1

Microwave–Material Interactions and Dielectric Properties, Key Ingredients for Mastery of Chemical Microwave Processes

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1.1

Fundamentals of Microwave–Matter Interactions

The main focus of the revised edition of this first chapter is essentially the same as the original – to explain in a chemically intelligible fashion the physical origin of microwave–matter interactions and, especially, the theory of dielectric relaxation of polar molecules. This revised version contains approximately 60% new material to scan a large range of reaction media able to be heated by microwave heating. The accounts presented are intended to be illustrative rather than exhaustive. They are planned to serve as introductions to the different aspects of interest in comprehensive microwave heating. In this sense the treatment is selective and to some extent arbitrary. Hence the bibliography contains historical papers and valuable reviews to which the reader anxious to pursue particular aspects should certainly turn.

It is the author's conviction, confirmed over many years of teaching experience, that it is much safer – at least for those who rate not trained physicists – to deal intelligently with an oversimplified model than to use sophisticated methods which require experience before becoming productive. Because of comments about the first edition, however, the author has included more technical material to enable better understanding of the concepts and ideas. These paragraphs could be omitted, depending on the level of comprehension of the reader. They are preceded by two different symbols – 🛠 for TOOLS and 💣 for CONCEPTS.

After consideration of the history and position of microwaves in the electromagnetic spectrum, notions of polarization and dielectric loss will be examined. The orienting effects of electric fields and the physical origin of dielectric loss will be analyzed, as also will transfers between rotational states and vibrational states within condensed phases.

Dielectric relaxation and dielectric losses of pure liquids, ionic solutions, solids, polymers and colloids will be discussed. Effect of electrolytes, relaxation of defects within crystals lattices, adsorbed phases, interfacial relaxation, space charge polarization, and the Maxwell–Wagner effect will be analyzed. Next, a brief overview of

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thermal conversion properties, thermodynamic aspects, and athermal effects will be given.

1.1.1
Introduction

According to the famous chemistry dictionary of N. Macquer edited in 1775, "All the chemistry operations could be reduced to decomposition and combination; hence, the fire appears as an universal agent in chemistry as in nature" [1]. Heating remains the primary means of stimulating chemical reactions which proceed slowly under ambient conditions, but several other stimulating techniques – photochemical, ultrasonic, high pressure and plasma – can be used. In this book, we describe results obtained by use of microwave heating. Microwave heating or dielectric heating is an alternative to conventional conductive heating. This heating technique uses the ability of some materials (liquids and solids) to transform electromagnetic energy into heat. This "in situ" mode of energy conversion is very attractive for chemistry applications and material processing.

If the effect of the temperature on reaction rates is well known, and very easy to express, the problem is very different for effects of electromagnetic waves. What can be expected from the orienting action of electromagnetic fields at molecular levels? Are electromagnetic fields able to enhance or to modify collisions between reagents? All these questions are raised by the use of microwave energy in chemistry.

1.1.1.1 History

How it all began There is some controversy about the origins of the microwave power cavity called the magnetron – the high-power generator of microwave power. The British were particularly forward-looking in deploying radar for air defense with a system called Chain Home which began operation in 1937. Originally operating at 22 MHz, frequencies increased to 55 MHz. The superiority of still higher frequencies for radar was appreciated theoretically but a lack of suitable detectors and of high-power sources stymied the development of microwaves. Magnetrons provide staggering amounts of output power (e.g. 100 kW on a pulse basis) for radar transmitters. The earliest description of the magnetron, a diode with a cylindrical anode, was published by A.W. Hull in 1921 [2, 3]. It was developed practically by Randall and Booth at the University of Birmingham in England ca 1940 [4]. On 21 February 1940, they verified their first microwave transmissions: 500 W at 3 GHz. A prototype was brought to the United States in September of that year to define an agreement whereby United States industrial capability would undertake the development of microwave radar. In November 1940 the Radiation Laboratory was established at the Massachusetts Institute of Technology to exploit microwave radar. More than 40 types of tube would be produced, particularly in the S-band (i.e. 300 MHz). The growth of microwave radar is linked with Raytheon Company and P.L. Spencer who found the key to mass production. Microwave techniques were developed during and just before World War II when most effort was concentrated on the design and manufacture of microwave navigation and communications equipment for military use. Originally, microwaves played a leading role during the World War II, especially during the Battle of Britain when English planes could fight one against three thanks to radar. It hardly seems surprising that with all this magnetron manufacturing expertise that microwave cooking would be invented at Raytheon and that the first microwave oven would be built there.

Since these beginnings the heating capability of microwave power has been recognized by scientists and engineers but radar development had top priority. A new step began with the publication of microwave heating patents by Raytheon on 9 October 1945. Others patents followed as problems were encountered and solutions found. Probably the first announcement of a microwave oven was a magazine article describing a newly developed Radarange for airline use [5, 6]. This device, it was claimed, could bake biscuits in 29 s, cook hamburgers in 35 s, and grill frankfurters in 10 s. This name Radarange almost became generic name for microwave ovens. An early prototype picture is shown in the book of Decareau and Peterson [7]. This first commercial microwave oven was developed by P.L. Spencer from Raytheon in 1952 [8]. The legend says that P.L. Spencer, who studied high-power microwave sources for radar applications, noticed the melting of a chocolate bar put in his pocket. Another story says that P.L. Spencer had some popping corn in his pocket that began to pop as he was standing alongside a live microwave source [7].

These first oven prototypes were placed in laboratories and kitchens throughout the United States to develop microwave cooking technology. The transition from crude aircraft heater to domestic oven took almost eight years. The turning point in the story of the microwave oven was 1965, which saw the beginning of a flurry of manufacturing activity and the issue of hundreds of patents on different aspects of oven design, processes, packaging, food products, appliance and techniques. The widespread domestic use of microwave ovens occurred during the 1970s and 1980s as a result of the generation of the mass market and also of Japanese technology transfer and global marketing.

From cooking to microwave processing The first studies of the effects of microwave heating were carried out at the Massachusetts Institute of Technology's Department of Food Technology on blanching of vegetables, coffee roasting, effect of cooking, with the hope of vitamin retention [9]. Microwave and conventional freeze-drying of foods were compared by Jackson et al. [10]. The Food Research Laboratory of Raytheon have made extensive studies that led to the first microwave freeze-drying pilot plant unit [11–16].

Microwave processing began on a commercial scale in the early 1960s when Cryodry Corporation of San Ramon, California, introduced the first conveyor system for sale. The first market was the potato chip finish drying process with several systems operating in United States and Europe [17, 18]. These systems operated at 915 MHz. Several 5 to 10 kW pilot plant conveyor systems were sold during this time to food manufacturers by Raytheon and Litton Industries Atherton Division. These systems all operated at 2450 MHz. One poultry-processing system [19] had a total output of 130 kW, split between two conveyor units. This system combined microwave power and saturated steam to precook poultry parts for the institutional and restaurant food service market. This system also operated at 2450 MHz.

Food applications included microwave tempering of frozen foods, pasta drying, precooking of bacon, poultry processing, meat pie cooking, frankfurter manufacturing, drying egg yolk paste, baking, sterilization, potato processing, cocoa bean roasting, and vacuum drying [7, 20]. Curiously, microwave heating of industrial applications was initiated by the domestic oven.

Pre-historical foundations Many histories of electromagnetic waves and especially microwaves begin with publication of the *Treatise on Electricity and Magnetism* by James Clerk Maxwell in 1873. These equations were initially expressed by J.C. Maxwell in terms of quaternions. Heaviside and Gibbs would later reject quaternions in favor of a classical vector formulation to frame Maxwell's equations in the well known form. Students and users of microwave heating, perhaps benumbed by divergence, gradient, and curl, often fail to appreciate just how revolutionary this insight was. The existence of electromagnetic waves that travel at the speed of light were predicted by arbitrarily adding an extra term (the displacement current) to the equations that described all previously known electromagnetic behavior. According to Lee [21], and contrary to the standard story presented in many textbooks, Maxwell did not introduce the displacement current to resolve any outstanding conundrums but he was apparently inspired more by an aesthetic sense that nature simply should provide for the existence of electromagnetic waves. Maxwell's work was magical and arguably ranks as the most important intellectual achievement of the 19th century. According to the Nobel physicist R. Feynman, future historians would still marvel at this work, long after another event of that time – the American Civil War – has faded into merely parochial significance [21].

Maxwell died in 1879 (48 years old), and H. Von Helmholtz sponsored a prize for the first experimental evidence of Maxwell's forecasting. H. Hertz verified that Maxwell's forecasting was correct in 1888 at the Technische Hochschule in Karlsruhe. According to Lee [21] another contestant in the race, was O. Lodge, a professor at University College in Liverpool, who published his own experimental evidence one month before H. Hertz. Hertz is the German word for heart and human heart beats approximately once per second, it is perhaps all for the best that Lodge didn't win the race and that lodgian waves with frequencies measured in gigalodges never appeared.

How was it possible to produce and detect electromagnetic waves in the 1880's? The first experiment of H. Hertz produced microwaves (frequency close to GHz). His basic transmitter-receiver is shown in Fig. 1.1. The generator is a Ruhmkorff coil or a transformer able to produce very high potential (1). This device is very similar to starter of car. The high voltage in the secondary causes spark discharge within straight wire connections to produce the desired resonant frequency (2). The detector is a ring antenna with a spark gap (3). Detection is based on induction

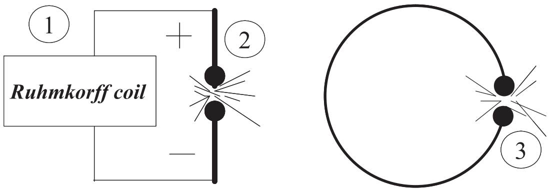

Fig. 1.1. Spark transmitter and receiver of Hertz's original experiment.

of sufficient voltage in the ring antenna to produce a visible spark. Hertz demonstrated the essential physics of wave phenomena, for example polarization and reflection. He died of blood poisoning from an infected tooth in 1894 at the age of 36. The commercial applications of wireless would be developed by G. Marconi. Many details about the whole history of microwave technology can be found elsewhere [21].

1.1.1.2 **The Electromagnetic Spectrum**

In the electromagnetic spectrum, microwaves occur in a transitional region between infrared and radiofrequency radiation, as shown in by Fig. 1.2. The wavelengths are between 1 cm and 1 m and frequencies between 300 GHz and 300 MHz.

The term "microwave" denotes the techniques and concepts used and a range of frequencies. Microwaves may be transmitted through hollow metallic tubes and

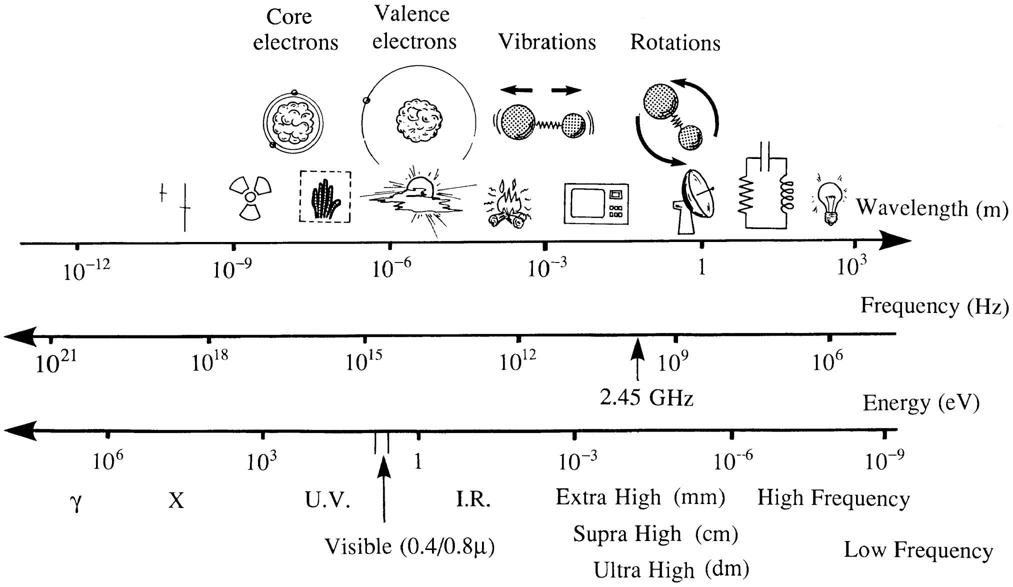

Fig. 1.2. The electromagnetic spectrum.

may be focused into beams by the use of high-gain antennas. Microwaves also change direction when traveling from one dielectric material into another, similar to the way light rays are bent (refracted) when they passed from air into water. Microwaves travel in the same manner as light waves; they are reflected by metallic objects, absorbed by some dielectric materials and transmitted without significant absorption through other dielectric materials. Water, carbon, and foods with a high water content are good microwave absorbers whereas ceramics and most thermoplastic materials absorb microwaves only slightly.

The fundamental connection between energy E, frequency, ν, wavelength, λ, and angular frequency, ω, is given by Eq. (1):

$$E = \hbar\omega = h\nu = \frac{hc}{\lambda} \tag{1}$$

To avoid interference with telecommunications and cellular 'phone frequencies, heating applications must use ISM bands (Industrial Scientific and Medical frequencies) which are 27.12 and 915 MHz and 2.45 GHz (i.e. wavelengths of 11.05 m and 37.24 and 12.24 cm, respectively). Domestic ovens and laboratory systems usually work at 2.45 GHz. At frequencies below 100 MHz, when conventional open wire circuits are used, the technique will be referred to as radio-frequency heating. The object to be heated is placed between the two electrodes of a capacitor. At frequencies above 500 MHz, however, wired circuits cannot be used and the power is transferred to the applicator containing the material to be processed. Hence, the microwave applicator is a metallic box in which the object to be heated is placed. These operating conditions will be referred as microwave-heating processes. In the microwave band the wavelength is of the order of the size of production and transmission elements. The elements cannot, therefore, be regarded as points in comparison with the wavelength, in contrast with circuit theory. In the same way, it is impossible to consider them far larger than the wavelength, as in geometrical optics. Hence, because of the position of microwaves in the electromagnetic spectrum, both quantum mechanics (corpuscular aspects) and the Maxwell equations (wavelike aspects) will be used. Detailed analysis of these phenomena is beyond the scope of this work.

1.1.1.3 **What About Chemistry? Energetic Comments**

It is well known that γ or X photons have energies suitable for excitation of inner or core electrons. We can use ultraviolet and visible radiation to initiate chemical reactions (photochemistry, valence electron). Infrared radiation excites bond vibrations only, whereas microwaves excite molecular rotation.

Energy associated with chemical bonds and Brownian motion are compared in Table 1.1. The microwave photon corresponding to the frequency used in microwave heating systems, for example domestic and industrial ovens, has energy close to 0.00001 eV (2.45 GHz, 12.22 cm). According to these values, the microwave photon is not sufficiently energetic to break hydrogen bonds; it is also much smaller than that of Brownian motion and obviously cannot induce chemical reactions. If

Tab. 1.1. Brownian motion and bond energies.

	Brownian motion	**Hydrogen bonds**	**Covalent bonds**	**Ionic bonds**
Energy (eV)	~0.017 (200 K)	~0.04 to 0.44	~4.51 (C–H); ~3.82 (C–C)	~7.6
Energy (kJ mol^{-1})	1.64	~3.8 to 42	~435 (C–H); ~368 (C–C)	~730

no bond breaking can occur by direct absorption of electromagnetic energy, what, then, can be expected from the orienting effects of electromagnetic fields at molecular levels? Are electromagnetic fields able to enhance or to modify collisions between reagents? Do reactions proceed with the same reaction rate with and without electromagnetic irradiation at the same bulk temperature? In the following discussion the orienting effects of the electric field, the physical origin of the dielectric loss, transfers between rotational and vibrational states in condensed phases, and thermodynamic effects of electric fields on chemical equilibrium will be analyzed.

🛠 TOOLS More about energy partition of molecular systems Rotational motion of molecular systems are much slower than the vibrational motion of the relatively heavy nuclei forming chemical bonds, and even slower than the electronic motion around nuclei. These vastly differing time scales of the different types of motion lead to a natural partitioning of the discrete energy spectrum of matter into progressively smaller subsets associated with electronic, vibrational, and rotational degrees of freedom.

