, has been given for ionic crystals containing vacancies.*

4. Application of Theory to a Real System.

Urea occlusion compounds containing polar chain molecules, such as ketones or secondary bromides, provide an ideal type of system for checking the theory of dielectric relaxation outlined above. In these solids, the urea molecules form a sort of regular honeycomb in which the pencil-like

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* Dielectric relaxation effects have been observed in alkali halide crystals containing divalent cation impurities [See J. S. Dryden and R. J. Meakins, *Faraday Soc. Discussions*, *23*, 39 (1957) for recent measurements, and references to earlier experimental work.] The loss curves observed by Dryden and Meakins were of the Debye type, or a close approximation thereto. These loss curves are a result of " dipolar " orientation caused by a motion of the effective negative charge of the vacancy relative to the positive charge of the neighboring divalent impurity. Lidiard treated the " dipole orientation " effects caused by the motion of the charges in these ionic crystals using the equivalent of our *S-J* hypothesis; mathematically, in the nearest-neighbor approximation, his theory strongly resembles our three-position case, and in the second-nearest neighbor approximation it resembles our (orthogonal) six-position case. [See A. B. Lidiard, *Report on Conference of Defects in Crystalline Solids* (Bristol, 1954), p. 283.] The predicted loss curve in the nearest-neighbor approximation is Debye-type, while that predicted with the second-nearest neighbor approximation is slightly broader, having two narrowly-spaced relaxation times.

polar chain molecules act like single-axis rotators. The compounds are strictly stoichiometric. All of the dielectric loss in these materials is a result of the motion of the dipole on the occluded molecule; the molecule turns about its long axis. The structure of hydrocarbon-urea adducts is well known due to the careful X-ray work of Smith [22]. Thus the crystalline field acting on each rotator can be estimated reasonably closely.

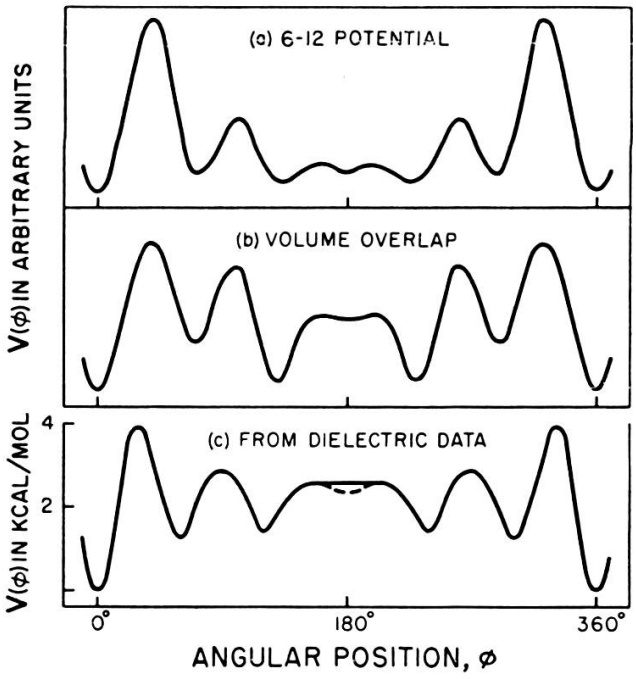

Fig. 1.
Potential energy as a function of angular position for 16-hentriacontanone in urea.

The existence of the urea honeycomb assures that the interaction between rotators is extremely weak, so cooperative interaction does not enter: the rotators may be treated as independent. The crystalline field interaction having to do with rotational motion is almost entirely a result of interaction of the protruding dipole (keto or bromide group) on the hydrocarbon with the urea lattice. Finally, dielectric data on such materials are available in the extensive investigation of Meakins [23]. Meakins gave an approximate analysis of his results, and concluded that the relaxation phenomena encountered were related to the motion of the dipole on the occluded molecule in the crystalline field of the urea honeycomb.

Lauritzen [24] of the Dielectrics Section of the National Bureau of Standards has carried out rigorous analysis of the dielectric behavior [23]

of urea adducts of 16-hentriacontanone and 12-bromotricosane. The crystalline field interactions for both of these compounds in urea were estimated using two methods. In method *(a)*, Lauritzen calculated the interaction of the protuberance of the rotator (i.e., the dipole) using the well-known Lennard-Jones 6-12 potential together with standard values for the van der Waals radii.

