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COOPERATIVE MOLECULAR BEHAVIOR AND FIELD EFFECTS ON LIQUIDS: EXPERIMENTAL CONSIDERATIONS

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CONTENTS

I. INTRODUCTION

We are taught at an early stage of our scientific training that there exist three states of matter—gas, liquid, and solid. Our understanding of the solid state of matter is advanced because the periodicity of molecules within the structured lattice simplifies solution of the equations involved. And, of course, it is possible to solve the Schrödinger equation itself for the dilute gas when the intermolecular interactions are insignificant. As we compress the gas, two- and three-body interactions become important and complicate such analyses. In the condensed liquid state the proximity of molecules is of the order of the internuclear separations within the molecules, the liquid is held together by attractive forces, and the whole ensemble behaves as an entity. A liquid flows freely, takes the shape of a containing vessel, and may even form droplets in free space held together by surface-tension forces in the peripheral regions, where the intermolecular forces are modified. Analyses are now enormously complicated. The intermolecular potentials are complex, time-varying quantities composed of attractive and repulsive forces. The phase is a cooperative molecular one in which a vast number of molecules move and interact cohesively.

The calculation of the intermolecular forces is considered to be at the root of the problem. But an intermolecular potential has been calculated for the simplest of liquid systems—argon and neon—only recently. This was achieved by measurement of the differential cross sections of argon and neon using modulated molecular beam techniques.[1] It is significant that the potentials calculated differed greatly from the Lennard-Jones potential, the potential that is even now being used extensively in the Monte Carlo and molecular-dynamics computer calculations of condensed-phase systems. In fact, the potentials for neon and argon themselves have different shapes and are not related by any simple scaling factors.

Thus, the elucidation of the liquid state of matter, the life-supporting state and the state in which most of our chemistry takes place, eludes us. As Berne and Harp[2] have said, "understanding the liquid state has proven to be both a challenge and an embarrassment to generations of outstanding chemists and physicists." Onsager's 50-year-old theory accounting for the dielectric constant of a polar fluid and the conductivity of a salt is still used extensively. Only recently has a full quantum calculation for the gas-phase exchange reaction

$$H + H_2 \rightarrow H_2 + H$$

been achieved. Obviously, we cannot yet contemplate extending such calculations to the solution state. This can be achieved only when we have detailed knowledge of the intermolecular potentials. In fact, the state of the art is such that we usually cannot calculate the solubility of one substrate in another *even where no reaction takes place*. Engineers and applied scientists, of course, would wish to be able to predict such solubilities, but it is only recently that theories of solution have reached the stage at which the right sign of volume change and a correct order of magnitude may be estimated.[3] As Hildebrand[4] has said, "of the various thermodynamic functions for the mixing process, the volume change on mixing at constant pressure has intrigued scientists for years. However, it is still little understood."

A. Intermolecular Forces

The actual study of liquids has provided little information on intermolecular forces. The numerous polymorphs in the solid states of many substances testify to the complexity and diversity of these forces. One still often sees in the literature the use of hard sphere potentials that neglect attractive energy completely.

The ideas behind such potentials have been used for over a century.[5] The work of Van der Waals[6] in 1873 implied that the structure of a liquid is primarily determined by repulsive forces, with the attractive forces providing only a uniform background energy. The liquid could thus be regarded as a system of hard spheres. At that time the properties of such a system were not known. Such information has become available only with the recent rapid progress in computer methods for studying molecular dynamics. The properties of such a system are obviously not compatible with many of the pertinent facts. Though the Lennard-Jones interaction is a significant improvement, it does not represent satisfactorily the liquid-state interactions even between neon and argon. When we recall that the R-12 repulsive energy (unlike the R-6 attractive energy) has no physical justification, this is not so surprising.

The failure of liquid studies to provide information on potentials is exemplified by the fact that information for calculating the potentials is still commonly derived from the macroscopic properties of dilute gases: from the second virial coefficient (at low gas densities), from the transport properties of gases, from the scattering of molecular beams by gases, and from X-ray determinations (again at low densities). All of these techniques have limitations. The second-virial method is not discriminating in distinguishing between potentials. Even if B_2 is known for all temperatures, this determines only the positive part of the potential curve and the area beneath the "negative" part of the abscissa. The experiments should be carried out to the extremes of temperature.[7] At the lowest accessible temperatures below the boiling point, the 12-6 potential gives B_2 values that are less negative than the experimental ones, indicating that the minimum of the 12-6 potential is not deep enough and that the third virial coefficients, calculated using the Lennard-Jones potential derived from the second virial coefficients, are too small. As Prigogine[8] emphasizes, "we cannot determine the correct law of force using only the second virial coefficients."

Transport properties used to measure the potential suggest that model potentials cannot be used to fit data over a whole temperature range. Quoting Prigogine[8] again: "For high temperature, there is a significant deviation of the calculated transport properties from the Lennard Jones potential." There are severe problems with the scattering-of-beams technique, the most serious being the inapplicability of the Born approximation and the need to use complicated quantum-mechanical calculations.

Even assuming we have a pair potential between two molecules accurate enough for the calculation of measureable bulk quantities, we then have to assume that the potentials are additive, so that the potential energy of the bulk is the sum of interactions between all possible pairs of molecules in the ensemble. This is probably an oversimplification. Hildebrand[4] reminds us that "the molar volume V_t is defined as that volume at which soft molecules begin to be sufficiently separated between collisions to acquire fractions of their momentum in free space. At volumes smaller than V_t they are in fields of force not appropriately described by pair potentials. The role of temperature is only to determine volume. Values of V_t depend on the capacity of a molecular species to absorb collision momentum by bending, vibrating or rotating." Three-body forces are thought to be important even in the calculation of certain properties of rare-gas solids, such as the zero-point energy and the Debye temperature. In light of this it may seem surprising that two-body interactions can form the basis for a discussion of intermolecular forces in liquids. Buckingham[9] sums up the situation thus: "In spite of our increasing knowledge of interaction energies, we must confess that we do not know accurately the potentials for any organic systems, not even $(CH_4)_2$. So we are forced to use empirical or semi-empirical potentials." And these, of course, in spite of obvious deficiencies. For example, a long-standing objection to the Lennard-Jones potential is that an assembly of such molecules has a configuration of minimum potential energy in the hexagonal close-packed structure. However, all inert gases except helium crystallize in the cubic close-packed structure. The fault probably lies in the neglect of small nonadditive terms in the potential energy of the assembly. If we wish to consider polyatomic, polarizable molecular liquids, electrostatic terms have to be added and the shapes of molecules accounted for so that repulsive forces will change with the orientation[5] of the molecule. As discussed in the first article of this volume, the hydrogen atoms are important in a computer simulation of CH_2Cl_2 for describing its molecular dynamics. Narten et al.[10] reported a similar observation in their X-ray-diffraction study of liquid neopentane.