The Born–Oppenheimer approximation is based on this assumption and enables reduction of the mathematically intractable spectral eigenvalue problem to a set of separable spectral problems for each type of motion. According to this approximation, energy levels associated with each type of motion are proportional to the ratio of electronic mass (m_e) to the nuclear mass (M_N). This ratio, ξ, quite smaller than unity, is given by Eq. (2):

$$\zeta \propto \left(\frac{m_e}{M_N}\right)^{1/4} \tag{2}$$

The electronic energy (ΔE_{elec}) is of the order of ξ, the vibrational energy (ΔE_{Vib}) of the nuclei is of the order of ξ^2, and the rotational energy (ΔE_{Rot}) of the molecule is of the order of ξ^4. In quantum mechanics, states are described by wave functions or Hamiltonian operators, whose discrete eigenvalues define the set of energy levels and whose corresponding eigenfunctions are the basis states. Hence, the total quantum wave function Ψ for a molecule can be written in separable form as described by Eq. (3):

$$\Psi = \Psi_{Elec}(r, R_0)\Psi_{Vib}(R)\Psi_{Rot}(\varphi_i) \tag{3}$$

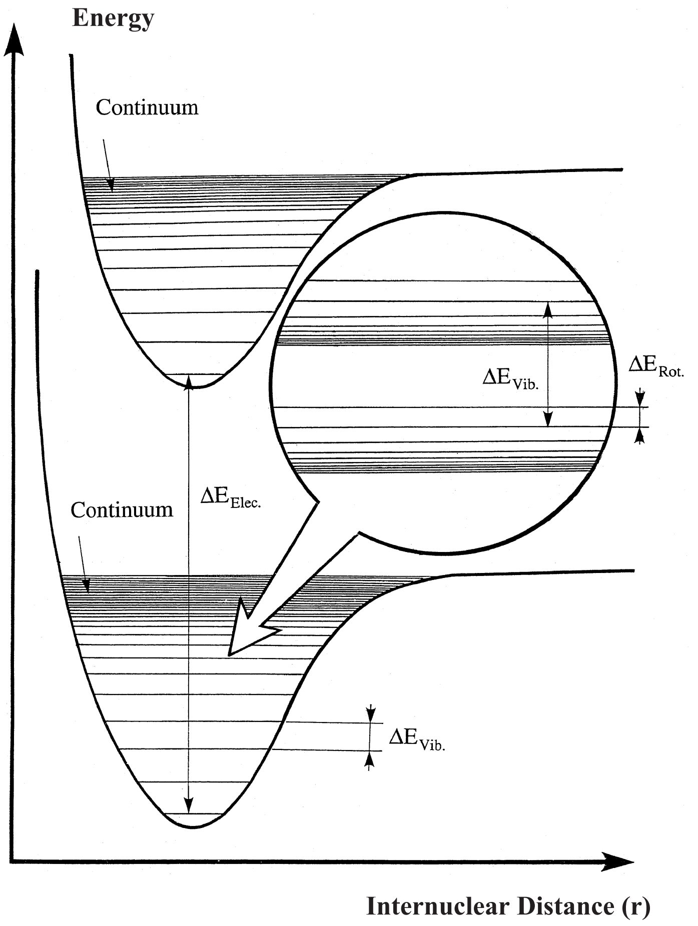

Fig. 1.3. The energy spectrum of matter.

where r is the electron coordinate, R the displacement of the nucleus from its equilibrium position, R_0, and φ_i is the Euler angle determining the orientation of the molecule in space. Figure 1.3 shows the energy spectrum of matter as it is probed on a progressively finer energy scale clearly revealing the different partition states. The fundamental and the first excited states are shown.

A resonance of a system can be produced by excitation that oscillates at a frequency close to the natural frequency of the system, unlike a relaxation, which is the restoring action of a diffusive force of thermodynamic origin. Direct resonance or a one-photon process can occur within isolated intervals of the electromagnetic spectrum from ultraviolet to visible frequencies close to 10^{15} Hz (electronic oscillator), in infrared with frequencies close to 10^{13} Hz (vibrational modes), and in the far infrared and microwave range with frequencies close to 10^{11} Hz (rotational modes).

1.1.2
The Complex Dielectric Permittivity

Insulating materials can be heated by applying high-frequency electromagnetic energy. The physical origin of this heating conversion lies with the ability of the electric field to induce polarization of charges within the heated product. This polarization cannot follow the extremely rapid reversals of the electric field and induce heating of the irradiated media.

The interaction between electromagnetic waves and matter is quantified by the two complex physical quantities – the dielectric permittivity, $\tilde{\varepsilon}$, and the magnetic susceptibility, $\tilde{\mu}$. The electric components of electromagnetic waves can induce currents of free charges (electric conduction that can be of electronic or ionic origin). It can, however, also induce local reorganization of linked charges (dipolar moments) while the magnetic component can induce structure in magnetic moments. The local reorganization of linked and free charges is the physical origin of polarization phenomena. The storage of electromagnetic energy within the irradiated medium and the thermal conversion in relation to the frequency of the electromagnetic stimulation appear as the two main points of polarization phenomena induced by the interaction between electromagnetic waves and dielectric media. These two main points of wave–matter interactions are expressed by the complex formulation of the dielectric permittivity as described by Eq. (4):

$$\tilde{\varepsilon} = \varepsilon' - j\varepsilon'' = \varepsilon_0\varepsilon'_{\mathrm{r}} - j\varepsilon_0\varepsilon''_{\mathrm{r}} \tag{4}$$

where ε_0 is the dielectric permittivity of a vacuum, ε' and ε'' are the real and imaginary parts of the complex dielectric permittivity and $\varepsilon'_{\mathrm{r}}$ and $\varepsilon''_{\mathrm{r}}$ are the real and imaginary parts of the relative complex dielectric permittivity. The storage of electromagnetic energy is expressed by the real part whereas the thermal conversion is proportional to the imaginary part.

⚒ TOOLS More about polar molecules A polar molecule has a permanent electric dipole moment. The total amounts of positive and negative charges on the molecule are equal, so the molecule is electrically neutral. Distributions of the two kinds of charge are different, however, so that the positive and negative charges are centered at points separated by a distance of molecular dimensions forming an electric dipole. A dipole made up of charges $+q$ and $-q$, separated by a distance d, of magnitude qd. The dipole moment usually represented by the symbol μ is approximately 10^{-18} Coulomb (the electronic charge is of the order of 10^{-10} SI units whereas d will be of order of molecular dimensions – 10^{-10} m). The unit 10^{-18} Cb m is called the Debye (abbreviation D).

The magnitude of the dipole moment depends on the size and symmetry of the molecule. Molecules with a center of symmetry, for example methane, carbon tetrachloride, and benzene are apolar (zero dipole moment) whereas molecules with no center of symmetry are polar. Table 1.2 gives relative static dielectric permittivity

Tab. 1.2. Relative static dielectric constant, refractive index (measured at the frequency of sodium D lines) and dipole moment for a few molecules.

Molecules	ε_{Sr}	n_D^2	μ
Apolar			
n-Hexane, C_6H_{14}	1.89	1.89	–
Carbon tetrachloride, CCl_4	2.23	2.13	–
Benzene, C_6H_6	2.28	2.25	–
Polar			
Methanol, CH_3OH	33.64	1.76	1.68
Ethanol, CH_3CH_2OH	25.07	1.85	1.70
Acetone, CH_3COCH_3	21.20	1.84	2.95
Chlorobenzene, C_6H_5Cl	5.64	2.32	1.69
Water, H_2O	80.37	1.78	1.94

or dielectric constants (very low frequency or frequency close to zero), refractive indices, and dipole moments for few simple polar and apolar molecules.

From Maxwell's theory of electromagnetic waves it follows that the relative permittivity of a material is equal to the square of its refractive index measured at the same frequency. Refractive index given by Table 1.2 is measured at the frequency of the D line of sodium. Thus it gives the proportion of (electronic) polarizability still effective at very high frequencies (optical frequencies) compared with polarizability at very low frequencies given by the dielectric constant. It can be seen from Table 1.2 that the dielectric constant is equal to the square of the refractive index for apolar molecules whereas for polar molecules the difference is mainly because of the permanent dipole. In the following discussion the Clausius–Mossoti equation will be used to define supplementary terms justifying the difference between the dielectric constant and the square of the refractive index (Eq. (29); The Debye model).

The temperature dependence of the dielectric constant of polar molecules also differs from that of nonpolar molecules. Change of temperature has a small effect only for nonpolar molecules (change of density). For polar molecules, the orientation polarization falls off rapidly with increasing temperature, because thermal motion reduces the alignment of the permanent dipoles by the electric field. In the following discussion we will see that it is possible to have increasing values of dielectric permittivity with increasing temperature.

As discussed above, a molecule with a zero total charge may still have a dipole moment because molecules without a center of symmetry are polar. Similarly, a molecule may have a distribution of charge which can be regarded as two equal and opposite dipoles centered at different places. Such a distribution will have zero total charge and zero total moment but will have a quadrupole moment. Carbon disulfide, which is linear, has a quadrupole moment. Two equal and opposite quadrupole moments centered at difference places form an octupole moment. The potential arising as a result of the total charge falls off as $1/r$, that because of the dipole moment as $1/r^2$, and that because of the quadrupole moment as $1/r^3$. At large distances from the origin, the higher moments have negligible effects. The intermolecular distances in liquids and solids are not large compared with molecular dimensions, however, so quite strong interactions may arise because of higher moments.

🛠 **TOOLS More about dielectrics and insulators** An insulator is a material through which no steady conduction current can flow when it is submitted to an electric field. Consequently, an insulator can accumulate electric charge, hence electrostatic energy. The word dielectric, especially if it is used as adjective, covers a wide range of materials including electrolytes and even metals.

If we consider a capacitor comprising two planes parallel with S and d, the surface area of the plates and the distance between the plates, respectively (S is large compared with d so that edge effects are negligible), the vacuum capacitance is given by Eq. (5):

$$C = \varepsilon_0 \frac{S}{d} \tag{5}$$

If an alternating voltage $V = V_0 \exp(j\omega t)$ is applied to this capacitor, a charge $Q = CV$ appears on the electrode, in phase with the applied voltage. The current in the external circuit is the time-derivative of the charge Q is given by Eq. (6):

$$I = \dot{Q} = j\omega CV \tag{6}$$

This current is 90° out of phase with the applied voltage. It is a nondissipative displacement or induction current. If the volume between the electrodes is filled with a nonpolar, perfectly insulating material, the capacitor has a new capacitance, and the ratio between the vacuum and filled capacitance is the relative permittivity of the material used. The new current is larger than that above but it is still out of phase with the current. Now, if the material is either slightly conducting or polar, or both, the capacitor is not longer perfect and the current is not exactly out of phase with the voltage. Hence, there is a component of conduction in phase with the applied voltage. The origin of this current is the motion of charges. The current is composed of a displacement current and a conduction current. The loss angle is given by Eq. (7):

$$\tan\delta = \frac{\text{Dissipative term}}{\text{Capacitive term}} \tag{7}$$

The current is composed of two quantities, real and imaginary, so the dielectric permittivity will also have a complex form which will depend on the types of interaction between the electromagnetic field and matter. This discussion refers to isotropic dielectrics. Many products falls into this class but the situation is different for crystalline solids, for which the permittivity becomes a tensor quantity (values different according to crystallographic axis).

CONCEPTS The dielectric properties are group properties The physical origin of polarization phenomena is the local reorganization of linked and free charges. The interaction between a dipole and an electric or magnetic field is clearly interpreted by quantum theory. For electric fields the coupling is weaker and there is such demultiplication of quantum levels that they are very close to each other. The Langevin and Boltzman theories must be used because interaction energy is continuous. Because of the weak coupling between dipole and electric field there are no quantified orientations and study of the interaction between a dipole in an electric field gives more information about the surroundings of the dipole than about the dipole itself. Dipoles are, moreover, associated with chemical bonds, and any motion of the dipole induces a correlative motion of molecular bonds whereas motion of a magnetic moment is totally independent of any molecular motion. In contrast with magnetic properties, dielectric properties are group properties and cannot be modeled by an interaction between a single dipole and electric field. A group of dipoles interacting among themselves could be considered.

The origin of confusion between the behavior of a single species and a collection, or the difference between dilute and condensed phases, is the most important problem and the source of illusions within microwave athermal effects.

1.1.2.1 Effect of the Real Part: Polarization and Storage of Electromagnetic Energy

The physical origin of polarization Polarization phenomena are expressed by the quantity $\vec{P}$ which gives contribution of matter compared with that of a vacuum. The electric field and the polarization are linked through Maxwell's equations. The constitutive equation for vacuum is Eq. (8):

$$\vec{D} = \varepsilon_0 \vec{E} \tag{8}$$

where $\vec{D}$ is the electric displacement, $\vec{E}$ the electric field. According to Eq. (8), dielectric permittivity is the ratio of the electric displacement to the electric field. For a dielectric medium characterized by $\tilde{\varepsilon}$, the constitutive equation is Eq. (9):

$$\vec{D} = \tilde{\varepsilon}\vec{E} = \varepsilon_0 \vec{E} + \vec{P} \tag{9}$$

In the global formulation of Eq. (9), we can express the term corresponding to vacuum and given by Eq. (8). Then the second and complementary term defines the contribution of matter to polarization processes or polarization $\vec{P}$. For any material, the higher the dielectric permittivity, the greater are Brownian ion processes. The polarization process described by $\vec{P}$ has its physical origin in the response of dipoles and charges to the applied field. Depending on the frequency, electromagnetic fields induce oscillation of one or more types of charge association. In any material there are a variety of types of charge association:

- inner or core electrons tightly bound to the nuclei,
- valence electrons,
- free or conduction electrons,
- bound ions in crystals,
- free ions as in electrolytes and non stoichiometric ionic crystals (for example, ionic dipoles such as OH^- have both ionic and dipolar characteristics),
- finally the multipole (mainly the quadrupole or an antiparallel association of two dipoles).

⚒ TOOLS More about photon–matter interaction Depending on the frequency, the electromagnetic field can induce oscillation of one or more types of charges association. For each configuration with its own critical frequency above which interaction with the field becomes vanishingly small, the lower the frequency the more configurations are excited. Electrons of the inner atomic shells have a critical frequency approximately that of X-rays. Consequently an electromagnetic field of wavelength more than 10^{-10} m cannot excite any vibrations, but rather induces ionization of these atoms. There is no polarizing effect on the material which has, for this frequency, the same dielectric permittivity as in vacuum. For ultraviolet radiation the energy of photons is sufficient to induce transitions of valence electrons. In the optical range an electromagnetic field can induce distortions of inner and valence electronic shells. Polarization processes, called electronic polarizability, result from a dipolar moment induced by distortion of electron shells. Electromagnetic fields in the infrared range induce atomic vibrations in molecules and crystals, and polarization processes result from the dipolar moment induced by distortion of the positions of nuclei. These polarization processes are called atomic polarization. In all these processes the charges affected by the field can be regarded as being attracted towards their central position by forces proportional to their displacement by linear elastic forces. This mechanical approach of electronic resonance is only an approximation, because electrons cannot be properly treated by classical mechanics. Quantitative treatment of these processes requires the formalism of quantum mechanics. The two types of polarization process described above can be connected together in distortion polarization.

The characteristic material response times for molecular reorientation are 10^{-12} s. Electromagnetic fields in the microwave band thus lead to rotation of polar molecules or charge redistribution; the corresponding polarization processes are called orientation polarization.

Orienting effect of a static electric field The general problem of the orienting effect of a static electric field (orientation of polar molecules) was first considered by Debye [22, 23], Frölich [24], and more recently by Böttcher [25, 26].

A collection of molecular dipoles in thermal equilibrium is considered. It is assumed that all the molecules are identical and they can take on any orientation.

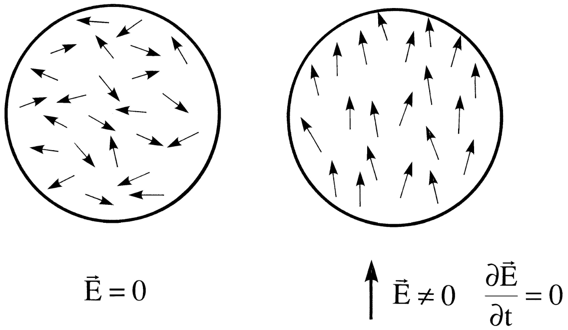

Fig. 1.4. Distribution of dipoles subjected to the effect of a static electric field.

Because of thermal energy each molecule undergoes successive collisions with the surrounding molecules. In the absence of an applied electric field, the collisions tend to maintain a perfectly isotropic statistical orientation of the molecules. This means that for each dipole pointing in one direction there is, statistically, a corresponding dipole pointing in the opposite direction as shown in Fig. 1.4.

In the presence of an applied electric field $\vec{E}$, the dipolar moment $\vec{\mu}$ of the molecule undergoes a torque $\vec{\Gamma}$. This torque tends to orientate the dipolar moment $\vec{\mu}$ parallel to the electric field. The corresponding potential energy (for a permanent or induced dipole) is minimum when the angle, θ, between the dipole and the electric field is zero. Consequently, the dipolar moment takes the same direction as the electric field. It is the same phenomena as the orientation of the compass needle in the earth's magnetic field. For molecular dipoles, however, the thermal energy counteracts this tendency and the system finally reaches a new statistical equilibrium which is depicted schematically in Fig. 1.4. In this configuration more dipoles are pointing along the field than before and the medium becomes slightly anisotropic.

The suitability of the medium to be frozen by the electric field is given by Langevin's function resulting from statistical theories which quantify competition between the orienting effect of electric field, and disorienting effects resulting from thermal agitation. The ratio of effective to maximum polarization versus the ratio of the potential interaction energy to the thermal agitation is shown in Fig. 1.5.

We can see that the Langevin function increases from 0 to 1 on increasing the strength of the electric field and/or reducing the temperature. The molecules tend to align with the field direction. For high values of the field, the orientation action dominates over the disorienting action of temperature, so that all the dipoles tend to become parallel to the applied field. Complete alignment corresponds to saturation of the induced polarization. Saturation effects only become detectable in fields of the order of 10^7 V m^{-1}. Because intermolecular distances are small in liquids and solids, however, the local field acting on molecule because of its neighbors may be very large, especially in strongly polar liquids (i.e. electric field close to

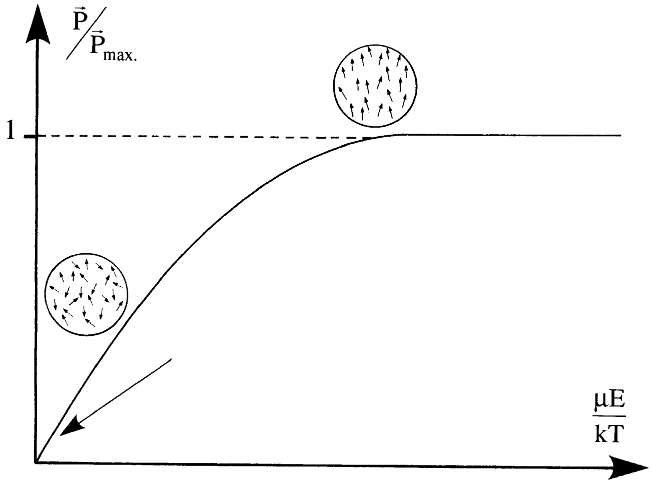

Fig. 1.5. Langevin's Function.