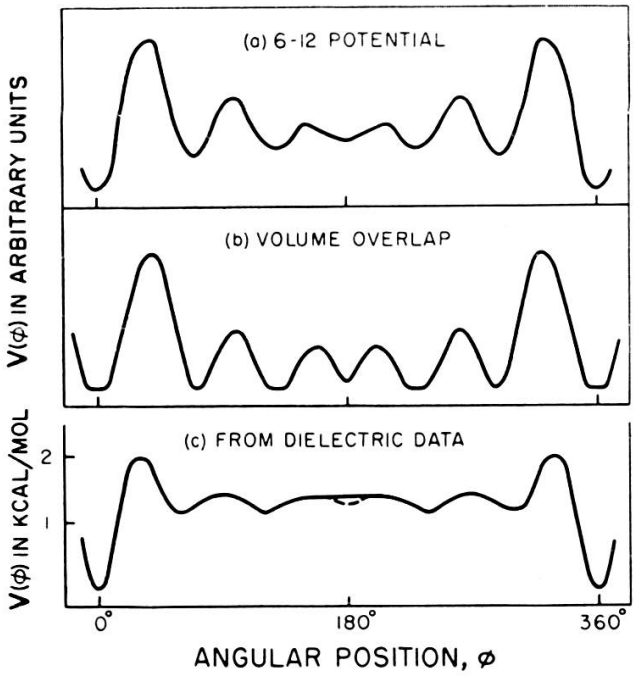

Fig. 2.
Potential energy as a function of angular position for 12-bromotricosane in urea.

The result obtained for the ketone-urea adduct is shown in figure 1*a*. The second method *(b)* of obtaining information concerning the nature of the crystalline field was to estimate the volume overlap in $Å^3$ as the dipole was rotated. This yielded the potential energy diagram for the ketone-urea adduct shown in figure 1*b*. The corresponding curves for the bromide-urea adduct are shown in figure 2*a* and 2*b*. The results render it perfectly clear that there is one most stable site, two pairs of higher energy sites, and one rather unstable orientational site. Dipole-dipole interactions between the lattice and the orienting dipole have the same symmetry as the van der Waals interactions, and no not materially change the potential energy of rotation.

With the symmetry of the crystalline field firmly established, it was then feasible to set down the differential equations analogous to equations (12). The " high " site is so shallow and little populated that it may be ignored, so that only five sites need be considered. Because of the symmetry of the crystalline field, only five different transition probabilities were involved in

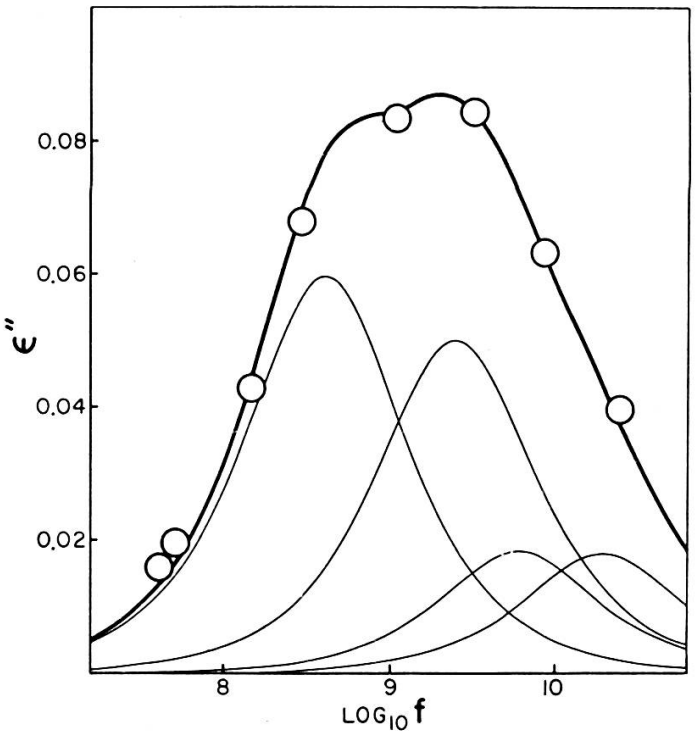

Fig. 3.
Experimental and calculated dielectric loss factor at 293° K for 12-bromotricosane in urea.
Circles represent values obtained by Meakins.
Light solid lines represent the four component Debye curves.
Heavy solid line represents the resultant dielectric loss factor.

these differential equations. These equations were solved to obtain the four relaxation times, and the corresponding orientational polarizabilities.