The influence of molecular shape on the intermolecular potentials may be observed straightforwardly by comparing different isomers of a given formula. For example, since the critical temperature (T_c) is roughly proportional to the pair potential, we can conclude that in the series of pentanes tabulated below cyclopentane has the largest energy of interaction and neopentane the smallest.

	n-Pentane	Isopentane	Neopentane	Cyclopentane
T_c	469.6	450.4	433.8	511.6
$\Delta S_M/R$	7	5.5	1.5	0.4

Account must also be made of the fact that the origins of the attractive and repulsive forces *need not be the geometrical centers of the molecules.* We shall consider the consequences of this in discussing the coupling of a molecule's rotation with its own (or a neighbor's) translation in later sections. Buckingham[9] again sums up: "We are still ignorant of energies near to the minima in the potential wells, and we know little of the effects of many body interactions. It is commonly assumed that the medium diminishes the interaction between polar species, but in fact polar or polarizable molecules placed between opposite electric charges increase their attraction."

It may easily be demonstrated that an external field stabilizes a liquid drop, increasing the attraction between those molecules whose diameters are smaller than a critical diameter (characteristic of the liquid under study), if the dipole moment of the drop is larger than the corresponding dipole moment of the same number of noninteracting dipoles. If the solution is assumed ideal, it is found, analogously to the case of supersaturated vapors,[11] that[12]

$$\log\left(\frac{P(r)}{P(\infty)}\right)=\frac{1}{kT}\left[\frac{2\sigma}{r\rho}-\mathbf{E}\cdot\left(\mathbf{M}_1-\mathbf{M}_2+\frac{r}{3}\frac{d\mathbf{M}_1}{dr}\right)\right]$$

where $\mathbf{M}_1$ is the dipole moment in the absence of an electric field, $\mathbf{M}_2$ is the dipole moment in the presence of the field, $P(r)=-(\partial F/\partial V)_T$ is the "pressure" over the drop of radius r (F is the free energy and V the volume of the drop), $P(\infty)$ is the corresponding pressure over a plane interface of the same liquid whose density is $\rho=(3N_r/4\pi r^3)$, (N_r is the number of noninteracting dipoles), $\mathbf{E}$ is the external electric field, and T is the temperature.

This equation shows that the external electric field favors the growth of regions where the concentration of dipoles is increased. This can be seen in a simple laboratory experiment if a large field is applied across two parallel brass electrodes to a nondipolar liquid such as CCl_4. *Small droplets* of liquid are quickly expelled through the top of the two sealed electrodes[13]. The electric field also induces bulk translational motion in molecular liquids. We shall consider this phenomenon in a later section.

Computer simulation is presently being used to refine our "trial potentials" by comparison with experimental data. As we shall see, new experintal results may also provide direct access to details of the interactions ween molecules in the liquid state.

B. The Liquid State and Its Range of Existence

Liquid argon is considered the model liquid because its dispersion energy ıssumed to be pairwise additive and its atoms have spherical symmetry. liquid argon the attractive energy is caused by mutual induction from the ctrons fluctuating in the electron clouds. As we have said, in molecular uids the pair potential depends on orientation and interactions between ctrostatic moments may contribute to the attractive energy. If the polariz- ılities are such that partial charges are located on the peripheries of the lecules, then temporary (chemical) bonds such as hydrogen bonds may m. The role of molecular shape in determining the properties of con- nsed-state systems is displayed even among the less complex molecular ecies. If molecules are flexible, coupling of intramolecular and intermolec- r modes of motion may occur. Coupling of rotational and translational otions may be seen in fairly simple molecular liquids, so the two modes y not always be separated, as is customary in, for example, the calcula- n of equilibrium properties (ΔH, ΔS, ΔE, and density) from the relevant rtition functions. The complexity of the interactions, and this coupling of odes of motion, has frustrated and delayed understanding of liquid-state havior. As Kohler[14] says, "at present there exists no model which would produce satisfactorily the properties of liquids over the whole density nge."

We will now ask some simple questions and see what answers may be ovided. We must not confine ourselves to macroscopic, bulk considera- ons. Bulk properties have their origin at the molecular level and it is here at many of the subtleties of condensed-state matter may be observed. Bulk nsiderations alone obscure many of these details.

At the triple point of a substance gas, liquid, and solid phases may co- ist—the states converge and are in equilibrium with each other. And the nventional belief that a sharp melting point indicates no continuous adation of properties between liquid and crystal is not strictly true. It is ssible for a liquid to be cooled below its normal melting point and to pass t into the crystalline solid but into a disordered solid in which there is *no ng-range order*. The important variable in this process is the *rate of cooling*. the rate is fast the liquid is changed into a glassy state with all its imper- ctions literally frozen in. The viscosity of the liquid increases steadily until approaches the glass-phase transition. The short-range order in the glass is rtually perfect, but there is no definite long-range order. Glasses are inter- ediate between liquids and solids; their high viscosities prevent rearrange- ent of molecules into the completely regular crystalline form. It is now widely believed that it should be possible to cool any liquid into a glassy state providing the cooling rate is fast enough and the final temperature low enough to prevent the glass from recrystallizing. These requirements are easily met in computer simulation studies as Evans[15] has described for one liquid system. Stillinger[16] has done similarly for water in a computer simulation. They observe that the diffusions are markedly slower because the hydrogen bonds are frozen in and are stronger.