10^6 V m^{-1} at a distance of 5×10^{-10} m from a dipole of 1 Debye). The consequence of this should, however, be reduced, even for strongly polar liquids, because the intermolecular distance is of the same order as the molecular dimensions and it is not justified to describe the molecule as a point dipole. The situation is totally different for solids and, especially, solid surfaces for which the magnitude of the static electric field is close to saturation value. These strong static electric fields occur independently of all external electric excitation and are the physical origin of adsorption phenomena. In these circumstances adsorption can lead to freezing of molecular motion and can also induce polarization because of distortion of electronic shells. Apolar molecule can obtain polar character because of adsorption. Free molecules without dielectric losses at the operating frequency (2.45 GHz) have the capacity to be heated by microwave irradiation after adsorption on solids such as clays or alumina catalysts.

In many practical situations field strengths are well below their saturation values. The arrow on Fig. 1.5 corresponds to the usual conditions of microwave heating (no adsorption phenomena, temperature close to room temperature, 25 °C, and electric field strength close to 10^5 V m^{-1}). According to these results, the electric field strength commonly used in microwave heating is not sufficient to induce consequent freezing of media.

Calculation of the dielectric permittivity of an isotropic polar material involves the problem of the permanent dipole contribution to polarizability and the problem of calculation of the local field acting at the molecular level in terms of the macroscopic field applied. Debye's model for static permittivity considers the local field equal to the external field. This assumption is valid only for gases at low density or dilute solutions of polar molecules in nonpolar solvents. Several workers have proposed theories containing assumptions about relationships between local and external electric fields. Detailed analysis of these phenomena is beyond the scope of this section. More information can be found elsewhere [27].

1.1.2.2 **Effect of Imaginary Part: Dielectric Losses**

Physical origin of dielectric loss The foregoing conclusions correspond to a static description or cases for which the polarization can perfectly follow the oscillation of the electric field. Indeed, the electric field orientation depends on time with a frequency equal to 2.45 GHz (the electric field vector switches its orientation approximately every 10^{-12} s). The torque exercised by the electric field induces rotation of polar molecules, but they cannot always orient at this rate. The motion of the particles will not be sufficiently rapid to build up a time-dependent polarization $\vec{P}(t)$ that is in equilibrium with the electric field at any moment. This delay between electromagnetic stimulation and molecular response is the physical origin of the dielectric loss.

The polarization given by Eq. (9) becomes a complex quantity with the real part in phase with the excitation whereas the imaginary part has a phase lag with the excitation. This last part is the origin of the thermal conversion of electromagnetic energy within the irradiated dielectric.

CONCEPTS More about delay and phase lag Matter does not respond instantaneously to stimulation induced by electromagnetic waves. In an isotropic medium this delay can be expressed by the specific formulation of polarization given by Eq. (10):

$$\vec{P} = \varepsilon_0 \int_{-\infty}^{+\infty} \chi(t-\tau)\vec{E}(\tau)\,\mathrm{d}\tau \tag{10}$$

Because of the causality principle, Eq. (11), in which χ is the electric susceptibility, t the time, and τ the delay must be verified:

$$\chi(t-\tau) = 0, \quad t-\tau < 0 \tag{11}$$

The electric susceptibility can comprise any combination of dipolar, ionic, or electronic polarization processes. This formulation leads to relationships between the real and imaginary parts of the complex electric susceptibility, known as the Kramers–Kronig relationships [28–31] which are very similar to the frequency relations between resistance and reactance in circuit theory [30].

Consequently, after this short section on electric susceptibility, we shall always use classical elementary models which yield good results, as can be expected from correspondence principle.

Macroscopic theory of dielectric loss The main interest in dielectric theories is the frequency region at which the dispersion and absorption processes occur (the dipolar polarization can no longer change fast enough to reach equilibrium with the polarization field). When a steady electric field is applied to a dielectric, the distortion polarization (electronic and vibrational modes) will be established very quickly, essentially instantaneously compared with characteristic time of electric field. The remaining dipolar part or orientation polarization takes time to reach equilibrium state. Relaxation processes are probably the most important of the interactions between electric fields and matter. Debye [22, 23] has extended the Langevin theory of dipole orientation in a constant field to the case of a varying field. It shows that the Boltzmann factor of the Langevin theory becomes a time-dependent weighting factor. A macroscopic description, more usable, can use an exponential law with a macroscopic relaxation time, τ, or the delay in the response of the medium to the electric stimulation given by Eq. (12):

$$\vec{P}_{\text{Orientation}} = (\vec{P}_{\text{Total}} - \vec{P}_{\text{Distorsion}})\left(1 - \exp\left(-\frac{t}{\tau}\right)\right) \tag{12}$$

Similarly, when the electric stimulation is removed, the distortion polarization falls immediately to zero whereas the distortion polarization falls exponentially. If the electric stimulation oscillates with time (angular frequency, ω; electric field strength, $\vec{E}_0$) as described by Eq. (13):

$$\vec{E} = \vec{E}_0 \exp(jwt) \tag{13}$$

The static permittivity, ε_{S}, (frequency close to zero) and very high-frequency permittivity ε_∞ could be defined in term of total polarization and distortion polarization as described by Eqs (14) and (15):

$$\vec{P}_{\text{Total}} = \vec{P}_{\text{Distorsion}} + \vec{P}_{\text{Orientation}} = (\varepsilon_{\text{S}} - \varepsilon_0)\vec{E} \tag{14}$$

$$\vec{P}_{\text{Distorsion}} = (\varepsilon_\infty - \varepsilon_0)\vec{E} \tag{15}$$

According to the exponential law defined for orientation polarization (Eq. 9), the following differential equation could be defined:

$$\frac{\mathrm{d}\vec{P}_{\text{Orientation}}}{\mathrm{d}t} = \frac{(\vec{P}_{\text{Total}} - \vec{P}_{\text{Orientation}})}{\tau} = \frac{(\varepsilon_{\text{S}} - \varepsilon_\infty)\vec{E}_0 \exp(j\omega t) - \vec{P}_{\text{Orientation}}}{\tau} \tag{16}$$

The ratio of orientation polarization to electric field becomes a complex quantity. This means that the dipolar part of the polarization is out of phase with the field, as depicted by Eq. (17):

$$\begin{aligned}\vec{P}_{\text{Total}} &= \vec{P}_{\text{Orientation}} + \vec{P}_{\text{Distorsion}} \\ &= (\varepsilon_\infty - \varepsilon_0)\vec{E}_0 \exp(j\omega t) + \frac{(\varepsilon_{\text{S}} - \varepsilon_0)\vec{E}_0 \exp(j\omega t)}{1 + j\omega t}\end{aligned} \tag{17}$$

Debye's model The Debye model could be built with these assumptions, and polarization and permittivity become complex as described by Eq. (18) where n is the refractive index and τ the relaxation time:

$$\tilde{\varepsilon} = \varepsilon' - j\varepsilon'' = n^2 + \frac{\varepsilon_s - n^2}{1 + j\omega\tau} \tag{18}$$

All polar substances have a characteristic time τ called the relaxation time (the characteristic time of reorientation of the dipolar moments in the electric field direction). The refractive index corresponding to optical frequencies or very high frequencies is given by Eq. (19):

$$\varepsilon_\infty = n^2 \tag{19}$$

whereas ε_S is the static permittivity or permittivity for static fields.

The real and imaginary parts of the dielectric permittivity of Debye's model are given by Eqs. (20) and (21):

$$\varepsilon' = n^2 + \frac{\varepsilon_s - n^2}{1 + \omega^2\tau^2} \tag{20}$$

$$\varepsilon'' = \frac{\varepsilon_s - n^2}{1 + \omega^2\tau^2}\omega\tau \tag{21}$$

Changes of ε' and ε'' with frequency are shown in Fig. 1.6. The frequency is displayed on a logarithmic scale. The dielectric dispersion covers a wide range of frequencies. The dielectric loss reaches its maximum given by Eq. (22):

$$\varepsilon''_{\text{max}} = \frac{\varepsilon_s - n^2}{2} \tag{22}$$

at a frequency given by Eq. (23):

$$\omega_{\text{max}} = \frac{1}{\tau} \tag{23}$$

This macroscopic theory justifies the complex nature of the dielectric permittivity for media with dielectric loss. The real part of the dielectric permittivity expresses the orienting effect of electric field, with the component of polarization which follows the electric field, whereas the other component of the polarization undergoes chaotic motion leading to thermal dissipation of the electromagnetic energy. This description is well adapted to gases (low density of particles). For a liquid, however, we must take into account the effect of collisions with the surroundings, and the equilibrium distribution function is no longer applicable.

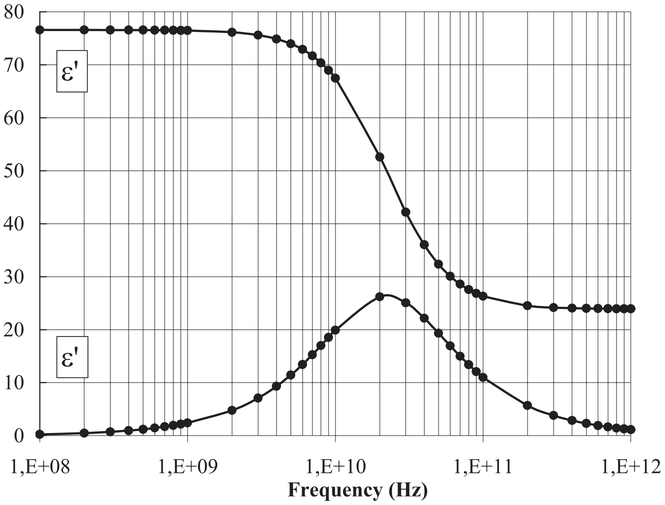

Fig. 1.6. Dependence of the complex dielectric permittivity on frequency (ε' and ε'' are, respectively, the real and imaginary parts of the dielectric loss at 25 °C; dielectric properties are: $\varepsilon_{\mathrm{Sr}} = 78.2$, $\varepsilon_\infty = 5.5$, and $\tau = 6.8 \times 10^{-12}$ s).

CONCEPTS More about the effect of collisions on distribution functions: microscopic theory of dielectric loss The Debye theory can define a distribution function which obeys a rotational diffusion equation. Debye [22, 23] has based his theory of dispersion on Einstein's theory of Brownian motion. He supposed that rotation of a molecule because of an applied field is constantly interrupted by collisions with neighbors, and the effect of these collisions can be described by a resistive couple proportional to the angular velocity of the molecule. This description is well adapted to liquids, but not to gases.

Molecular orientations can be specified by ϕ and θ. The fraction of molecules whose dipole moments lie in an element of solid angle $\mathrm{d}\Omega$ is $f(\phi, \theta)\,\mathrm{d}\theta$. The number of representative points which pass across unit length of θ in unit time is described by Eq. (24):

$$\frac{\partial q}{\partial \theta} = -K\frac{\partial f(\theta)}{\partial \theta} + f(\langle\dot{\theta}\rangle) \tag{24}$$

where the first term describes a diffusive process with a specific constant K and the second term describes the effect of the electric field which sets the molecules in rotation with an average terminal angular velocity depending of the orientating couple and on resistive constant or damping constant of inner friction given by Eq. (25):

$$\zeta(\langle\dot{\theta}\rangle) = \frac{-\partial p\vec{E}\cos\theta}{\partial \theta} \tag{25}$$

At equilibrium, molecular energies will be distributed according to Boltzman's law and, finally, the general formulation which defines the factor f is given by Eq. (26):

$$\frac{\partial f}{\partial \theta} = \frac{1}{\zeta \sin \theta} \frac{\partial}{\partial \theta}\left(kT \sin \theta \frac{\partial f}{\partial \theta} + fpE \sin^2 \theta\right) \tag{26}$$

The distribution function of the f factor is given by Eq. (27):

$$f = 1 + \frac{pE \cos \theta}{kT(1 + j\omega\tau)} \tag{27}$$

So the average moment in the direction of the field is given by Eq. (28) which can define the microscopic relaxation time that depends on the resistive force experienced by the individual molecules (for more details, see MacConnell [32]).

$$\langle p \cos \theta \rangle = \frac{\displaystyle\int_0^{\pi} \cos \theta \left(1 + \frac{pE \cos \theta}{kT(1 + j\omega\tau)}\right) 2\pi \sin \theta \, \mathrm{d}\theta}{\displaystyle\int_0^{\pi} \left(1 + \frac{pE \cos \theta}{kT(1 + j\omega\tau)}\right) 2\pi \sin \theta \, \mathrm{d}\theta} \tag{28}$$

The general equation for the complex dielectric permittivity is, then, given by Eq. (29):

$$\frac{\tilde{\varepsilon}_\mathrm{r} - 1}{\tilde{\varepsilon}_\mathrm{r} + 2} = \frac{\rho N}{3\varepsilon_0 M}\left(\alpha + \frac{\mu^2}{3kT(1 + j\omega\tau)}\right) \tag{29}$$

where N is the Avogadro number, M is the molar mass, ρ the specific mass, and α the atomic polarizability. The relaxation time τ is a microscopic relaxation time that depends on the average resistive force experienced by the individual molecules. In the limit of low frequency the Debye expression is obtained for the static permittivity whereas in the high frequency limit the permittivity will fall to a value which may be written as the square of the optical index (see Table 1.2, Section 1.1.2). The first term of the left side corresponds to distortion polarization whereas the other term corresponds to orientation polarization. For apolar molecules, we obtain the famous Clausius–Mosotti–Lorentz equation.

Relaxation times Debye [22, 23] suggested that a spherical or nearly spherical molecule could be treated as a sphere (radius r) rotating in a continuous viscous medium of bulk viscosity η. The relaxation time is given by Eq. (30):

$$\tau = \frac{8\pi\eta r^3}{2kT} \tag{30}$$

The relaxation time evaluated from experimental measurements is the effective time constant for the process observed in the medium studied, even for solutions.

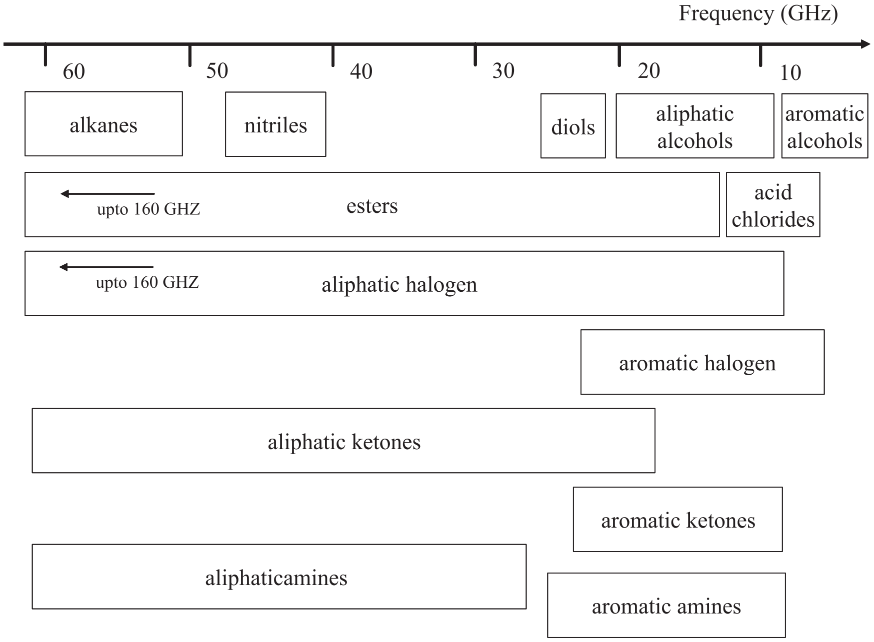

Fig. 1.7. Relaxation time range for classical organic functions.

Because of the incidence of the internal field factor, this is not the value of the molecular dipole relaxation. Depending upon the internal field assumption a variety of relationships between theoretical and effective relaxation times have been defined. Relaxation times for dipole orientation at room temperature are between 10^{-10} s for small dipoles diluted in a solvent of low viscosity and more than 10^{-4} s for large dipoles in a viscous medium such as polymers (polyethylene) or dipole relaxations in crystals (the relaxation associated with pairs of lattice vacancies).

The relaxation times of ordinary organic molecules are close to a few picoseconds. Figure 1.7 gives relaxation frequency range for classical organic functions: alkanes [33, 34], alcohols [35–39], alcohol ether [40], acid chlorides [41, 42], esters [43, 44], aliphatic [45–54] and aromatic halogens [55, 56], aliphatic [57, 58], aromatic ketones [59], nitriles [60], and aliphatic [61, 62] and aromatic amines [63].

Thus, for a frequency of 2.45 GHz these molecules can follow electric field oscillations, unlike substances which are strongly associated, for example water and alcohols, and therefore have dielectric loss at 2.45 GHz. Consequently the solvents which have dielectric loss are water, MeOH, EtOH, DMF, DMSO, and CH_2Cl_2. Dielectric loss is negligible for nonpolar solvents such as C_6H_6, CCl_4, and ethers, although addition of small amounts of alcohols can strongly increase the dielectric loss and microwave coupling of these solvents.