By relatively minor adjustments of the k_{ij} around their predicted values, it was possible to closely match the observed dielectric loss curves at a given temperature. An example of this is shown in figure 3 for the bromide. The particular k_{ij} that give the close fit shown in figure 3 imply the potential energy curve shown in figure 2*c*. The similarity of this curve with that calculated with the 6-12 law is rather striking. The barrier system that leads to a close fit of the dielectric data for the ketone-urea adduct is shown in figure 1*c*. The temperature-dependence of the shape of the loss curves

can also be predicted. A comparison of theory with experiment is shown in figure 4. These results leave little doubt that the anisotropy of the crystalline field is the principle source of the set of dielectric relaxation times in these materials.

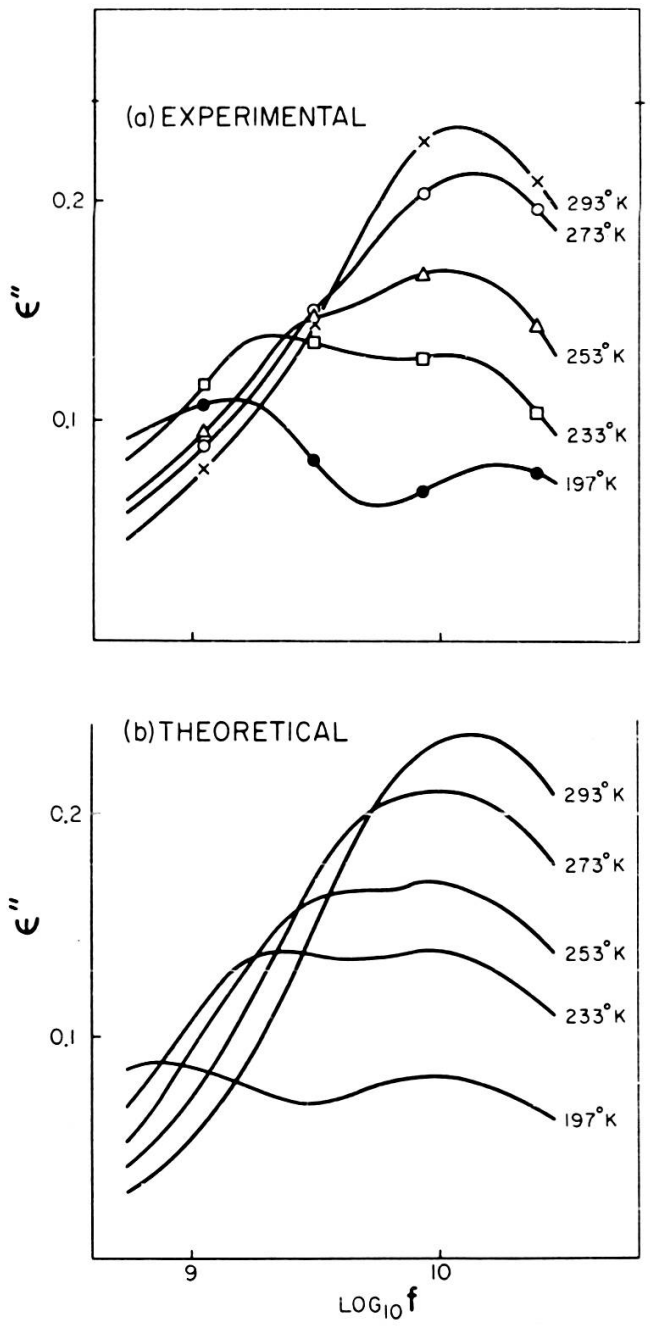

Fig. 4.
Comparison of experimental and theoretical dielectric loss factor of 16-hentriacontanone in urea at various temperatures. Experimental curves are those published by Meakins.

It is of interest to point out that the barrier system calculated with both the 6-12 law and the volume overlap method lead with no adjustments whatever to a successful prediction of the general features of the shape of the loss curves, as well as their behavior with changing temperature [24]. In particular, both the bimodal character of the loss curves at low temperatures, and their coalescence at higher temperatures, was predicted from the barrier system calculated theoretically. When the procedure is essentially reversed, the details of the barrier system can be even more closely determined from a combination of structural and dielectric data. The latter provides a powerful tool for investigating the details of the crystalline field.

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