Glasses are interesting in their own right and offer challenging "test situations" for the molecular dynamicist. A few degrees' change in temperature near the glass-phase transition (T_g) may vary the viscosity of the system by several orders of magnitude. This has fascinating spectral consequences, as Evans et al.[17] have discussed. Recent interest has been directed toward quenching liquid metals into glassy states because the unique physical properties so acquired (e.g., the combination of high mechanical strength, ductility, and remarkable magnetic properties)[18] have technological importance. By changing alloy composition, one can make paramagnets, ferromagnets, ferrimagnets, and spin glasses. In ferromagnetic glasses consisting primarily of transition metals it is found that coercive forces are extremely low.[19] These materials make good soft ferromagnets. Another property they may exhibit is a high resistance to corrosion[20] compared with their crystalline equivalents.

As we have said, the numerous polymorphs of many solids testify to the significant range of structures, and consequently properties, that a solid may have. But what of a liquid? Does a similar gradation of molecular behavior exist in the liquid phase? Liquid helium has fascinated scientists more than any liquid apart from water and is the only known system in which two liquid phases almost certainly exist. Important quantum effects are found in this simple system (and some hydrogen-isotope systems). It remains a liquid down to 0 K and may be solidified only under considerable external pressure. Interestingly, Dyson[21] has suggested that all matter is "liquid" at 0 K because of quantum-mechanical barrier penetration. The lifetimes for such processes are so long that even the most rigid materials cannot preserve their shapes or their chemical structures for comparable times. Dyson says that on such a time scale "every piece of rock behaves like a liquid, flowing into a spherical shape under the influence of gravity. Its atoms and molecules will be ceaselessly diffusing around like the molecules in a drop of water."

Some liquids obviously have, at certain densities, properties similar to those of compressed and even dilute gases. Liquids are known in which *rotational spectral detail* may be resolved at submillimeter (far infrared) frequencies,[22] as in the gas phase. If HCl is dissolved in argon, spectral fine rotational detail is resolved for argon densities between 100 and 480 Amagat. The density dependence of the different linewidths is distinctly nonlinear and different for different lines. Such behavior is the same as in the compressed gas state, but in striking contrast to that observed in dilute gas systems. If HCl is dissolved in SF_6 and CCl_4, rotational fine structure is resolved in the former in the liquid state, but not in the latter, *even though* the Lennard-Jones parameters and masses of SF_6 and CCl_4 are quite similar.[23] Such observations provide vital clues to details of the dynamics. It is apparent that the ratios of mass and size of the probe to the mass and size of the solvent are significant in determining the dynamics, and that it is not just the translational motion but also the rotational motion of the solvent that modulates local density fluctuations. In fact it can be established straightforwardly that rotational and translational motions are strongly coupled even in such simple liquids. Expressed in classical terms, since translational frequencies in the liquid are usually comparable to rotational frequencies, these motions become easily coupled.

The simplest spectroscopic example that shows the effect of this coupling is the induced rotational absorption of HD in liquid argon.[24] The observed experimental rotational energy states of H_2 or D_2 in liquid argon are, within experimental error, equal to their gas-phase values. Because the electrical center and the center of interaction of the HD molecule are located halfway between the two nuclei *but the center of mass is somewhat displaced*, a HD molecule may rotate about its center of mass, in an argon liquid environment, only if the electrical center, which is displaced from the center of the cavity, simultaneously translates back into the center of the cavity and is restored to a position of minimum potential energy. As Ewing[25] says, "for HD or any molecule whose center of interaction does not coincide with its center of mass, rotational and translational motions are coupled by the solvent cavity." The spectral consequences are such that resolved far-infrared rotational details show large half-widths, erratic frequency shifts, and additional absorptions arising from the relaxation of the rotational selection rules. Transitions +1, +2, +3, and +4 are all observed for the HD–argon liquid system, a consequence of the rotation–translation coupling perturbation.

In such systems, when spectroscopic detail is resolved, molecular-dynamics analyses are greatly simplified. So Marteau et al.[26], examining the far-infrared collision-induced absorption of liquid Kr–Ar mixtures, were able to assign certain features of their spectra to *nonlocalized phonon* (*collective translational*) *modes in the liquid*. So too, Bulanin and Tonkov[27] have assigned a feature at 38 cm^{-1} in their spectra of D_2–argon solutions to phonon absorption by the liquid argon. And Chantry et al.[28] attributed features in the far-infrared spectra of CS_2 and benzene to lattice modes of the translational type. In recent years it has become customary to attribute the *broad absorptions* of these latter two liquids to rotational motions, that is, to the motions of dipoles induced by neighboring molecular quadrupoles or octopoles in the liquid. However, it is generally *not possible* to distinguish between rotational and translational molecular contributions, whether single-molecule or collective, to such broad and featureless profiles. By considering simple molecular liquid systems we may easily establish the importance of both rotational and translational modes of motion in determining the total dynamics of the system.

We may now envisage instances in which one of these two modes of motion (rotation and translation) is constrained in the liquid because of, for example, the shapes of the molecules. Consider long, rodlike molecules. Rotation about certain axes will be hindered because an orientational order is introduced into the system. The molecules may remain positionally disordered, with their centers of mass delocalized. What effect does such order impose on the liquid system, and do such systems exist in nature? Edgar Allan Poe wrote in 1837:[29]

> I am at a loss to give a distinct idea of the nature of this liquid, and cannot do so without many words. Although it flowed with rapidity in all declivities where common water would do so, yet never, except when falling in a cascade, had it the customary appearance of limpidity. It was, nevertheless, in point of fact, as perfectly limpid as any limestone water in existence, the difference being only in appearance. At first sight, and especially in cases where little declivity was found, it bore resemblance, as regards consistency, to a thick infusion of gum arabic in common water. But this was only the least remarkable of its extraordinary qualities. It was not colourless, nor was it of any uniform colour—presenting to the eye, as it flowed, every possible shade of purple, like the hues of a changeable silk. The variation in shade was produced in a manner which excited as profound astonishment in the minds of our party as the mirror had done in the case of Too-Wit. Upon collecting a basinful, and allowing it to settle thoroughly, we perceived that the whole mass of the liquid was made up of a number of distinct veins, each of a distinct hue; that these veins did not commingle; and their cohesion was perfect in regards to their own particles among themselves, and imperfect in regard to neighbouring veins. Upon passing the blade of a knife athwart the veins, the "water" closed over it immediately, as with us, and also, in withdrawing it, all traces of the passage of the knife were instantly obliterated. If, however, the blade was passed down accurately between the two veins, a perfect separation was effected, which the power of cohesion did not immediately rectify.