Effect of temperature Relaxation data for pure water play an important role in discussion of the dielectric behavior of aqueous solutions. Another practical interest is

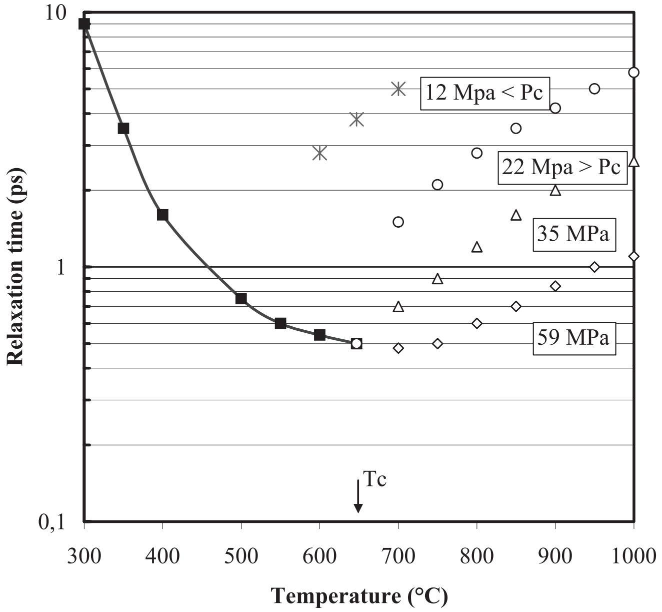

Fig. 1.8. Effect of temperature and pressure on the dielectric relaxation time of pure water. The arrow indicates the critical temperature.

the demand for dielectric reference materials suitable for calibrating and checking the performance of equipment for measurement of dipolar liquids. The design of microwave moisture measurement systems for food and other materials is another interest. The thermal and pressure dependency of the relaxation time of pure water is shown by Fig. 1.8 [64].

The critical temperature and pressure are $T_c = 647$ K and $P_c = 22.1$ MPa. In the liquid state (continuous curve) the relaxation time decreases rapidly with increasing temperature irrespective of pressure. In the gaseous state, the relaxation time is strongly pressure-dependent (positive temperature-dependence at constant pressure). The relaxation time jumps to a larger value at the boiling temperature when the pressure is lower than the critical pressure. More generally, the most relevant property at lower temperatures or higher densities is the temperature whereas density is more important at higher temperatures or lower densities. The relaxation time increases with decreasing density. The microwave field can hardly change the thermal motion of water molecules as far as they are rotating. This situation can be easily understood by considering our common experience that rapidly rotating top remains standing against gravity. The orientation of the dipolar moment may be changed when the molecule lose angular momentum, owing to collisions with other molecules. In gaseous phase, the dielectric relaxation is governed by binary collisions. Recently molecular dynamics simulations have been performed to study the dielectric properties of supercritical water. These results show that

Debye's model assumptions are not valid for supercritical water, because the dilute limit is doubted. Microscopically there are many degrees of freedom and all these motions are not totally decoupled from the others, because the eigenstate of motions are not well known the structurally disordered matter. Dielectric measurements can only probe slow dynamics which can be described by stochastic processes and classical Debye's model could be rationalized [65, 66].

The temperature and pressure dependence for methanol is quite similar to that for water. Although alcohol molecules also form hydrogen bonds, the maximum coordination is two, unlike water. The methanol molecule can form both chain and ring structures, in the same way as liquid selenium [67]. Breaking of the hydrogen-bond network occurs because of librational motion for water and stretching for methanol and most other alcohols.

At high densities, for example supercritical conditions, experimental relaxation time deviates strongly from Debye's values, owing to hydrogen bonding. In the gaseous phase free molecules are responsible for the classical dielectric relaxation and molecules incorporated within the hydrogen-bond network should be added; the general relaxation function for supercritical fluids with hydrogen bonds is given by Eq. (31):

$$\tilde{\varepsilon} = \varepsilon_\infty + (\varepsilon_S - \varepsilon_\infty)\left(\frac{1-\alpha}{1 + j\omega\tau_{\text{free}}} + \frac{\alpha}{1 + j\omega\tau_{\text{bound}}}\right) \tag{31}$$

where α is the fraction of bound molecules and τ_{free} and τ_{bound} and the relaxation times for free and bound molecules, respectively. The average relaxation time is given by Eq. (32):

$$\tau = (1-\alpha)\tau_{\text{free}} + \alpha\tau_{\text{bound}} \approx \tau_{\text{free}} + \alpha\tau_{\text{bound}} \quad \text{if } \alpha \ll 1 \tag{32}$$

τ_{free} can be assumed to be the binary collision time given by Eq. (33):

$$\tau_{\text{free}} = \frac{1}{4n\pi r_{\text{eff}}^2}\sqrt{\frac{m\pi}{k_B T}} \tag{33}$$

where m is the mass of the molecule, n the number density, and r_{eff} is the effective radius hard sphere diameter of molecule, equal to intramolecular distance from Raman scattering data. In the gaseous state α becomes small and eventually vanishes in the dilute limit whereas at low temperatures in the liquid state it is replaced by an enhancement factor, because of the highly correlated nature of molecular motion. Hydrogen-bonding enthalpy (vibration or stretching energy) can be obtained from Eq. (34):

$$\tau_{\text{bound}} = \tau \exp\left(\frac{\Delta H}{k_B T}\right) \tag{34}$$

For water, a liquid characterized by a discrete relaxation process in the temperature

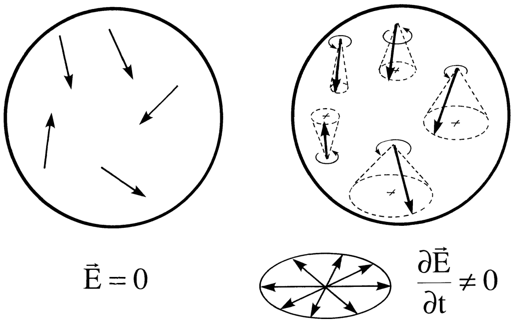

Fig. 1.9. Precession motion of the dipole of a distribution of molecules undergoing irradiation by a time dependent electric field.

range of interest, this activation enthalpy is 4.9 kcal mol^{-1}, or the hydrogen-bond energy of water.

Dynamic consequences of dielectric losses It is clear that for a substance with dielectric loss, for example water and the alcohols, the molecules do not perfectly follow the oscillations of the electric field. For media without dielectric loss, and for the same reasons as under static conditions, the strength of the electric field cannot induce rotation for all polar molecules, but statistically only for a small part (less than 1%). This means that all the molecules oscillate round an average direction (precession motion), as shown in Fig. 1.9.

The principal axis of the cone represents the component of the dipole under the influence of thermal agitation. The component of the dipole in the cone is because of the field that oscillates in its polarization plane. In this way, the dipole follows a conical orbit if Brownian movement is prevented. In reality the cone changes its direction continuously because of Brownian movement faster than the oscillation of the electric field which leads to chaotic motion. Hence the structuring effect of electric field is always negligible because of the value of the electric field strength, even more so for lossy media.

In condensed phases it is well known there are energy transfers between rotational and vibrational states. Indeed, molecular rotation does not actually occur in liquids – rotational states turn into vibrational states because of an increase in collisions. For liquids, the collision rate is close to 10^{30} collisions per second. Microwave spectroscopic studies of molecular rotation only use dilute gases to obtain pure rotational states with a sufficient lifetime. Broadening of rotational transitions induced by molecular collisions occurs because pressures are close to a few tenths of a Bar as described for Fig. 1.10.

In conclusion, for condensed phases molecular rotations have quite a short lifetime because of collisions. The oscillations eventually induced by the electric field are dissipated in liquid state leading to vibration. At densities of the collisions corresponding to those in liquids, the frequency of the collisions become comparable

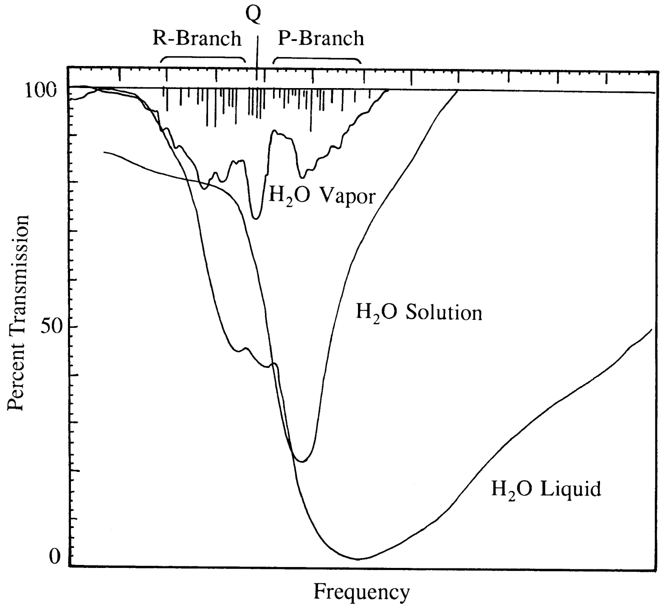

Fig. 1.10. Absorption spectrum for water (gaseous, solution, and liquid). Above the vapor band is the Mecke rotational analysis [68, 69].

with the frequency of a single rotation and, because the probability of a change in rotational state on collision is high, the time a molecule exists in a given state is small. From these remarks it is obvious that the electric field cannot induce organization in condensed phases such as the liquid state.

1.1.2.3 **Thermal Dependency of Dielectric Permittivity**

In contrast with Eq. (18), Eq. (29) gives the frequency behavior in relation to the microscopic characteristics of the studied medium (polarizability, dipolar moment, temperature, frequency of the field, etc). Then, for a given change of the relaxation time with temperature, we can obtain the change with frequency and temperature of the dielectric properties – the real and imaginary parts of the dielectric permittivity. In fact, for a given molecular system, it is better to use a formula containing $\tau_{\text{Inter}}(T)$, a part which depends on the temperature, and a part totally independent of the temperature, τ_{Steric}, as in Eq. (35):

$$\tau(T) = \tau_{\text{Steric}} + \tau_{\text{Inter}}(T) \tag{35}$$

Depending on the frequency of the field and the relaxation time band in relation to the temperature considered, one can observe three general changes of dielectric properties with temperature. Figure 1.11 gives the three-dimensional curves depicting the dependence dielectric properties on frequency and temperature [70].

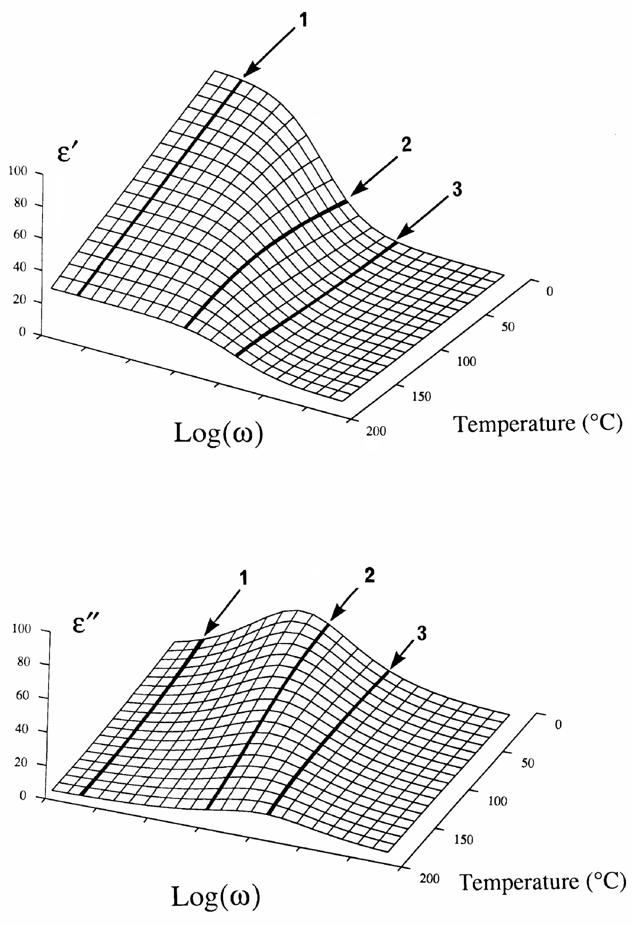

Fig. 1.11. Change of the complex dielectric permittivity with frequency and temperature (ε' is the real part and ε'' is the imaginary part of the dielectric loss) [70].

Depending on the values of the working frequency and the relaxation frequency, three general cases can be observed:

- case 1, where the real and imaginary parts of the dielectric permittivity decrease with temperature (working frequency lower than relaxation frequency);
- case 2, where the real and imaginary parts of the dielectric permittivity increase with temperature (working frequency higher than relaxation frequency); and
- case 3, where the real and/or imaginary part of the dielectric have a maximum (working frequency very close to relaxation frequency).

The two solvents most commonly used in microwave heating are ethanol and water. Values for water are given by Kaatze [71, 72] and values for ethanol by Chahine et al. [73]. Water fits most closely with case 1 because both values decrease with temperature. In contrast, for ethanol the real part increases and the dielectric loss reaches a maximum at 45 °C (case 2). For ethanol, in fact, the working frequency is higher than the relaxation frequency at room temperature. Ethanol has a single relaxation frequency close to 1 GHz at 25 °C and, furthermore, its relaxation frequency rises fairly rapidly with temperature (3 GHz at 65 °C). For water the working frequency is smaller than the relaxation frequency at all temperature (17 GHz at 20 °C and 53 GHz at 80 °C).

The pioneering work of Von Hippel [74] and his coworkers, who obtained dielectric data for organic and inorganic materials, still remains a solid basis. Study of dielectric permittivity as a function of temperature is less well developed, however, particularly for solids.

1.1.2.4 Conduction Losses

For highly conductive liquids and solids the loss term not only results from a single relaxation term as given by Eq. (21) but also from a term containing ionic conductivity, σ, as shown by Eq. (36):

$$\varepsilon'' = \frac{\varepsilon_s - n^2}{1 + \omega^2\tau^2}\omega\tau + \frac{\sigma}{\omega} \tag{36}$$

A conducting material can be regarded as a nonconducting dielectric with resistance in parallel. The alternative graphical representation as a plot of the logarithm of dielectric losses against the logarithm of the frequency enables the a.c. conductivity associated with the relaxation dipoles to be distinguished easily from the d.c. conductivity arising from the free charges. From Eq. (36) two different ranges could be defined as shown in Fig. 1.12:

$$\text{for } \omega\tau \ll 1 \quad \varepsilon'' = \frac{\sigma}{\omega} \text{ range } I \tag{37}$$

$$\text{for } \omega\tau \gg 1 \quad \varepsilon'' = \frac{\varepsilon_S - \varepsilon_\infty}{\omega t} \text{ range } II \tag{38}$$

The second term of Eq. (36) is usually small compared with the first (typical values: $\sigma = 10^{-8}$ S, $\tau = 10^{-10}$ s, $\sigma\tau = 10^{-18}$ Ss). This is quite small compared with first term, which is of the order of 10^{-11}; it can therefore be neglected.

The hydroxide ion is a typical example of an ionic species with both ionic and dipolar characteristics. For solutions containing large amount of ionic salts this conductive loss effect can become larger than the dipolar relaxation.

For solids, conduction losses are usually very slight at room temperature but can strongly change with temperature. A typical example is alumina with very slight

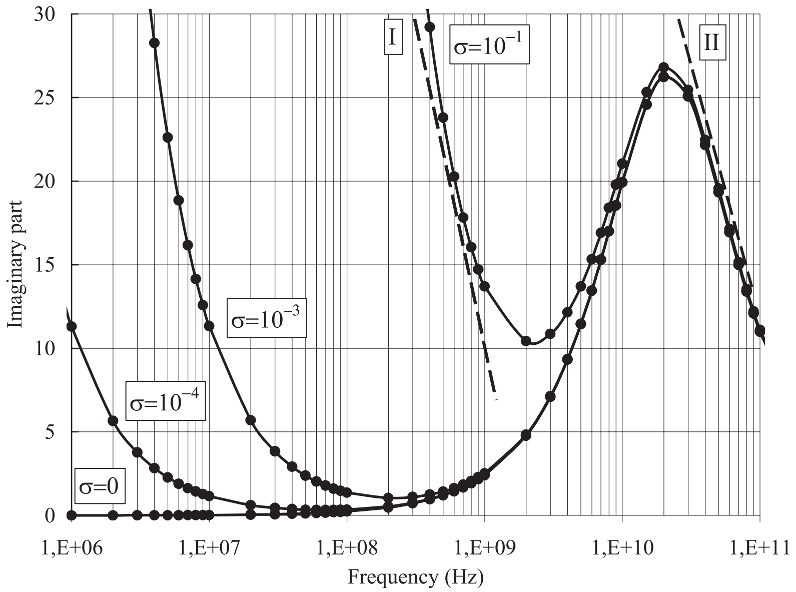

Fig. 1.12. Dependence on conductivity of change of dielectric losses.

dielectric losses at room temperature (close to 10^{-3}) and can reach fusion temperatures in several minutes in a microwave cavity [75]. This effect is a consequence of a strong increase of conduction losses associated with thermal activation of the electrons which pass from the oxygen 2p valence band to the 3s3p conduction band. In solids, moreover, conduction losses are usually enhanced by material defects which sharply reduce the energy gap between the valence and conduction bands. Because conduction losses are high for carbon black powder, the material can be used as lossy impurities or additives to induce losses within solids for which dielectric losses are too small. This trick has long been used by people using microwaves for heating applications and explains problems encountered with chocolate in microwave cookers. Chocolate contains lipid polymers with strong microwave losses. On microwave heating, chocolate degraded very quickly leading to carbon black. This increases local microwave heating. As a result microwave heating of chocolate can quickly induce a strong burning taste.

Although conductivity is usually a thermally activated process, as given by Eq. (39):

$$\sigma(T) = \sigma_0 \exp\left(-\frac{U}{k(T - T_0)}\right) \tag{39}$$

where U is the activation energy and σ_0 the conductivity at T_0, Joule heating within the sample cannot be removed quickly enough by conduction and/or convection, so the temperature of the sample increases to the fusion temperature. The temperature dependence of solid static permittivity can lead to a large increase of dielectric permittivity just below the melting point for most of crystalline or amorphous (glass) materials.