This remarkable account of the character of *liquid crystals*, first brought to our attention by Gray,[30] introduces us to another state of matter—the liquid crystalline state. Liquid crystals in which the molecules are positionally disordered, but orientationally ordered, are called nematics. Because of the forces arising from their mutual interaction, the molecules adopt a com-

mean parallel orientation. Such systems have fascinating properties and
nological applications, which are discussed at length in many texts.[31]
What if there is positional as well as rotational order, but only in one or
directions (and not three directions, as in the crystalline solid)? Again,
h situations do exist in nature and are also classified as liquid crystals.
h positional order in only one direction, they are called smectics. “In ad-
on to possessing mean longitudinal parallelism (rotational order) each
lecule conditions the mean position of its neighbour so that the mean dis-
ce between their centres (or ends) is minimized. This results in planes of
uctural discontinuity which are perpendicular to the direction of parallel-
. The layers of molecules so constituted can slide with equal facility in all
ections over the planes of discontinuity.”[31(ii)]

There are tricks that we may play even on these liquid crystalline systems
produce additional phases of matter. Let us return to the nematic phase
d recall some more elementary chemistry—the chemistry of chiral sys-
ns. Chiral molecules (containing, for example, an asymmetric carbon atom
ached to four different elementary groups) display the fascinating prop-
y of handedness; that is, the separate atoms (or groups of atoms) may be
anged (if we envisage a planar representation of the molecule) in clock-
se or anticlockwise directions. The two different molecules are then mirror
ages of each other; that is, they possess a plane of symmetry. If we dis-
lve such a molecule in a nematic liquid crystal we cause the structure to
ist and to undergo a helical distortion. Some liquid crystals are twisted in
is way in their natural form and may be considered distorted nematics; they
e called cholesterics and are chiral liquid crystalline systems.

Optically active, isotropic molecular systems, even those consisting of
nall molecules, display more clearly than any others the importance of
olecular shape and of the size of the atoms of a molecule in determining
e packing and molecular dynamics of the liquid state, and consequently
s physical properties.[32] A computer simulation of 1,1-fluorochloroethane
veals that spectra obtained with all of the spectroscopic techniques (dielec-
ic, infrared, Raman, neutron scattering, Kerr-effect measurement, nuclear
agnetic resonance, and light scattering) will be the same for the R and S
nantiomers, but *may be different* for the racemic mixture. This is a conse-
uence of a subtle detail of the molecular dynamics—the coupling of a
olecule's rotation *to its own* translation. Certain cross elements of a mixed
otation–translation matrix are opposite in sign for the two enantiomers
because they are mirror images). However, this has no effect on the mea-
ured spectral properties of each individual enantiomer. If *R* and *S* species
re mixed to form the corresponding racemic mixture, the elements of op-
osite sign must cancel and vanish, this being the only observable dynami-
al difference. This has remarkable effects on measured spectra and, indeed,

on physical properties. In 1,1-fluorochloroethane the effect is sufficient to shift, for example, the far-infrared frequency of maximum absorption of the enantiomers (which occurs at 35 cm^{-1}) to ~ 65 cm^{-1} in the racemic mixture (the phenomenological Debye loss time is approximately halved). The differences in the dynamics are most pronounced. The role of the molecular atoms in determining condensed-state properties may now be easily examined, because if we replace the chlorine atom in this molecule with a larger iodine atom to obtain 1,1-fluoroiodoethane, the dynamics and physical properties are dominated by the mass and assumed sphericity of the iodine atom. That even physical properties may be modified in the racemate relative to the individual enantiomeric systems may be seen by considering lactic acid ($CHOHCH_3COOH$). At room temperature the racemic mixture is a liquid, whereas both enantiomers form solids (melting points 18°C and 53°C, respectively). A consideration of these optically active systems brings to the fore the subtlety of the roles of rotation and translation and the coupling between the two in determining condensed-state properties.

In a molecular crystal there may exist positional order (the centers of gravity of the molecules are located on a three-dimensional periodic lattice), but rotational disorder. Crystals so arranged are often called cubic mesophases or plastic crystals. The molecules are globular and may undergo thermal rotatory motions freely, in some cases more freely than in the liquid.[33] That these rotary motions are accompanied by translational displacements (the motions are coupled in the solid) is illustrated by the blurred X-ray-diffraction patterns that are always obtained in such systems. However, computer simulation shows[34] that in bromoform, for example, a solid rotator phase is formed below the freezing point at 281 K, rototranslation functions, which may be observed in a frame of reference with moving axes, are relatively small in these very liquids that form rotator-phase states. It is proposed, therefore, that a dynamical prerequisite for the existence of certain types of rotator phases is that rotation be largely decoupled from translation.[15(b)]

Submillimeter spectra (Fig. 1) firmly substantiate the existence of a solid rotator phase in bromoform. The rotator-phase spectrum is shifted slightly to higher frequencies relative to the liquid spectrum, but remains a broad and featureless band. No lattice modes, which are characteristic of the crystalline solid, are resolved until the sample is cooled below −2°C. In tertiary butyl chloride, in which two solid rotator phases exist between the isotropic liquid and nonrotator crystalline solid states, *a marked hysteresis may be observed as the sample is cooled and reheated through the phase-transition regions* (Fig. 2). Using a spot frequency at 84 cm^{-1} from a tunable far-infrared laser, spectroscopic changes were monitored as the sample was first slowly cooled through the transition region. The first transition, liquid to ro-

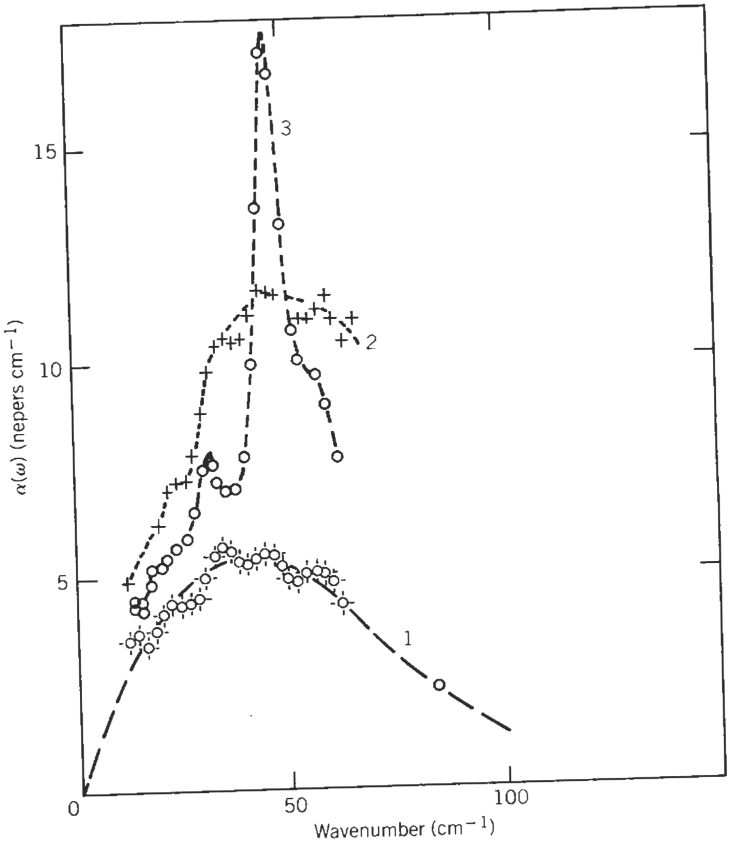

Figure 1. Far-infrared absorption of bromoform in the liquid and rotator-phase states: (*1*) -○- , The liquid state at 295 K; ○, laser point at 84 cm^{-1}. (*2*) +, The rotator phase at 273 K (as for the liquid, a broad, featureless band). (*3*) ○, The crystalline solid (note that lattice modes are resolved).

tator solid phase I, is barely observable at 247.53 K. The second transition, rotator phase I to rotator phase II, is more pronounced at 219.25 K. The third transition, rotator phase II to crystalline solid, involves the most significant drop in throughput intensity, at 182.9 K. The most striking feature of these curves is the marked hysteresis seen as the sample is reheated through the phase-transitions region (slowly over about 1½ h). There is no indication whatsoever that the crystalline solid passes into rotator phases II and I. Instead, the sample melts *at a higher temperature* (~ 268 K) than any of the transition temperatures. Using such "molecular probes" (the various spectroscopies) to follow phase transitions provides us with valuable insight into the freezing and melting processes.

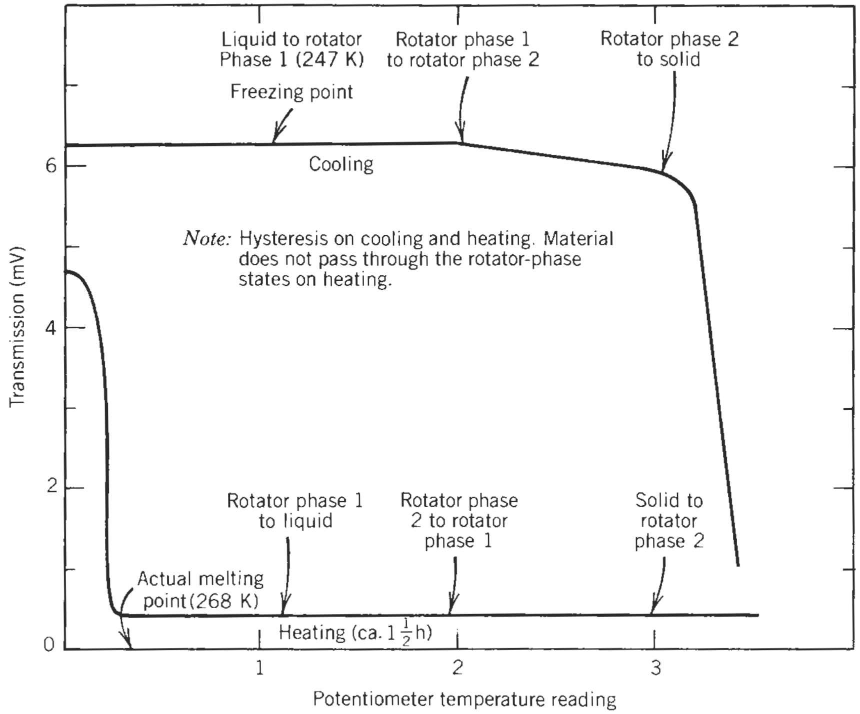

Figure 2. Far-infrared microscopic probe of the freezing and melting processes in *t*-butyl chloride.

Sciesinska and Sciesinski reported similar observations for cyclohexanol.[35] As they said, "the phase situation in solid cyclohexanol still remains unclear. The number of ascertained solid phases varies from four to seven depending on the method of investigation and the authors." In Fig. 3 we reproduce a diagram of theirs that gives the temperature dependences of integral transmission (the transmitted power over a given frequency region) for cooling (b, c, e, g, and h) and heating slowly from liquid-nitrogen temperature (points f, d, and a). The various phase transitions are exposed distinctly because they most often cause a change of integral transmission due to increased scattering even when the absorptions are similar for both phases. Nor is this hysteresis confined to those substances that form rotator-phase solid states. Michel and Lippert[36] reported on "two ways of freezing acetonitrile" (CH_3CN). Their phase transitions for acetonitrile are reproduced in Figs. 4 and 5 which show the results of monitoring the ν_3 symmetric CH_3 deformation mode, the ν_4 C—C stretch, the ν_5 C—H antisymmetric stretch, and the combination modes $\nu_2 + \nu_4$ (C—N + C—C) and $\nu_3 + \nu_4$ (CH_3 def + C—C).