1.1.2.5 Magnetic Losses

Chemical reagents are primarily dielectric liquids or solids. Magnetic losses are, however, observed for microwave-irradiated metal oxides, for example ferrites. As for dielectrics, a complex magnetic permeability is defined as given by Eq. (40):

$$\tilde{\mu} = \mu' - j\mu'' \tag{40}$$

The real part is the magnetic permeability whereas the imaginary part is the magnetic loss. These losses are quite different from hysteresis or eddy current losses because they are induced by domain walls and electron spin resonance. These materials should be placed at the position of magnetic field maxima for optimum absorption of microwave energy. For transition metal oxides, for example those of iron, nickel, and cobalt, magnetic losses are high. These powders can thus be used as lossy impurities or additives to induce losses within solids for which dielectric losses are too small.

1.1.3
Dielectric Properties and Molecular Behavior

1.1.3.1 Dielectric Properties Within a Complex Plane

The Argand diagram Another graphical representation of substantial interest is obtained by plotting the imaginary part against the real part – the Argand diagram.

The function can be obtained by elimination of ω between Eqs (20) and (21). For simple dipole relaxation, a circle is obtained:

$$\left(\varepsilon' - \frac{\varepsilon_S - \varepsilon_\infty}{2}\right)^2 + (\varepsilon'')^2 = \left(\frac{\varepsilon_S - \varepsilon_\infty}{2}\right)^2 \tag{41}$$

The dielectric permittivity is represented by the semicircle of radius:

$$r = \frac{\varepsilon_S - \varepsilon_\infty}{2} \tag{42}$$

centered at:

$$\varepsilon' = \frac{\varepsilon_S + \varepsilon_\infty}{2} \tag{43}$$

The top of this semicircle corresponds to $\tau\omega = 1$.

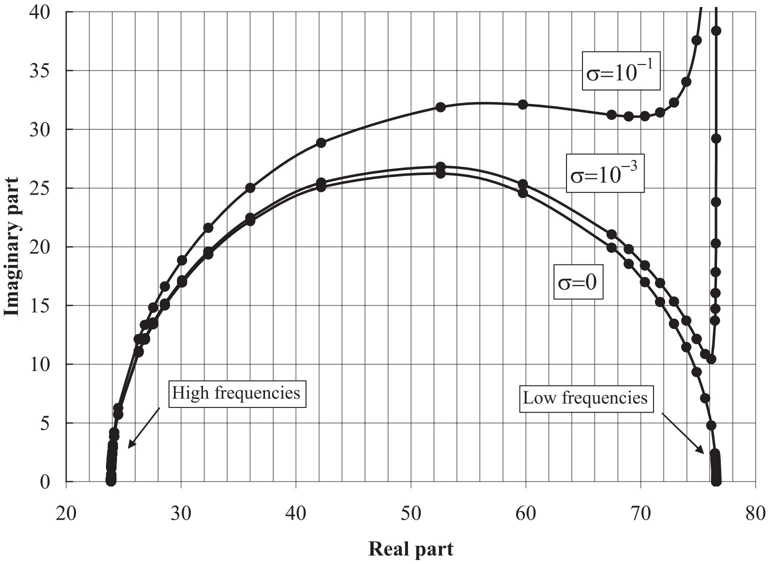

Fig. 1.13. Argand's diagram for different values of conductivity (Sm^{-1}).

This plot of experimental values is a convenient graphical test of the applicability of Debye's model. The effect of the last term on the shape of the diagram can be seen in Fig. 1.13. The larger the conductivity, the further the actual diagram departs from Debye's semicircle.

The Cole–Cole model Argand's diagram for many polar molecules in the liquid phase is actually a semicircle as predicted by Debye's model. Typical examples are pure alcohols or symmetrical molecules such as chlorobenzene in a nonpolar solvent (alkane). Many plots deviate from Argand's plot. This deviation is usually explained by assuming there is not just one relaxation time but a continuous distribution. Long molecules for which the permanent dipole moment is not aligned with the long molecular axis and polymers have broader dispersion curves and lower maximum loss than would be expected from Debye relationships. If the molecule is aligned with the field, only the longitudinal component of the dipole moment is active during the relaxation process. The molecule tends to rotate about a short molecular axis with a long relaxation time because of inertial and viscous forces. In contrast, if the molecule is perpendicular to the field the transverse component of the dipole is active and the molecule relaxes by rotating rather quickly about its long axis, because inertial and viscous forces are smaller in this configuration. If the molecules are randomly oriented relative to the field, the corresponding relaxation time is distributed between these two extreme cases. If $f(\tau)$ is the distribution function of the relaxation time between τ and $d\tau$, the corresponding Eq. (44) for dielectric loss is:

$$\varepsilon'' = \varepsilon_\infty + (\varepsilon_S - \varepsilon_\infty)\int_0^\infty \frac{f(\tau)\,d\tau}{1 + j\omega\tau} \tag{44}$$

Because this leads to circular arc centered below the axis, Cole and Cole have proposed a modified form of Debye's formula with a term h characterizing the flattening of the diagram (Eq. 45) ($h = 0$ corresponds to the classical Debye model):

$$\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{1 + (j\omega\tau)^{1-h}} \quad \text{with } 0 \le h \le 1 \tag{45}$$

The value of h found experimentally has a tendency to increase with increasing number of internal degrees of freedom in the molecules and with decreasing temperature [76]. The high relaxation is associated with group rotation and molecular tumbling. Normalized skewed arc plots give evidence of asymmetric distribution of relaxation time. The value of h increases with decreasing chain length, i.e. the distribution of relaxation time tends toward symmetric distribution with decreasing chain length. Skewed arc behavior in liquids has been reported by many workers and has been explained in terms of cooperative phenomenon and multiple relaxation processes. The molecule becomes less rigid with increasing chain length and can relax in more than one way. The different groups may rotate, as also may the whole molecule. The relaxation time for the former process is smaller than that for the latter. The intramolecular process has similar effects to the intermolecular cooperative phenomenon observed in pure polar liquids.

The Cole–Davidson model These kinds of diagram are also symmetrical or nonsymmetrical and may be fairly described by an analytical relationship proposed by Davidson and Cole [77] (Eq. 46):

$$\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{(1 + j\omega\tau)^{\alpha}} \quad \text{with } 0 \le \alpha \le 1 \tag{46}$$

When α is close to unity this again reduces to Debye's model and for α smaller than unity an asymmetric diagram is obtained. The Cole–Cole diagram arise from symmetrical distribution of relaxation times whereas the Cole–Davidson diagram is obtained from a series of relaxation mechanisms of decreasing importance extending to the high-frequency side of the main dispersion.

Glarum's generalization Glarum [78] has suggested a mechanism which leads to a dispersion curve barely distinguishable from the empirical skewed-arc of Davidson and Cole. Glarum suggests that dipole relaxation occurs by two coexistent mechanisms. Because of lattice defects in the liquid or solid, a dipole can adapt its orientation almost instantaneously to an electric field. The presence of a hole might drastically reduce the resistance to rotation. At the same time, dipole relaxation can occur without the help of defects. Glarum believes these two processes are independent and the general correlation function is the product of the correlation function of the two mechanisms, assuming that the motion of defects is governed by a diffusion equation. If the relaxation because of arrival of a defect is rare, classical Debye relaxation is obtained ($\alpha = 1$). If defect diffusion is the dominant process, a circular arc is obtained with $\alpha = 0$. If the two processes coexist, a Cole–Davidson term $\alpha = 0.5$ is obtained. Glarum's theories have been extended by Anderson and Ulman [79]. They assumed that the orientation process is function of an environmental property called the free volume. These theories raise the possibility of deducing the rate of fluctuation of environmental conditions from dielectric measurements.

Molecules with two or more polar groups Molecules comprising of skeleton with two polar groups give two adsorptions overlapping significantly on the frequency scale. If we use subscripts 1 and 2 for the lower and higher-frequency relaxation, six quantities must be evaluated. If the processes are quite independent these can be unequivocally established from the experimental data. Coexistence of two classical Debye relaxations is described by Eqs (47) and (48):

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_{\infty 1}}{1 + \omega^2 \tau_1^2} + \frac{\varepsilon_S - \varepsilon_{\infty 2}}{1 + \omega^2 \tau_2^2} \tag{47}$$

$$\varepsilon'' = \frac{\varepsilon_S - \varepsilon_{\infty 1}}{1 + \omega^2 \tau_1^2}\omega\tau_1 + \frac{\varepsilon_S - \varepsilon_{\infty 2}}{1 + \omega^2 \tau_2^2}\omega\tau_2 \tag{48}$$

Within the complex plane, two circles are obtained. The overlapping of these two circles depends on the vicinity of the relaxation time or relaxation frequency of the two polar groups. This assumption could be applied to more than two polar groups. Are there two isolated Debye's relaxations or a distribution of relaxation times for a single relaxation process? If the latter, it is better to use the Cole and Cole or Davidson and Cole models. Results from permittivity measurements are often displayed in this type of diagram. The disadvantage of these methods is that the frequency is not explicitly shown.

1.1.3.2 **Dielectric Properties of Condensed Phases**

In this section dipole moment values and complex dielectric permittivity are surveyed more particularly in terms of their frequency dependency for a variety of liquid and solid state systems. The varieties of dielectric phenomena encountered are described briefly. They are selected to illustrate relationships between dielectric data and the structure and behavior of molecular units.

In contrast with condensed phases, intermolecular interactions in gases are negligibly small. The dipole moment found in the gas phase at low pressure is usually accepted as the correct value for a particular isolated molecule. The molecular dipole moment calculated for pure liquid using Debye's model gives values which are usually very different from those obtained from gas measurements. Intermolecular interactions in liquids produce deviations from Debye's assumptions.

Short-range interactions lead to a strong correlation between the individual molecules and enhance the polarization. Hydrogen bonding aligns the molecules either in chain-like structures (e.g. water or alcohols) or in antiparallel arrangements (e.g. carboxylic acids). The atomic polarization increases and in the second example the orientation polarization decreases as a result of mutual cancellation of the individual molecular dipoles, leading to liquid permittivity smaller than values calculated for nonassociated liquids. If intermolecular interactions in gases are negligibly small, the Debye model enables adequate representation of the relationship between polarization and molecular dipole moment. The dipole found in the gas phase is usually accepted as the correct value [80]. The dipole moment of chlorobenzene is 1.75 D measured in the gas phase whereas it is 1.58 D in benzene, 1.68 D in dioxane and 1.51 D in carbon disulfide. In dilute solution the solution's molar polarization could be expressed as the weighted sum of the molar polarization of the individual components. Significant solute–solute effects are still present even at high dilutions.

Pure liquids – water and alcohols Water and peroxides (HO–OH) represent a limiting state of such interactions. In the liquids state, water molecules associate by hydrogen-bond formation. Despite its apparently complex molecular structure, because of its strong association, water closely followed simple Debye relaxation (at 25 °C: $\varepsilon_{\mathrm{Sr}} = 78.2$, $\varepsilon_{\infty\mathrm{r}} = 5.5$, $\tau = 6.8 \times 10^{-12}$ s, and $h = 0.02$, the Cole–Cole term). In such systems the molecules have usually been rigid dipoles without interaction with neighbors. The situation significantly changes when hydroxyl groups are considered. Such molecules have a dipolar group with appreciable mobility. For alcohols or phenols the hydroxyl group can rotate about the axis of the oxygen–carbon bond and can relax intramolecularly. In the liquid phase, however, hydroxyl groups of different molecules can interact forming hydrogen bonds which link molecules. The alcohols 1- and 2-propanol give almost ideal semicircles in Argand's plot. Skewed-arc is found for halogenated alkane derivatives. The skewed-arc pattern is characteristic for higher alcohols. For solutions of electrolytes in methanol and ethanol the decrease of permittivity is even more marked than that observed for water. Calculations suggest that the ionic field is probably not effective beyond the first solvation layer. Maybe for the alcohols ion solvation and its local geometrical requirements lead to proportionally greater disruption of the hydrogen-bond chains than in aqueous solutions.

Effects of electrolytes Relaxation processes are represented by several types of Argand diagram, for example the Debye diagram (I), the Cole–Cole diagram (II), the Davidson–Cole diagram (III) or a diagram with a few separated Debye regions. Original studies of aqueous salt solutions by Hasteed afforded diagrams I and II only [81, 82]. Since this pioneering work, experimental evidence suggests the occurrence of four types of diagram for ionic solutions. Unfortunately, experimental data are meager and dielectric measurements for these kinds of solution are quite limited.

Recent work has led to precise measurement of complex dielectric permittivity over a wide frequency range which covers the decimeter, centimeter, and millimeter spectral regions (7–120 GHz [83–91]). Knowledge of these data is even more crucial when moving to study of concentrated solutions and solutions at elevated temperature. In these, ion–water, water–water, and ion–ion interactions are more diverse and the corresponding relaxation processes become more complicated. The contribution to ionic losses of electric conductivity also increases, specially in the centimeter wavelength range. Increasing the temperature and concentration of the electrolytes induce an increase in relaxation frequency or a decrease in relaxation time, adding noticeable error to the determination. Experimental evidence from measurements in a wide frequency range makes it possible to describe the whole dispersion region. At high frequencies the contribution from electrical conductivity is smaller.

Figure 1.14 shows the change with frequency of the real and imaginary parts of dielectric permittivity for aqueous solutions of NaCl of high concentration. The d.c. conductivity has been avoided by the authors, who made measurements at 1 kHz using conventional methods. Addition of electrolytes usually increases conductivity, as shown in Fig. 1.15 (arrows indicate values of dielectric losses at 2.45 GHz). No resonance or relaxation processes other than the Debye rotational diffusion of water molecule occur in the high-frequency part of the millimeter wavelength range. This gives evidence that ionic losses are described by Eq. (36). The structural model of an electrolyte solution that reflects different water molecule dynamics at

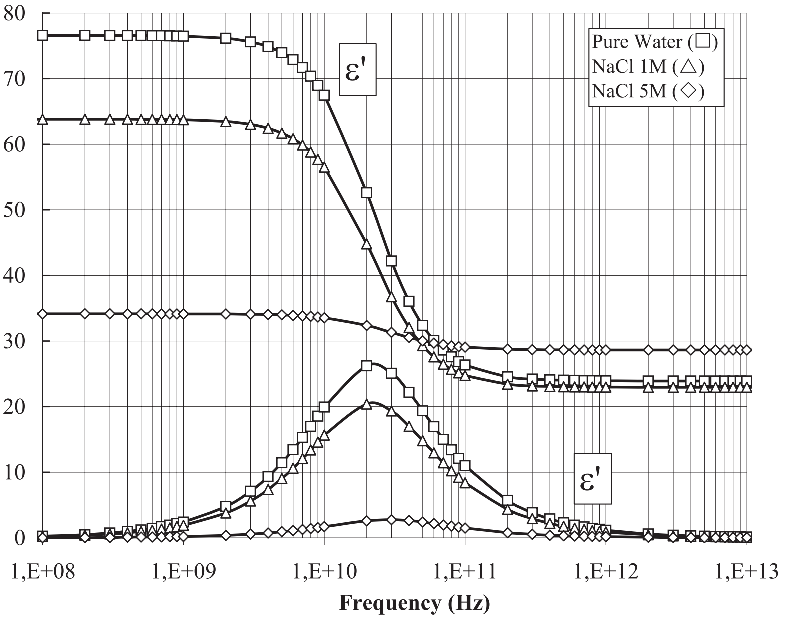

Fig. 1.14. Change of the real and imaginary parts of the dielectric permittivity.

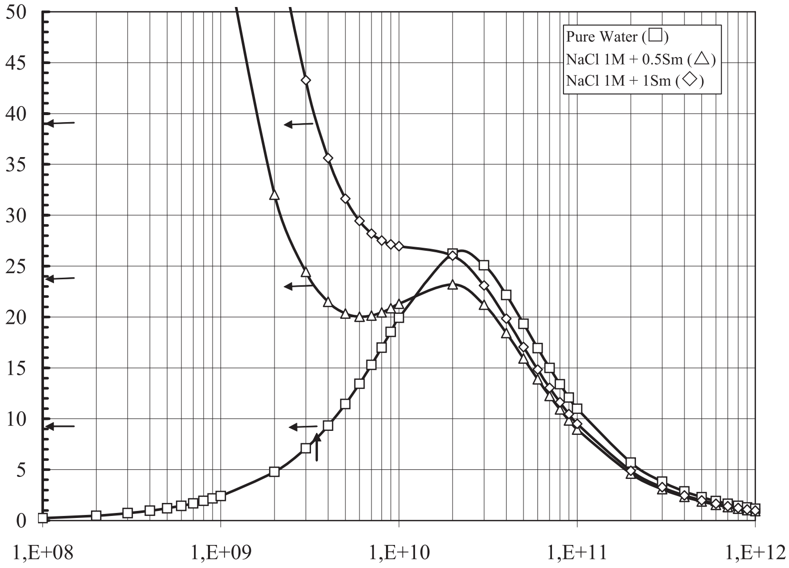

Fig. 1.15. Effect of ionic conductivity on dielectric losses.

different concentrations can be represented by the following description. In the dilute regions, water molecules can be divided into those whose state is modified by the presence of ions (hydration shell of cations and anions) and those that retain all the properties of pure water (bulk water). In highly concentrated solutions, in which bulk water is absent, the model implies the occurrence of two states of water molecules – water molecules bound by one ion, a fragment of the hydration shell, and molecules shared by cations to form ion–water clusters [92–102]. These different structural subsystems should be found within the dispersion region. LiCl and $MgCl_2$ solutions lead to two simple Debye dispersions (free and hydration-shell molecules).