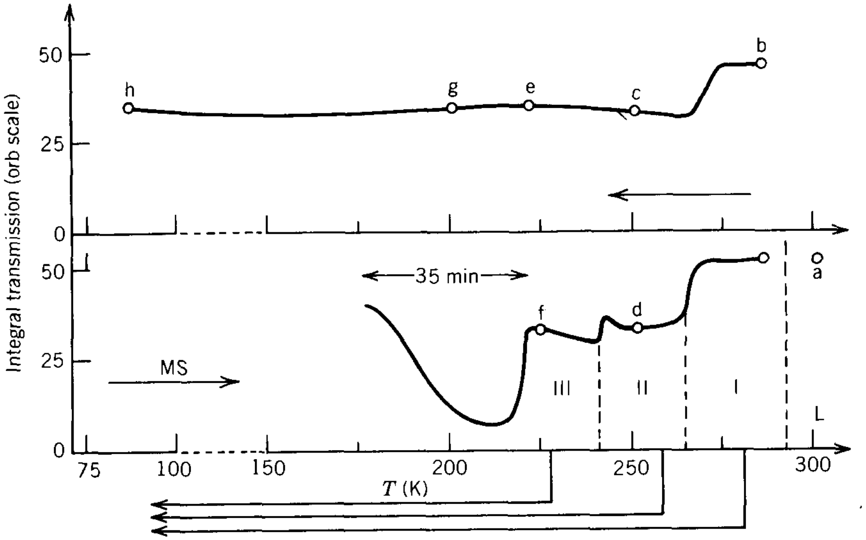

Figure 3. Integral transmission for cyclohexanol, obtained using an IRIS Spectrometer. Points b, c, e, g, and h represent the cooling process; points f, d, and a, the heating process. The phases are as follows: a, liquid; b, supercooled liquid; c and e, rotator phases; d, crystal II; f, crystal III; and h, crystal (metastable). *Note:* Again the material passes through rotator phases on cooling but not on reheating. (Reproduced by permission from ref. 35.)

Michel and Lippert stated that

> presolid states, metastable processes, and hysteresis can be observed as a continuous function of temperature and speed of cooling... hysteresis effects occur in both directions while acetonitrile is passing through presolid and metastable states. When cooling very slowly, one can observe a presolid state with a lifetime of less than half a second. It is characterized by a rapid decrease of the maximum intensities of the combinations modes. A definite melting point is not found when reheating, but rather a transition region with a shape similar to a titration curve. The first sign of the phase transition can be observed *eight degrees before melting*. The proper melting region is contained within two degrees. Directly after melting the liquid is different from the one before freezing at the same temperature. After some minutes or after reheating, the old situation returns.

We shall consider the nucleation process in molecular liquids in more detail in a later section, and shall see that *external electric fields can be used to induce nucleation.*

We have tended to label some condensed-phase properties as anomalous when they have failed to fit our restrictive preconceptions about condensed-state matter. For example, the 10% contraction of ice on melting is not anomalous at all. As Eyring et al.[37] point out, "when a normal system, such as argon, melts it expands twelve per cent. Such an expansion is typical. The atypical ten percent contraction of ice upon melting can be made to disappear if one first applies some 2,500 atmospheres pressure at an appropriate temperature, to the hydrogen bonded tetrahedral ice I and so transform it into close packed ice III, which is a fifth more dense. Ice III then melts with a normal ten percent expansion." Problems have arisen because of our desire to label matter strictly as solid or liquid, making no allowance for intermediate states that may exist. The numerous ice polymorphs that exist attest

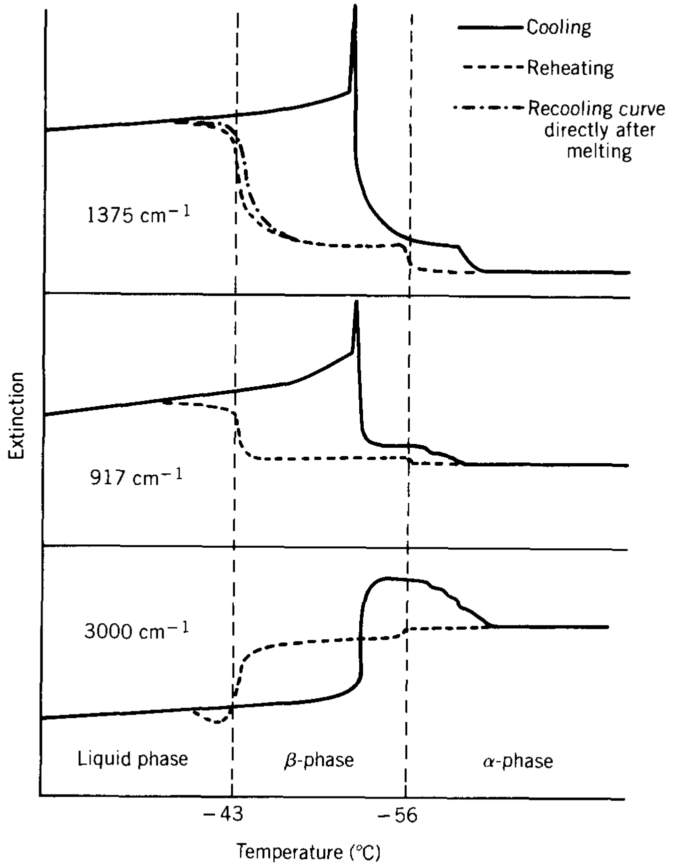

Figure 4. Acetonitrile phase transitions: ν_3, symmetric CH_3 deformation; ν_4, C—C stretch; and ν_5, C—H asymmetric stretch. Note the existence of hysteresis and presolid states. The diagrams show intensities at fixed wavenumbers on cooling and reheating. (Reproduced by permission from ref. 36.)