First, depending on concentration ions may associate producing ion-pairs or similar solute species with an appreciable dipole moment. Such species will make their own contribution to dielectric relaxation processes. Because of their strong localized electric field, ions affect the solvent's molecular interactions. Addition of sodium chloride to water leads to a strong decrease of the real part of the dielectric permittivity equivalent to a temperature increase (e.g. 0.5 M sodium chloride at 0 °C has the same value as pure water at 30 °C). The value of relaxation time is shifted in the same sense but to a far smaller extent. The sodium chloride ions markedly change the geometric pattern of molecular interactions. According to X-ray and neutron diffraction studies, the electrostatic field neighborhood of a sodium or chloride ion is such that the interaction energy with the water molecule dipole greatly exceeds that of typical hydrogen bond between the solvent species. This means that an appreciable number of water molecules will be frozen around each ion – a change in molecular pattern from the liquid. The freezing of these water molecules forming a hydrating sheath around the ions means their dipoles are not free to re-orientate in the applied electric field. This causes the permittivity decrease. This effect has been quantitatively defined by Hasted et al. [81, 82] – for 3 M sodium chloride solution the value is one-half that for the pure solvent (e.g. nine water molecules immobilized per pair of sodium chloride ions). Neutral solute molecules such as ethyl alcohol noticeably increase the dielectric relaxation time of water [103–105]. This is frequently expressed by saying that the water tends to freeze to an ice-like configuration in the immediate neighborhood of the solute molecule. Many physicochemical data (entropies, partial vapor pressures, viscosities) agree in this respect. The situation is not simple, however, because ionized salts, for example alkyl ammonium lead to breaking down of the structure but nevertheless cause an increase in relaxation time. It is possibly contrary effects are occurring: these salts are known to form crystalline hydrate structures of the clathrate type.

Foodstuffs contain much water. Many people believe the water content is responsible for the microwave heating of food. According to Fig. 1.15, dielectric relaxation of water and corresponding dielectric losses are quite negligible for ionic solutions. Conduction losses are preponderant. Ionic species such salts (sodium chloride) induce dielectric losses in soup and microwave heating results from ionic conduction.

Intermolecular interactions and complexes Dielectric measurements on interacting solutes in inert solvents provide information about molecule complex formation. Some such dipoles induced by intermolecular interactions and molecular complexes in benzene solution are listed in Table 1.3. The dipole moment of the complex is a function of the relative strengths of the acid and base and the intramolecular equilibrium is described by Eq. (49):

$$\text{X-H} \ldots \text{Y} \Leftrightarrow \text{X}^{-} \ldots \text{H-Y}^{+} \tag{49}$$

Stronger acid–base complexes with proton transfer induce formation of ion-pair systems leading to high dipole moments. The OH–N interactions of pyridine in

Tab. 1.3. Dipole moments of molecular complexes in benzene solution (from Ref. [27]).

Components		μ(X–H)	μ(Y)	μ(H–Y)
CH_3COOH	C_5H_5N	1.75	2.22	2.93
$ClCH_2COOH$	C_5H_5N	2.31	2.22	4.67
$Cl_2CHCOOH$	C_5H_5N		2.22	5.24
Cl_3CCOOH	C_5H_5N		2.22	7.78
CH_3COOH	$(C_2H_5)_3N$	1.75	0.66	3.96
$s\text{-}C_6H_2(NO_3)_3OH$	$(n\text{-Bu})_3N$	1.75	0.78	11.4

acetic and chloroacetic acids lead to a polarity increase. Thus at least 70% ionic character is expected in the trichloroacetic acid–pyridine complex. The very high dipole moment of the picric acid–base complex is indicative the predominantly ionic form.

Solutions of two nonpolar compounds often have polar properties. For iodine solutions in benzene polarization is greater than expected for nonpolar compounds. Interactions usually involve partial electron transfer from one component to another. One component has a positive charge (donor) and the other has negative charge (acceptor). In the benzene–iodine complex partial electron transfer can be envisaged between electrons of benzene π orbitals and the lowest unfilled orbital of iodine. The extent of electron transfer determines the dipole moment observed. Such systems, called charge-transfer complexes, lead to changes of other physical properties, for example magnetic properties.

The relaxation times of trihalogenated esters in solution in benzene, dioxane, and carbon tetrachloride reveal another typical type of anomalous behavior which can be explained by solute–solvent interactions. It is well known that the ester molecule is a resonance hybrid in which the carbonyl group assumes positive character. This character is further accentuated by the three electron attracting halogen group. This positive carbonyl carbon interacts strongly with the oxygen lone-pair electrons in dioxane and the π electrons of the benzene ring forming complexes with these solvents and resulting in large value of relaxation time [54].

Intermolecular interactions and hydrogen bonding Hydrogen bonding is a form of molecular orientation involving an A–H group and an electron-donor component Y. A is usually oxygen sometimes nitrogen, and less frequently carbon. Hydrogen-bond formation alters the electron distribution within the molecules, changes the polarization, and could induce a dipole moment. The polarization of N-substituted amides in solution increases with increasing concentration. Association into polar chains occurs with a dipole moment greater than that of the monomer unit. Intermolecular hydrogen bonding occurs if the NH group is at a position trans to the CO group. The two group dipole moments reinforce each other, producing an enhanced dipole. Solute–solvent interactions caused by hydrogen bonding can also increase the dipole moment. The increase is much larger than expected from the inductive effect alone – HBr has dipole moment equal of 1.08 in benzene solution compared with 2.85 in dioxane solution.

Macromolecules and polymers Because of their partial use in the electrical industry and because of the partial relevance of dielectric studies to questions of molecular mobility and relaxation time, extensive studies of polymer behavior have been performed by dielectric methods. Only the salient features can be outlined here.

Nonpolar polymers such as polyethylene, polytetrafluoroethylene, and polystyrene are especially significant because of their low loss values over the widest frequency range. For polar polymers such as poly(vinyl chloride)s, poly(vinyl acetate)s and polyacrylates dispersion is observed at lower frequencies than for the monomers, as expected. Two or more dispersion regions are commonly observed. They are referred to as α, β, and γ bands beginning with the lowest-frequency dispersion. The α dispersion is broader than a Debye process. Dielectric losses have a lower maximum and persist over a wide range of frequency. Fusoos and Kirwood [106] have successfully described this behavior. It is widely believed that α dispersion caused by Brownian motion of the polymer chain whereas the β dispersion is because of oscillatory motion or intramolecular rotation of side groups.

Small molecules adopt reasonably well defined geometric configurations and calculation of dipole moment is possible. For polymers mobile configurations with rotations about single bonds in the chain skeleton and may occur for many side groups. The measured dipole moment is the statistical average of the mobile configurations and is proportional to the square root of the number of polar groups present in the polymer. The dipole moment, μ, of a polymer is usually expressed as given by Eq. (50):

$$\langle \mu^2 \rangle = ng\mu_0^2 \tag{50}$$

where n is the number of polar groups in the chain, μ_0 the group dipole moment of the polar unit, and g a factor depending on nature and degree of flexibility of the chain. Theoretical calculations of g have been extensively studied by Birshtein and Ptitsyn [107] for polymers with a polar group in rigid side chains and Marchal and Benoit [108] for polymers with polar groups within the chain backbone. In both polymers g is a function of the energy barrier restricting rotation within the chain backbone.

The very large dipole moment of polymers results in strong intermolecular forces in solution. Atactic and isotatic polymers have different dipole moments. The dipole moment of the atactic poly(vinyl isobutyl ether) is 10% lower than that of the isotactic form, showing that the isotactic polymer adopts a more ordered structure with group dipoles tending to align parallel to each other.

Rigid polymers have dipole moments which are proportional to the degree of polymerization. The alpha-helical form of polypeptides (e.g. gamma-benzyl glutamate) leads to a very high dipole moment, because the group dipole moments are aligned parallel. In the alpha-helix the carbonyl and amino groups are nearly parallel to the axis of the helix, which is stabilized by hydrogen bonding between these two groups. The calculated moment for this arrangement is 3.6 D for the peptide unit (2.3 D and 1.3 D, respectively, for carbonyl and amino groups) in agreement with the experimental value.

Solids and dipole relaxation of defects in crystals lattices Molecules which become locked in a solid or rigid lattice cannot contribute to orientational polarization. For polar liquids such as water, an abrupt fall in dielectric permittivity and dielectric loss occur on freezing. Ice is quite transparent at 2.45 GHz. At 273 °K, although the permittivity is very similar (water, 87.9; ice, 91.5) the relaxation times differ by a factor of 10^6 (water, 18.7×10^{-12} s; ice, 18.7×10^{-6} s). Molecular behavior in ordinary ice and a feature which may be relevant to a wide variety of solids has been further illuminated by the systematic study of the dielectric properties of the numerous phases (ice I to VIII) formed under increasing pressure. Davidson was the first to publish an exhaustive study [109]. A molecule may have equilibrium positions in a solid which correspond to potential energy minima separated by potential barrier, because of interactions with neighbors. Such molecules change their orientation either by means of small elastic displacements or by acquiring sufficient energy to jump the potential barrier. When an electric field is applied to a crystalline dipolar solid, polarization could occur by three mechanisms. The first is the distortion polarization, the second is the elastic displacement of dipoles from their equilibrium positions, and the third is a change in the relative orientations of the dipoles.

Typical lattice defects include cation vacancies; substitutional or interstitial ions are other types of more complicated structural defects. A cation vacancy behaves like a negative charge. If the temperature is high, ions are sufficiently mobile that an anion could be expelled from the lattice by the Coulomb potential of the cation vacancy. Cation and anion vacancies could form a dipole oriented along one of the six crystallographic axes. This vacancy coupling is then able to induce a crystalline dipole. Similar dipoles can also appear when an ion is substituted for the host ion. A divalent atom such as calcium substituted for a monovalent cation in alkali halides releases two electrons and becomes a doubly charged ion. The new atom of calcium has excess positive charge which can couple with a negative defect, for example an alkali metal vacancy or an interstitial halide, to create a dipole.

In the following discussion an LiF lattice with a lattice parameter containing N substitutional Mg ions per unit volume is considered. According to Langevin's model and Maxwell–Boltzmann statistics polarization arising from the dipole defects is given by Eq. (51):

$$P_{\mathrm{dd}} = \frac{Na^2e^2}{6kT(1 + j\omega\tau)}E \tag{51}$$

An Li ion has been replaced by an Mg ion. This ion with its positive charge forms a dipole with a negative lithium vacancy sitting on one of the twelve nearest-neighbor sites normally filled with Li ions. In the absence of an electric field, these twelve positions are strictly equivalent and the lithium vacancy hops between them giving a zero average dipole moment for the defect. In the presence of an electric field the twelve sites are no longer equivalent. The twelve sites usually split into three categories in relation to the interaction energy with electric field. Hence, the value of the dipole moment is given by Eq. (52):

$$\mu = \frac{ae}{\sqrt{2}} \tag{52}$$

Finally, the complex permittivity of the substituted lattice takes the familiar form given by Eq. (53):

$$\varepsilon'' = \varepsilon_\infty + \frac{N\mu^2}{3kT(1 + j\omega\tau)} \tag{53}$$

Equation (53) describes Debye relaxation. Magnesium and calcium-doped lithium fluorides have a characteristic Debye relaxation diagram from which the dopant concentration and the relaxation time can be deduced. Many others crystals containing mobile lattice defects have similar Debye's relaxation processes. Major understanding of the structure of color centers results from dielectric relaxation spectra. Nuclear magnetic resonance, optical and Raman spectroscopy can be used efficiently in conjunction with dielectric spectroscopy.

Solids and adsorbed phases Solid surfaces almost invariably have absorbed molecules derived from the gas or liquid medium to which the surface is exposed. The amount of such absorbed material depends upon the chemical nature of the solid surface. The absorbed layer can greatly affect the properties of the solid surface. The absorbed molecules may reorient by libratory oscillation between defined orientational positions (see *Orienting effect of a static electric field* in Section 1.1.2.1). Such a restricted process could account for the reduced effective permittivity. The extensive use of silicates (clays and soils) as catalysts in chemistry adds interest to their study.

CONCEPTS More about relaxation process within solids Typical loss peaks are broader and asymmetric in solids, and frequency is often too low compared with Debye peaks. A model using hypotheses based on nearest-neighbor interactions predicts a loss peak with broader width, asymmetric shape, and lower frequency [27]. This behavior is well suited to polymeric, glassy materials and ferroelectrics. Low temperature loss peaks typically observed for polymers need many-body interactions to be obtained. Although current understanding of these processes is not yet sufficient to enable quantitative forecasting the dielectric properties of solids may offer insight into the mechanisms of many-body interactions.

Interfacial relaxation and the Maxwell–Wagner effect Dielectric absorption quantifies energy dissipation and for most systems lose energy from processes other than dielectric relaxation. These processes usually are related to the d.c. conductivity of the medium. The corresponding loss factor for higher conductivity persists at high frequencies and even in the microwave heating range. The incidence of d.c. conductivity appears for fused ionic salts as a distorting feature. In addition to d.c. conductance loss, energy dissipation can occur by scattering of the radiation at interfacial boundaries in inhomogeneous materials. In the visible region, distribution of small particles of a second material (e.g. air bubbles) in an otherwise transparent medium can render it opaque. The same feature arises in dielectric media when particles are dispersed within a matrix. The general aspect of this absorption is referred as the Maxwell–Wagner process.

If the dielectric material is not homogeneous but could be regarded as an association of several phases with different dielectric characteristic, new relaxation processes could be observed. This relaxation processes called Maxwell–Wagner processes occur within heterogeneous dielectric materials. An arrangement comprising a perfect dielectric without loss (organic solvent) and a lossy dielectric (aqueous solution) will behave exactly like a polar dielectric with a relaxation time which becomes greater as the conductivity becomes smaller. Such an arrangement, leading to a macroscopic interface between two immiscible solvents, could be extended to dispersion of slightly conducting spherical particles (radius a, permittivity and conductivity) in a non conducting medium (dielectric permittivity equal to ε_M). To calculate the effective permittivity of the dispersion, consider a sphere of radius R containing n uniformly distributed particles. These particles coalesce to form a concentric sphere of radius $\sqrt[3]{na^3}$. The effective dielectric permittivity of this heterogeneous medium is given by Eq. (54):

$$\tilde{\varepsilon} = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{1 + j\omega\tau} \tag{54}$$

where the static dielectric permittivity ε_S is given by Eq. (55):

$$\varepsilon_S = \varepsilon_M \left(1 + \frac{3na^3}{R^3}\right) \tag{55}$$

The system relaxes with a relaxation time given by Eq. (56):

$$\tau = \frac{\varepsilon_P + 2\varepsilon_M}{\sigma} \tag{56}$$

These interfacial polarization effects can explain strong enhancement of microwave heating rate observed by some workers with phase-transfer processes which associate organic solvents with high lossy aqueous solutions or with a dispersion of solids within liquids which are essentially nonpolar. The Maxwell–Wagner loss will not occur in homogeneous liquid systems. For supercooled liquids in particular, for example glasses or amorphous solids, the three loss processes d.c. conductivity, Maxwell–Wagner effect, and dipolar absorption occur simultaneously. Consequently, even if dielectric loss for these media is low at room temperature, slight heating will lead to a increase of dielectric loss resulting in fusion. For example, an empty drinking glass placed within a domestic microwave oven can melt easily, depending on oven power. Obviously, if a wave-guide or cavity is used, fusion can result for an empty test tube, for a test tube partially filled with lossy products, for or a test tube filled with products without dielectric loss. For products with slight dielectric loss it is better to avoid glass and use a test tube made from quartz or silica without dielectric loss at 2.45 GHz.

Colloids Colloidal solutions are the most difficult systems to measure and analyze dielectrically. If the solute particles have dipole moments, the solution should show anomalous dispersion and loss at low frequencies if orientation of the dipole involves orientation of the whole particle. If there are substantial differences among the dielectric constants or conductivity of the particles and the matrix, interfacial polarization can cause dielectric loss and frequency belongs to the low frequency range. In aqueous colloidal solutions the presence of electrolytes even in small amounts in the water should commonly cause sufficient conductivity difference to result in interfacial polarization. Another effect is that of the electric double layer at the particle surface, even in the absence of the electric field. The effect of these factors must be taken into account. Errera [110] reported the first results of large apparent permittivity for vanadium pentoxide, and Schwan [111] was the first to provide experimental evidence of the large increase of static permittivity for a suspension of polystyrene spheres in water. Values of 10 000 for diameters close to a micron have been reached for static permittivity. The dynamics of charge distribution within these systems lead to interesting dielectric properties with occur over a timescale determined by different characteristics of the system. The properties of colloids have been studied at radiofrequency but very little attention has been devoted to their properties at microwave frequencies. This is probably because the charge dynamics for particles several micrometers in diameter are too slow to result in significant losses at microwave frequencies.

Charged colloids typically consist of charged particles suspended in an electrolyte. Surface charges attract counterions leading to a double layer charge. When a microwave field is applied to a charged particle, the tangential component of the electric field around the particle surface causes azimuthal transport of the double layer ions across the particle. This results in asymmetric charge distribution within the double layer around the particle. This charge redistribution induces a change in the dipole strength, leading to a resultant electric field around the particle which opposes the applied field [112–114]. O'Brien [114] showed that flow of counterions result in a high frequency, low-amplitude relaxation with a relaxation time τ_1 given by Eq. (57):

$$\tau_1 \approx \frac{1}{\kappa^2 D} \tag{57}$$

where κ is the reciprocal of the double layer thickness and D the ion diffusivity [112]. After this charge redistribution of the double layer, a slower relaxation process occurs within the electrolyte. The low-frequency relaxation time τ_2 is given by Eq. (58):

$$\tau_2 = \frac{R^2}{D} \tag{58}$$

where R is the radius of the particle. The size dependence of this dissipative process is of particular interest for microwave heating. Hussain et al. [115] have recently shown that polystyrene particles with surface charge resulting from sulfate groups suspended in pure distilled water (diameter between 20 and 200 nm) had relaxation beyond 10 GHz associated with the dipolar relaxation of water. The dielectric permittivity and dielectric loss induced by colloids over this region are slightly lower than those produced by water. Dielectric losses are in agreement with additional dc. static conductivity of the colloid given by Eq. (36). More recently, Bonincontro and Cametti [116] and Buchner et al. [117] have described how dielectric measurements can be used to obtain information about electric polarization mechanisms occurring on different time scales for ionic and nonionic micellar solutions, liposomes, and suspensions of biological cells. Jönsson et al. have [118] discussed the effect of interparticle dipolar interaction on magnetic relaxation for magnetic nanoparticles. It seems that superparamagnetic behavior could be replaced by spin-glass-like dynamics for those systems.