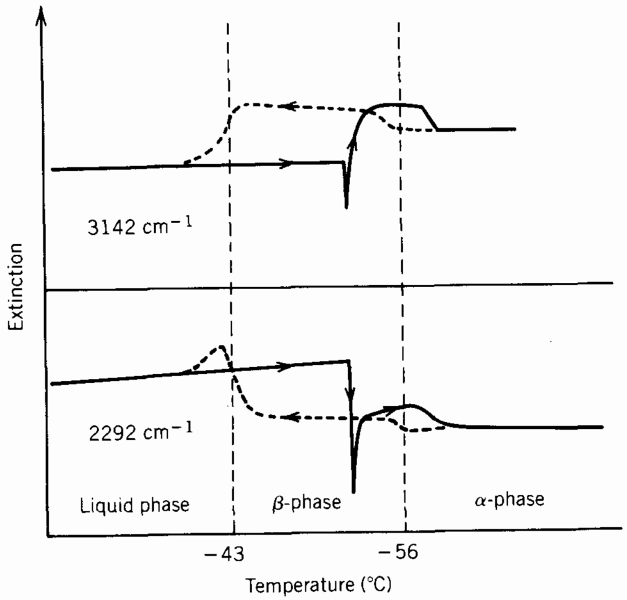

Figure 5. Acetonitrile phase transitions: $\nu_2 + \nu_4$, C—N + C—C; $\nu_3 + \nu_4$, CH_3 def. + C—C. The combination modes show a rapid decrease in the presolid state. (Reproduced by permission from ref. 36.)

to the slight molecular readjustments that are necessary to produce different phases—a gradual gradation of properties through the liquid and into the solid is in fact apparent.

Water, of course, is the most extensively studied of all liquids because informed opinion holds that life may arise in, and be supported by, only a suitable aqueous medium.[38] Quoting Stillinger,[16] "it is only since 1960 that it has become technically feasible to produce a quantitative and deductive theory [see Vol. 1 of this issue] for liquid water without large elements of uncertainty. It is no coincidence that this period coincides with the general availability of rapid digital computers. These computers have provided essential numerical advances in both the quantum mechanical and statistical mechanical aspects of the field that underlie present understanding." Submillimeter spectra reveal the complexity of the water-molecule interactions, as well as subsequent dynamics that even now no theoretical molecular modeling successfully reproduces.[17] Rahman and Stillinger observed that the molecular dynamics depends strongly on the form of the hydrogen bonding in the liquid: "There was no evidence of a hopping process, but, rather, translational diffusion proceeds via individual molecules participating in the continual restructuring of the labile, random, hydrogen bond network." It is possible to break up the hydrogen-bonding network by dilution.[17] The effect of the hydrogen bonding is to broaden the zero-teraHertz spectral profile so that it spans eight or nine decades of frequency, compared with only two when the bonds are absent. This typifies the extremes of molecular behavior and properties that the isotropic liquid state may adopt. A full, consistent understanding in accord with the pertinent facts must start at the molecular level itself. It is not possible to explain many recent phenomena of the liquid state (some of which are discussed in later sections) with, for example, hydrodynamic theories that set out to explain liquid-state behavior in terms of macroscopic data. These do not consider the detailed molecular structure of the medium, let alone the structure of the molecules, as is so often necessary.

From the foregoing it is apparent that within the liquid state there may be many variations of molecular behavior. Near the freezing points considerable molecular rearrangement may occur, and pretransitional phases have been proposed. There may exist a considerable short-range structure that extends even to macroscopic distances in some liquid systems (liquid crystals). This structure disintegrates at the boiling point and some liquids even display the freedom of motion associated with the gas phase itself. Recently, another "new state of matter" has been proposed—a liquid crystalline state in which the sample is a *solid* film. Certain solid films of PBLG that show liquid crystalline properties represent "a new and very interesting phase of matter. It is quite possible that other rodlike molecules which exhibit a liquid crystal phase such as DNA can be induced to form the same state, in vitro or in vivo."[39]

II. COLLECTIVE MODES IN LIQUIDS

A. Liquid Crystalline Systems

We have seen that because of molecular shape a molecule's rotation may cause a simultaneous translation of neighboring molecules. Rotation and translation are mutually coupled and cooperative molecular behavior in liquids has its origin on the molecular level itself. If the center of mass is displaced from the center of interaction a correlation between translation and rotational degrees of freedom is introduced. This permits the explanation of some thermodynamic anomalies, such as the higher vapor pressure of HT compared with D_2 discussed by Babloyantz.[40] At 20.3 K the vapor pressure of HT is about 36% higher than that of D_2 and the molar volume and vapor pressure of HD are larger than the expected values obtained by interpolation from the values for H_2, D_2, and T_2.

Since rotation–translation coupling effects are so pronounced in these simple systems, they must also be present in other liquids. However, they are not easily distinguished using spectroscopic methods. Recent advances in computer technology are shedding new light on the problem. Various elements of the autocorrelation matrix $\langle \mathbf{p}(0)\mathbf{J}^T(t)\rangle$ show that the coupling of rotation with translation exists *for most molecules* and indirectly affects laboratory-frame autocorrelation functions measured with the spectroscopies. Here **p** is the *linear* center of mass momentum and **J** the molecular angular momentum. This mixed function vanishes for all times t in an isotropic molecular liquid in the laboratory frame because the parity of **P** to time reversal is opposite in sign to that of **J**.‡ The second-moment autocorrelation functions $\langle \mathbf{P}^2(0)\mathbf{J}^2(t)\rangle$ are invariant to frame transformation and may be observed in the laboratory frame. They provide us with a detailed description of molecular rototranslation, as may be seen in Fig. 8 for CH_3CN. Evans[15(a)] concludes that "the dynamics in the region of the boiling point may not be significantly affected by R–T interaction but the liquid–solid transition and molecular behavior in this region may be severely affected." These coupling effects are so important because, as Warner[41] points out in reference to liquid crystalline systems, "the ordering of rods under the influence of their packing density and shape is a purely entropic process.... ordering results from a coupling between the rotational and translational entropy of the rod.... such a coupling would be revealed down to wavelengths of the order of the rod dimensions." Our picture is therefore one of a local molecular order arising from steric constraints and from the tendency for molecules to order themselves over short distances as a consequence of their shapes and the requirement that "hard" molecules confined to a limited volume do not overlap. This short-range molecular ordering must arise to some extent in all condensed systems. And, as Warner points out, "this steric aspect of ordering is, given constancy of volume, independent of temperature. Experiments at constant volume confirm the constancy of the steric component of the ordering process."[42] The effect of molecular asymmetry in dominating correlations and leading to a residual short-range *orientational* order is discussed by Wulf.[43]