Space charge polarization and relaxation Accumulation of charges in the vicinity of electrodes unable to discharge the ions arriving on them can induce relaxing space-charge. The ion behavior balances the effect of the field to accumulate charge on interfaces whereas thermal diffusion tends to avoid them (i.e. interfaces between two liquids with dielectric and conductivity differences). The layer can contain charge density and is therefore equivalent to a large dipole. Dipole reversal is a sluggish relaxation process. Unlike the classical Debye's model, it is impossible to separate dielectric permittivity into real and imaginary parts. Argand's diagram can be calculated and are found to be exactly semicircular and slightly flattened.

1.2
Key Ingredients for Mastery of Chemical Microwave Processes

After a brief overview of the thermal conversion data (thermal dependence of dielectric properties, electric field focusing effects, hydrodynamics) thermodynamic aspects and athermal effects of electric fields will be examined. Next, the effects of thermal path and hot spots induced by microwave heating will be analyzed in term of kinetic effects.

1.2.1
Systemic Approach

The tasks of chemical engineers are the design and operation of chemical reactors for converting specific feed material or reactants into marketable products. They must have knowledge of the rates of chemical reactions involved, the nature of the physical processes interacting with the chemical reactions, and conditions which affect the process. The rates of the physical processes (mass and heat transfer) involved in commonly used chemical reactors can often be estimated adequately from the properties of the reactants, the flow characteristics, and the configuration of the reaction vessel. Chemical process rate data for most industrially important reactions cannot, however, be estimated reliably from theory and must be determined experimentally.

In contrast, design of chemical microwave processes, especially scale-up of operating conditions, involves knowledge and control of several nonlinear feedback

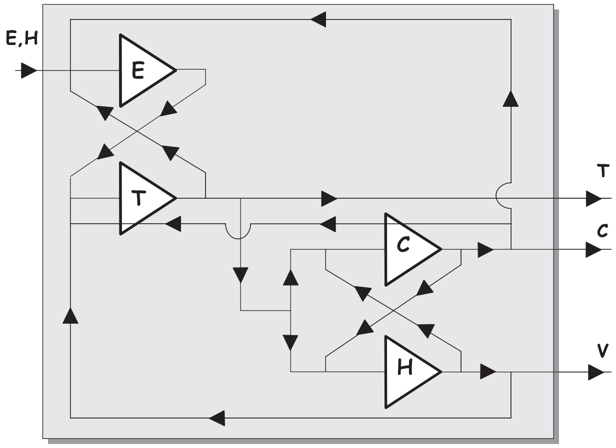

Fig. 1.16. Schematic diagram of the chemical microwave process [119].

loops. Figure 1.16 depicts chemical microwave processes in accordance with concepts of systemic theory, or the theory of systems, in cybernetic modeling. This theory studies systems in relation to feedback and coupling loops.

The microwave process includes the microwave oven, the reactors and the reactants. The inputs of the system are microwave energy (E, H) and reactants whereas the outputs are heat (T), products (C), and convection motions of fluid solutions (V). A processor is associated with each process. They are represented schematically by triangles in Fig. 1.16. In systemic theory, the meaning of a processor is a function linking input and output. These processors can be expressed by partial differential equations. The two first processors to be considered are electromagnetic (E) and the thermal (T) processors, leading to heating. The heating processor can supply the chemical (C) and hydrodynamic (H) processors. The chemistry can modify hydrodynamic conditions (viscosity, superficial tension, etc) whereas convective motion affects yield of reactions. Convective motion and chemical reactions can also modify thermal and dielectric properties. Hence, four coupling loops can be defined. Most of these coupling loops have highly nonlinear character. Since 1990, the author has studied all these couplings and separately now the general problem of a chemical microwave process can be solved with optimized devices and plants.

The importance of these phenomena cannot be overemphasized, because they have significant effects on the yields and the quality of the products. The characteristics and limitations of these systems which affect the reactor performance should be well understood to ensure successful design and operation of the plant. Consequently, a microwave plant could be optimized for several given compositions (i.e. dielectric properties and thermal dependency). An optimized microwave plant cannot be a versatile device in terms of dielectric properties or, in other words, chemical composition.

1.2.2
The Thermal Dependence of Dielectric Loss

According to Poynting's formulation, the time averaged dissipated power density $P_{\mathrm{Diss}}(r)$ at any position r within lossy liquids or solids is given by Eq. (59):

$$P_{\mathrm{Diss}}(r) = \frac{\omega}{2}\left(\varepsilon_0\varepsilon''\vec{E}(r)^2 + \mu_0\mu''\vec{H}(r)^2 + \frac{\sigma}{\omega}\vec{E}(r)^2\right) \tag{59}$$

where ω is the angular frequency, ε_0 the dielectric permittivity of a vacuum, $\varepsilon''(r)$ the dielectric loss, $\vec{E}(r)$ the electric field amplitude, μ_0 the magnetic permeability of a vacuum, μ'' the magnetic losses, $\vec{H}(r)$ the magnetic field amplitude, and σ the ionic conductivity.

According to dielectric and/or magnetic losses and electric and magnetic field strength, the dissipation of electromagnetic energy leads to heating of the irradiated medium. Hence estimation of dissipated power density within the heated object depends directly on the electric and magnetic fields, and dielectric and magnetic loss distributions. Maxwell's equations can be used to describe the electromagnetic fields in the lossy medium and an energy balance can be solved to provide the temperature profiles within the heated reactor.

The specificity of microwave heating results from the thermal dependence of dielectric properties. The complex dielectric permittivity is very dependent on temperature and the dynamic behavior of microwave heating is governed by this thermal change. The electric field amplitude depends on the real and imaginary parts of the dielectric permittivity, which themselves depend on temperature as described by Eq. (60):

$$P_{\mathrm{Diss}}(r, T) = \frac{\omega\varepsilon_0\varepsilon_r''(T)}{2}\vec{E}(r, \varepsilon_r'''(T), \varepsilon_r''(T))^2 \tag{60}$$

Figure 1.17 shows the thermal feedback induced by the thermal dependence of dielectric properties. The microwave applied energy results in dissipated microwave energy depending on dielectric properties. The heating rate depends on thermal properties (thermal diffusivity, specific heat). The thermal dependence of the thermal properties is, however, very slight compared with the thermal dependence of the dielectric properties. In contrast with conventional heating techniques, the heated medium acts as an energy converter. Consequently, thermal change of dielectric properties causes changes in the dissipated energy during heating. Depending on the nature on the thermal changes, this may result in thermal runaway or, occasionally, reduced material heating. Thermal runaway is a catastrophic phenomenon in which a slight change of microwave power causes the temperature to increase rapidly. The electric field depends on spatial location in relation to the wavelength within the heated material and thus inhomogeneous heating results in the deleterious effect of inhomogeneous material properties (e.g. densification

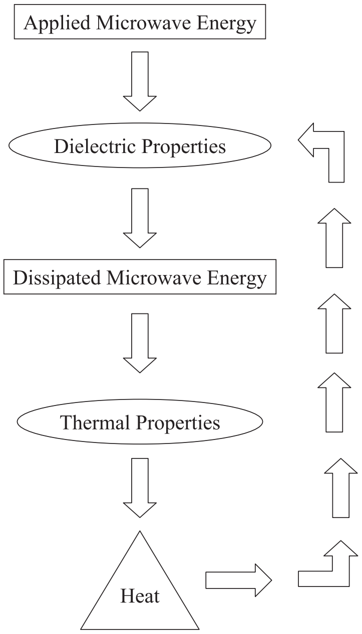

Fig. 1.17. Schematic diagram of dielectric thermal feedback [119].

and sintering in ceramics, or polymer curing and reticulation). A precise knowledge of the dielectric properties is therefore essential for any study of microwave heating or design of a microwave applicator. The thermal behavior of the heated material is, however, usually dependent not only on the dependence of dielectric losses but on the strength of the electric field applied. Both of these factors have to be known to optimize the operating conditions and microwave thermal processes. Consequently, basic understanding of microwave heating processes remains somewhat empirical and speculative, because of its highly nonlinear character.

1.2.3
The Electric Field Effects

The electric field is a crucial condition in microwave heating and the design of microwave ovens. If electric field distributions within empty microwave ovens are well known, the problem is totally different if loaded microwave ovens are considered. Perturbation theory can be used if the sample is very small. In fact, the magnitude of the perturbation is proportional to reactor-to-applicator volume ratio. The perturbation could be negligible if this ratio is close to 10^{-4} and most laboratory and industrial devices have higher ratios [120].

1.2.3.1 Penetration and Skin Depths

The wave equation of electromagnetic fields in the z direction is given by Maxwell's equations. The electric field takes the form given by Eq. (61):

$$E = E_0 \exp(j\omega t - \gamma z) \tag{61}$$

where γ is the propagation constant. Dielectric media without loss lead to a pure imaginary propagation constant given by Eq. (62):

$$\gamma = j\omega(\varepsilon_0 \varepsilon_r \mu_0 \mu_r)^{1/2} \tag{62}$$

The problem is totally different for dielectric loss. The wave is attenuated as it traverses the medium and, therefore, the power dissipated is reduced to an even larger extent. Consequently, the propagation constant becomes complex as described by Eq. (63):

$$\gamma = \alpha + j\beta \tag{63}$$

The real and imaginary parts of the complex propagation constant are called attenuation factor (Np m^{-1}) and the phase factor (Rad m^{-1}), respectively. They are given by Eqs (64) and (65):

$$\alpha = \sqrt{\frac{\omega^2 \varepsilon_0 \mu_0 \varepsilon_r'}{2}} \sqrt{\sqrt{1 + \left(\frac{\varepsilon_r''}{\varepsilon_r'}\right)^2} - 1} \tag{64}$$

$$\beta = \sqrt{\frac{\omega^2 \varepsilon_0 \mu_0 \varepsilon_r'}{2}} \sqrt{\sqrt{1 + \left(\frac{\varepsilon_r''}{\varepsilon_r'}\right)^2} + 1} \tag{65}$$

The simplified version of the attenuation factor α for highly lossy media, for example metallic or ionic conductors, is given by Eq. (66):

$$\alpha \approx \sqrt{\frac{\omega^2 \varepsilon_0 \mu_0 \varepsilon_r''}{2}} \tag{66}$$

Hence, the attenuation factor α could be defined by a distance δ which is the skin depth as described by Eq. (67):

$$\delta = \frac{1}{\alpha} \tag{67}$$

The attenuation factor leads to attenuation of electric field and power during propagation along the z coordinate as described by Eqs. (68) and (69):

$$E = E_0 \exp(-\alpha z) \exp j(wt - \beta z) \tag{68}$$

$$P = P_0 \exp(-2\alpha z) \tag{69}$$

The penetration depth P_d is defined as the distance from the surface of a lossy dielectric material at which the incident power drops to 37% (1/e). Skin depth is, in fact, equal to twice the penetration depth.

The field or power penetration increases with decreasing frequency. Penetration depths at frequencies below 100 MHz are close to meters. Penetration depths within pure water at 2.45 GHz are close to centimeters (7 mm at 3 °C and 2 cm at 40 °C). Consequently, the penetration depth within a microwave reactor filled with lossy media is obviously smaller. Microwave heating could results in unacceptable hot spots and vigorous stirring is often necessary.

Field penetration within metals is substantially smaller. Skin depth within the metallic enclosure of a microwave oven is close to several microns, depending on the nature of the metal. Although losses are larger for stainless steel than for most metals it is widely used as the internal wall of industrial microwave ovens because of its surface hardness and resistance to corrosion. Stainless steel should not be used in high-level devices, however. Skin depth within metals explains why sparks observe during microwave heating of plates with plating. The thickness of the plating is close to the skin depth and microwave heating induces plating vaporization leading to a plasma with colored sparks. This is a test enabling verification of whether the plating is made with aluminum, copper, gold, or silver!

1.2.3.2 **Dimensional Resonances**

According to the conclusions of the previous paragraph, microwave heating of high lossy media could be difficult in terms of thermal uniformity. Obviously, strong stirring could settle this problem. The aspect of energy profiles within lossy media is more complicated. Resonant devices and, especially, dimensional resonance according to the author's terminology can induce electric field-focusing effects. The Fig. 1.18 shows the dependence of temperature on electric field radial distribution within a water pipe of diameter 4 cm. Different radial distributions within air and water are observed and the focusing effect is observed at 10 °C, at which temperature dielectric losses are greater.

Electromagnetic field distributions within spherical and cylindrical bodies irradiated by a plane wave have been examined by several workers in relation to safety problems of radar and for medical purposes [122–126]. For spherical shapes it was found that the heating potential was higher than the value calculated by use of the average cross section model by a factor approximately ten under resonance conditions. Many common food items for example potatoes and tomatoes have diameters and dielectric properties that fall within the range for maximum core heating. Strong focusing effects are exhibited by geometrical shape of mushroom hat. Ohlsson and Risman [127] have shown that core heating releases steam which induces an energy impulse of sufficient power to cause mechanical stress within the heated material. This deleterious phenomenon is optimum for an egg of diameter close to 40 mm. This fact has been used as the well known effect that microwaves cook from inside. Accordingly, spheres and cylinders behave as dielectric resonators with strong focusing effects of electromagnetic energy. These effects are very dependent on temperature in relation to the balance between electric field distribu-

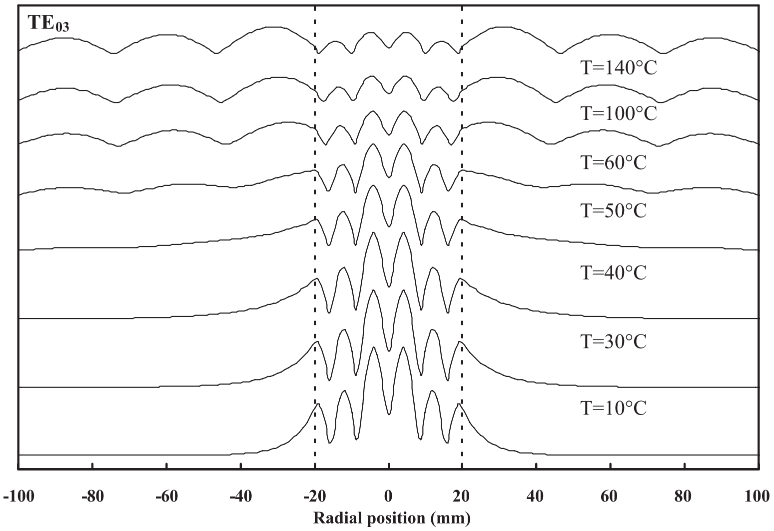

Fig. 1.18. Dependence of temperature on the radial electric field profile within a water pipe [121].

tions and dielectric properties. The same reagents placed within flasks of different shape can lead to different heating rate for the same microwave operating conditions.

In classical descriptions, thermal runaway is attributed to a strong increase of dielectric losses because of heating. So, the energy provided by microwave irradiation increases with temperature. The authors have shown it is possible to achieve thermal runaway with dielectric losses decreasing with temperature as a result of dimensional resonance or focusing effects of an electromagnetic field within the dielectric sample [128, 129].

1.2.4
Hydrodynamic Aspects

In many instances of heat transfer involving liquids, convection is an important factor. In most circumstances of heat-transfer within a conventional reactor, heat is being transferred from one fluid through a solid wall to another fluid and natural convection occurs. Density differences provide the body force required to move the fluid. As a result of thermal gradients induced by heating, vaporization and boiling can occur. Fluid motion results from different hydrodynamic instability. The author has exhaustively studied the microwave hydrodynamic behavior of water and ethanol which are two classical solvents in chemistry [130–133]. A brief overview of hydrodynamic instability (convective patterns for Rayleigh–Benard, Marangoni, and Hickman instabilities) and the design of experimental devices for heating of very polar liquids, for example water, can be found elsewhere [130], as can experimental results relating to the hydrodynamic behavior of water and

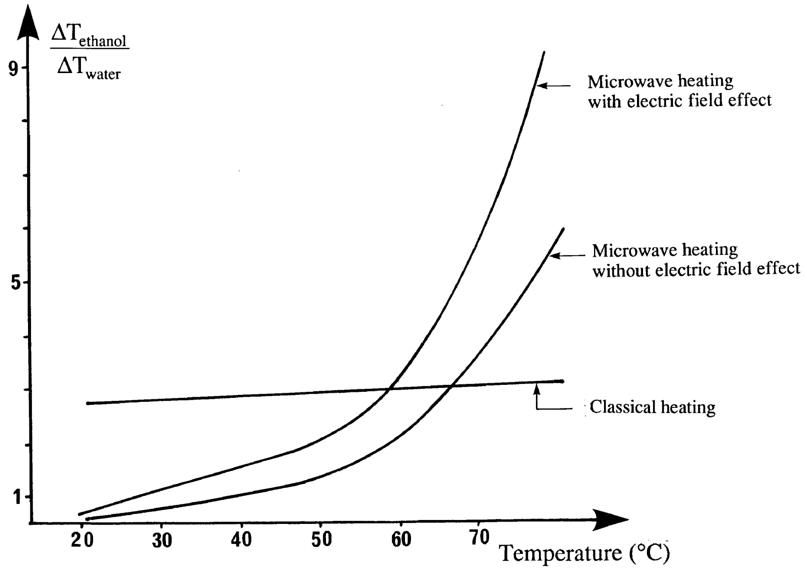

Fig. 1.19. Comparison of the effect of temperature on the heating expected with conventional and microwave heating (with and without the electric field effect) for water and ethanol [133].

ethanol under microwave heating at reduced pressure [131]. Coupling of hydrodynamic instability with linear stability analysis of experimental results is discussed in Ref. [132]. Microwave heating seems to be a tool which enables control of the spatial thermal profile in relation to the intrinsic properties of the liquid. Finally, modeling of microwave heating is described in Refs. [120] and [133].

The heating rates expected for water and ethanol as a result of conventional and microwave heating are compared in Fig. 1.19. For identical energy density and conventional heating, the ratio of the induced heating rates in water and ethanol does not change during heating. If no significant changes are observed for the temperature range, a significant difference appears when the dielectric loss effect is taken into account. In a third step, with the electric field correction, the difference is significantly amplified. Hence, we observe for temperatures below 50 °C that microwave heating is preponderant in water and for temperatures above 50 °C microwave heating is preponderant in ethanol. Thus this figure obviously proves the selectivity of classical heating and microwave heating in relation to the thermal dependence of the real and imaginary parts of the dielectric permittivity. For water or other liquids with dielectric losses decreasing with temperature, thermal conversion of electromagnetic energy is preponderant in cold areas. Thus, temperature fluctuations are eliminated by microwave heating. The intrinsic ability of microwave heating is to eliminate the thermal gradient between bulk and surface for an evaporating column. For ethanol or other liquids with dielectric losses increasing with temperature, in contrast with water, and for the same reasons, the thermal conversion of the electromagnetic energy is preponderant in hot areas. Microwave heating amplifies temperature fluctuations. Thus, we can understand why interfacial instabilities are preponderant in microwave evaporation of ethanol whereas bulk instabilities are preponderant in microwave evaporation of water.

The geometrical shape of the temperature profiles can be controlled in relation to the thermal dependence of the dielectric properties, and moreover, the absence of warming walls, as in classical heating, gives new dimensions to microwave heating. These two characteristics can make it possible to obtain specific and promising hydrodynamic effects as a result of thermal treatment of liquids.

1.2.5
Thermodynamic and Other Effects of Electric Fields

The thermodynamic effects of electric fields exist and are well known. The application of an electric field to a solution can induce an effect on chemical equilibrium. For example, the equilibrium of Eq. (18) where C has a large dipolar moment while B has a small dipole is shifted toward C under the action of an electric field:

$$A + B \rightleftharpoons C \tag{70}$$

Typical examples are the conversion of the neutral form of an amino acid into its zwitterionic form, the helix–coil transitions in polypeptides and polynucleotides, or other conformational changes in biopolymers. Reactions of higher molecularity where reactants and products have different dipole moments are subject to the same effect (association of carboxylic acids to form hydrogen-bonded dimers). Equilibrium involving ions are often more sensitive to the application of an electric field; the field induces a shift toward producing more ions. This is known as the dissociation field effect (DFE) or the “second Wien’s effect” [134].

In principle the effect of an electric field on chemical equilibria can be described by the thermodynamic relationship described by Eq. (71):

$$\left(\frac{\partial \ln K_{\text{Eq.}}}{\partial |\vec{E}|}\right)_{P,T} = \frac{\Delta\mu}{RT} \tag{71}$$

where K_{eq} is the equilibrium constant, $|\vec{E}|$ the field strength (V m^{-1}), and $\Delta\mu$ the molar change of the macroscopic electric moment or the molar polarization for nonionic systems. For ionic equilibria it must be pointed out that one can never reach a true thermodynamic equilibrium because of the field-induced flow of the ions. DFE theory has been developed by Onsager [135]. The most notable result is that $\Delta\mu$ is proportional to the field strength E. Hence, according to Eq. (72):

$$\int_0^E \mathrm{d} \ln K_{\text{Eq.}} = \frac{1}{RT}\int_0^E \Delta\mu \,\mathrm{d}E \propto E^2 \tag{72}$$

which results from integration of Eq. (71), the change in equilibrium constant is proportional to the square of the electric field strength and the effect on the equilibrium constant is noticeable only at high field strengths. In practice electric field strengths up to 10^7 V m^{-1} are required to produce a measurable effect on normal chemical reactions. For water at 25 °C, K_{eq} changes by approximately 14% if a field of 100 kV m^{-1} is applied. Smaller fields are required to achieve a comparable shift in less polar solvents. Nonionic equilibria can also be perturbed by the DFE if they are coupled to a rapid ionic equilibrium. A possible example is depicted by Eq. (73):

$$A^- + H^+ \rightleftharpoons AH \rightleftharpoons BH \tag{73}$$

in which the slow equilibrium is coupled to an acid–base equilibrium. This is the same principle as coupling a temperature-independent equilibrium to a strongly dependent one. Such a scheme has been studied for the helix–coil transition of the poly-alpha,L-glutamic acid by Yasunaga et al. [136], in which dissociation of protons from the side chains increases the electric charge of the polypeptide which in turn induces a transition from the helix to the coil form, for the dissociation of acetic acids by Eigen and DeMayer [137], and for dissociation of water by Eigen and Demayer [138].

Hence, if thermodynamic effects of an electric effect exist, the electric field strengths necessary are too high compared with the ordinary operating conditions of microwave heating.

1.2.6
The Athermal and Specific Effects of Electric Fields

A chemical reaction is characterized by a change of free energy between the reagents and the products. According to thermodynamics, the reaction is feasible only if the change of free energy is negative. The more negative the change of free energy, the more feasible the reaction. This change of the free energy for the reaction is the balance between broken and created chemical bonds. This thermodynamic condition is not sufficient to achieve chemical reaction in a short time (or with a significant reaction rate), however. Kinetic conditions must also be satisfied to achieve the reaction. The free energy of activation depends on the enthalpy of activation which expresses the height of the energy barrier to surmount. This energy condition is only a necessary condition and is not sufficient to ensure transformation of the reagents. The relative orientation of the molecules which react is crucial, and this condition is expressed by the entropy of activation. This entropic term expresses the need for a geometrical approach to ensure effective collisions between reagents.

Thus the essential question raised by the assumption of ‘‘athermal’’ or ‘‘specific’’ effects of microwaves is the change of these characteristic terms (free energy of reaction and of activation) for the reaction studied [139]. Hence, in relation to the previous conclusions, five criteria or arguments (in a mathematical sense) relating to the existence of microwave athermal effects have been formulated by the author

[140]. More details can be found in this comprehensive paper which analyses and quantifies the likelihood of nonthermal effects of microwaves. This paper provides some guidelines for clear definition what should characterize nonthermal effects.

Hence, according to these five criteria there is no doubt an electric field cannot have any molecular effect for solutions. First, the orienting effect of the electric field is small compared with thermal agitation, because of the weakness of the electric field amplitude. Even if the electric field amplitude were sufficient, the presence of dielectric loss results in a delay of dipole moment oscillations in comparison with electric field oscillations. Heating the medium expresses the stochastic character of molecular motion induced by dissipation of the electromagnetic wave. The third limitation is the annihilation of molecular rotation in condensed phases, for example the liquid state. According to our demonstration, under usual operating conditions it will be proved that the frequently propounded idea that microwaves rotates dipolar groups is, mildly speaking, misleading.

If molecular effects of the electric field are irrelevant in microwave heating of solutions, this assumption could be envisaged for operating conditions very far from current conditions. On one hand, it will be necessary to use a stronger electric field amplitude, or to reduce the temperature according to the Langevin function. This last solution is obviously antinomic with conventional chemical kinetics, and the first solution is, currently, technologically impossible. On the other hand, it will be necessary to avoid reaction media with dielectric loss. Molecular effects of the microwave electric field could be observed paradoxically for a medium which does not heat under microwave irradiation.

In conclusion, the interaction between a dipole and an electric field is clearly interpreted by quantum theory. The coupling is weaker than with magnetic fields, and when a dipole population is subjected to an electric field there is a such demultiplication of quantum levels that they are very close to each other. The interaction energy is continuous, and we have to use Boltzmann or Langevin theories. Because of the weak coupling between dipole and electric field, and the lack of quantified orientations, the study of electric dipole behavior gives less information about the dipole itself than about its surroundings. Indeed electric dipoles are associated with molecular bonds (the electric dipole moment results from the distribution of positive and negative charges on the molecule studied; if they are centered at different points the molecule has a permanent dipole and the molecule is polar). Any motion of electric dipoles, induced for example by interaction with an electric field, leads to correlative motion of molecular bonds, whereas motions of the magnetic moment are totally independent of any molecular motion. Consequently, studies of dielectric properties must be studies of "group properties". Those properties cannot be modeled by a single dipole; a group of dipoles interacting among themselves would be a key aspect of these models. The origin of the confusion between the behavior of a single dipole and a collection of dipoles (in other words differences between dilute and condensed phases) is the most important problem, and the source of illusions for people claiming microwave effects resulting from the orientating effect of the electric field.

In conclusion, is it necessary to obtain a microwave athermal effect to justify microwave chemistry? Obviously no, it is not necessary to present microwaves effects in a scientific disguise. There are many examples where microwave heating gives particular time–temperature histories and gradients which cannot be achieved by other means especially with solid materials. Hence, rather than claiming nonthermal effects it is better to claim a means or a tool to induce a specific thermal history.

1.2.7
The Thermal Path Effect: Anisothermal Conditions

According to the author, before claiming microwave heating effects in preference to collisional or mechanistic terms, it is necessary to estimate the effect of strong heating rates induced by microwave heating. The energy density used in a domestic oven is sufficient to raise temperature from ambient to 200 °C in less than 1 min, and so cause the total reaction time to be reduced by a factor close to 10^3.

This natural tendency for thermal racing is accentuated by these implicated energy densities which are usually different from those used with a water or oil bath, particularly for sealed vessels and autoclaves as used by organic chemists. The temperature and, especially, the thermal path $T(t)$ seems to be a crucial variable. The authors have shown theoretically and experimentally that strong heating rates (up to 5° s^{-1}) can induce selectivity or inversion between two competitive reactions [141].

The first case, depicted by Fig. 1.20, is called "induced selectivity". Numerical results correspond to a values of kinetic terms which give an optimum selectivity effect; exact values could be found elsewhere [141]. Under classical heating conditions, or a very slow heating rate, a mixture of the two products P_1 and P_2 is obtained. The ratio of the concentrations of P_1 and P_2 could be controlled by adjusting the rate of heating. Hence, under microwave heating conditions, pure P_1 or P_1

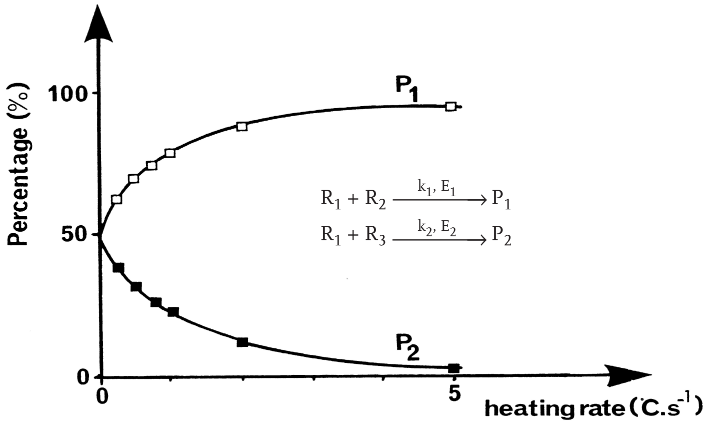

Fig. 1.20. Dependence of the amount (%) of P_1 and P_2 on heating rate. From Ref. [141].

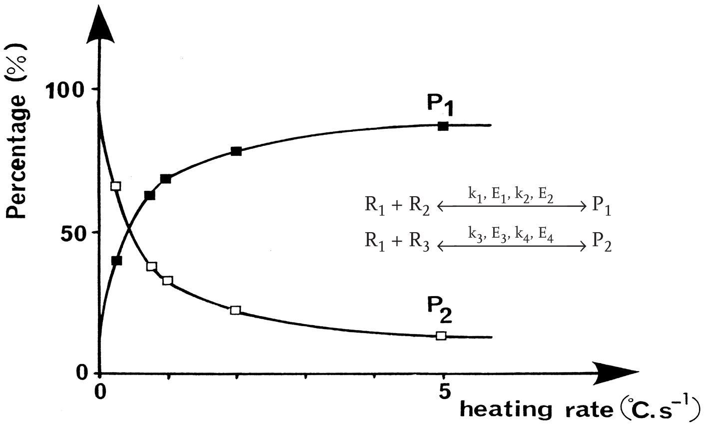

Fig. 1.21. Dependence of the amount (%) of P_1 and P_2 on heating rate from [141].

slightly contaminated by P_2 can be obtained. Chemical operating conditions (reactant concentrations) which are not selective conditions, because of side reaction leading to P_2, can become very selective when the rate of heating is very fast.

The second case, called "Isomeric inversion", is illustrated by Fig. 1.21. Under classical conditions P_1 alone is obtained whereas rapid heating or microwave heating leads to P_2. This situation is more interesting than the first because it forecasts reactivity changes induced by heating rate despite the same chemical operating conditions (reagent concentrations).

The author has illustrated these selectivity effects experimentally with a very classical reaction of much industrial interest – sulfonation of naphthalene. 2-Naphthalene sulfonic acid is a raw material used in the manufacture of pharmaceuticals, dyestuffs, and polymers. Sulfonation of naphthalene results in a mixture of 1- and 2-naphthalene sulfonic, di, tri, and tetrasulfonic acids and sulfones, depending on operating conditions. The reaction is first order with respect to naphthalene in concentrated aqueous sulfuric acid and the ratio of 1- to 2-sulfonic acid decreases slightly with increasing sulfuric acid concentration and temperature – the isomer ratio is 6 for 75% sulfuric acid and 4 for 95% sulfuric acid at 25 °C. The detailed operating conditions (concentrations, microwave applicator, heating rates, and analysis) can be found elsewhere [141]. Figure 1.22 shows the dependence of the percentage 1- and 2-sulfonic acids after reaction on the microwave power used. The isomer ratio can be controlled independently of the chemical operating conditions. This change of selectivity results from heating rate induced. At high temperature (close to 130 °C) 2-sulfonic acid is the major product rather than 1-sulfonic acid. The higher the heating rate, the more the ratio of 1- to 2-sulfonic acid changes.

To observe such kinetic effects of microwave heating, however, it is necessary to have reactions with reaction times close to heating time. Under most operating conditions reactions times are close to several tenths of minutes and anisothermal

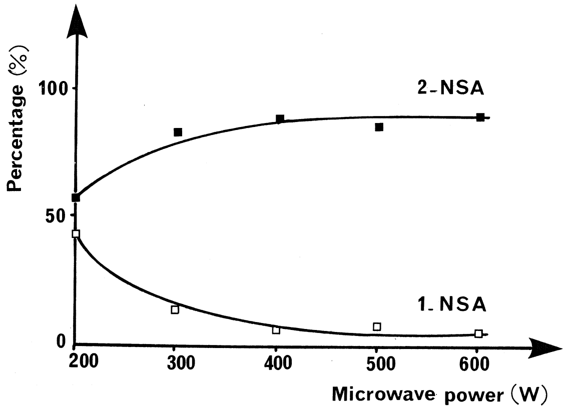

Fig. 1.22. Dependence of the percentage of P_1 and P_2 on heating rate from [141].

effects can be neglected. The use of sealed vessels and autoclaves should enable synthetic chemists to take advantage of the strong heating rate induced by microwave heating (heating times close to reaction times). Thus microwave heating seems to be an easy way of imposing very rapid heating rates for kinetic control of reactions.

1.2.8
Hot Spots and Heterogeneous Kinetics

Effects of temperature upon reaction rate and the heterogeneous character of microwave heating are well known. The wavelength of microwaves used is 12.2 cm (2.45 GHz). Within a dielectric medium, the wavelength is, to a first approximation, equal to the wavelength in air divided by the square root of real part of relative dielectric permittivity. Therefore, for very polar solvents, for example alcoholic or aqueous solutions, several local electric field maxima could be obtained within the heated sample [120, 142]. Baghurst and Mingos [143] have shown that boiling temperature of solvents under the action of microwave heating could be higher than under classical heating conditions. This temperature is referred to the nucleation-limited boiling temperature (NLBT). For most organic solvents the NLBT is within the range of a few degrees to thirty degrees above the conventional boiling point. Vigorous stirring or addition of nucleating materials (e.g. antibumping granules) can easily reduce this localized superheating. For solid reagents or materials, microwave heating can rapidly lead to fusion, depending on the thermal dependence of dielectric properties and, especially, on increase of conductivity with temperature (Section 1.1.2.4 and Ref. [75]). Consequently, most local thermal fluctuations can be amplified and temperatures close to 1000 °C can easily be reached in a few seconds. The association of organic reagents with inorganic solids as alumina, silica, and clays strongly enhances the capacity to absorb microwaves. Loupy et al. [144]

have shown that association of potassium acetate with alumina or silica leads to a reactive medium which strongly absorbs microwaves – the temperature is close to 600 °C after heating for 1 min. The author has made real-time infrared videos of powders (alumina, oxides, zeolites, water gels, etc.) under the action of microwave heating. Evidence of strong thermal gradients has been obtained (for ferrites, $50^\circ\ \mathrm{mm}^{-1}$). The author has shown that these hot spots or areas could induce localized reaction rate enhancement [145]. These results have shown that a very small density of superheating areas is sufficient to induce a consequent rate enhancement (2% of hot spots are sufficient to increase yield by 60%), even if their effects on averaged temperatures are not detectable.

In conclusion, microwave heating offers the possibility of realizing high power densities because of core thermal conversion of electromagnetic energy. There is, therefore, increasing industrial application of microwave energy for heating, drying, curing, and sintering of materials. Microwave applicators (traveling wave, multimode, and single-mode cavities) are designed by a trial and error procedure, however. Industrial in-line processing calls for the design of specific applicators which enable high-power densities and hence rapid rates of heating to be achieved. The development of electromagnetic models for such applicators would improve our understanding of microwave processing and heating and enable the rapid design of optimized microwave devices.

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