In the nematic phase of a liquid crystal, in addition to this short-range order (which must also be present in the isotropic phase), there exists a long-range order—molecules are oriented on the average with respect to a direction known as the "director." Long-range distortional fluctuations of this director exist, and new hydrodynamic modes (not present in normal liquids) associated with fluctuations of the director have been predicted.[44] Evans[45] has reported the resolution of new resonant modes in the nematic phase of a liquid crystal at submillimeter frequencies (Fig. 6).‡ He wrote that "the intensity and frequency of these modes are controlled by externally applied electric and magnetic fields. Their existence suggests that this spectroscopy may serve as a convenient tool for the study of liquid crystals." However, continuum theory shows that external fields damp out fluctuations in the director and reorient it so that it is either parallel or perpendicular to the fields. In strong enough fields (magnetic fields of > 1000 G), the director motion is prevented. Evans observed no indication of any disappearance of the modes in his experiment, even though electric fields an order of magnitude greater than the magnetic fields (a maximum of 1000 G) were used. Interestingly, Bulkin[46] reported that some mid-infrared bands disappear at the

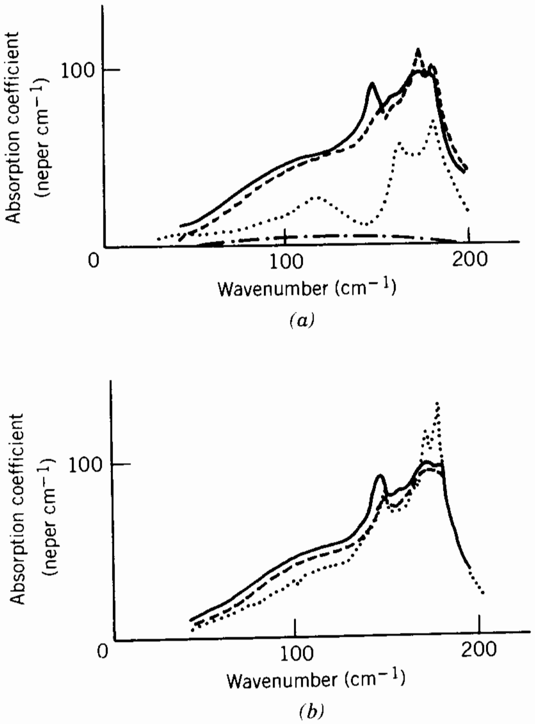

Figure 6. (*a*) Far-infrared spectrum of 4-cyano-4-*n*-heptyl biphenyl and related molecules: —— , 4-cyano-4-*n*-heptyl biphenyl at 296 K, nematic phase; ---, the same with a field of 7 kV cm^{-1} applied; · · · , 2.52 mol dm^{-3} 4-cyanobiphenyl in dioxan at 296 K corrected for solvent absorption; ·–·–, 0.9 mol dm^{-3} biphenyl in cyclohexane at 296 K corrected for solvent. (*b*) Far-infrared spectra of 4-cyano-4-*n*-heptyl biphenyl under external magnetic fields: —— , nematic phase with no field; ---, with a field of 400 G; · · · , with a field of 800 G. Note the appearance of sharp resonant modes in the nematic phase of the liquid crystal in strong electric and magnetic fields. (Reproduced by permission from ref. 45.)

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‡Evans has recently computed laboratory-frame rotation—translation cross-correlation functions in a polyatomic, chiral molecular liquid (M. W. Evans, *Phys. Rev. Lett.*, accepted, 1985).

crystal to nematic phase transition. Bulkin concluded that "these bands arise from sum and difference modes between lattice vibrations and internal vibrations...the disappearing bands are an indication of the coupling between molecules and hence are of importance in understanding ordering forces in the crystal as compared to those in the liquid crystal." Bulkin also reported pretransitional effects in the crystalline phase prior to melting, and that Schwartz and Wang[47] observed "striking changes in the relative intensity of several Raman bands as a function of applied external electric field strength in the nematic phase. Certain bands increased in integrated intensity, while others showed the opposite effect."

Evans has attributed his new modes to collective modes, that is, intermolecular or phonon vibrations. As Bulkin again says, "in the nematic phase we again have the possibility of observing 'pseudo-lattice' vibrations, i.e., intermolecular motions characteristic of the long range order in this phase...it may be possible to propagate phonons even in liquid crystals." There is not much evidence to support Evans's results in the nematic phase,[‡] but there is some in the case of more highly ordered smectic phases. Smectic phases, particularly such phases as smectics B and H, are, of course, much closer to crystalline phases than are nematics. So, Amer and Shen[48] observed that diethylazoxybenzoate and diethylazoxycinnamate, which have smectic A phases, each have a single low-frequency Raman mode in the crystalline phase, at 22 and 26 cm^{-1} respectively. In the smectic phase, this mode appears to shift, with the maximum at about 14 cm^{-1}. *It vanishes abruptly at the smectic A–liquid transition.* And Schnur and Fontana,[49] studying terpthal-bis-butyl aniline in the low-frequency, lattice-vibration spectrum region, observed that a number of bands in their spectra were almost the same in the smectic B phase as in the crystal. At the smectic B–smectic C transition most of this structure disappeared. Evans has reported the changes in the spectrum of 4-cyano-4-*n*-heptyl biphenyl as the sample was slowly cooled into the solid (Fig. 7). A constant magnetic field (600 G) was applied throughout the cooling process. It was anticipated that a uniaxial single crystal might be produced in this way. In this process the most intense absorption, at ca. 180 cm^{-1}, gradually shifts to the strongest lattice mode at ca. 165 cm^{-1} in the solid (Fig. 7 shows only two spectra), firmly establishing the common molecular origin of these two modes.

It is important to realize that the *local molecular order* may be as pronounced in the *isotropic* as in the nematic phase of a liquid crystal, and that the long-range order itself, which is characteristic of the nematic phase, is associated with and dependent on this well-established local order.

[‡] See also R. Chang, *Mol. Cryst. Liq. Cryst.* **12**, 105 (1971).

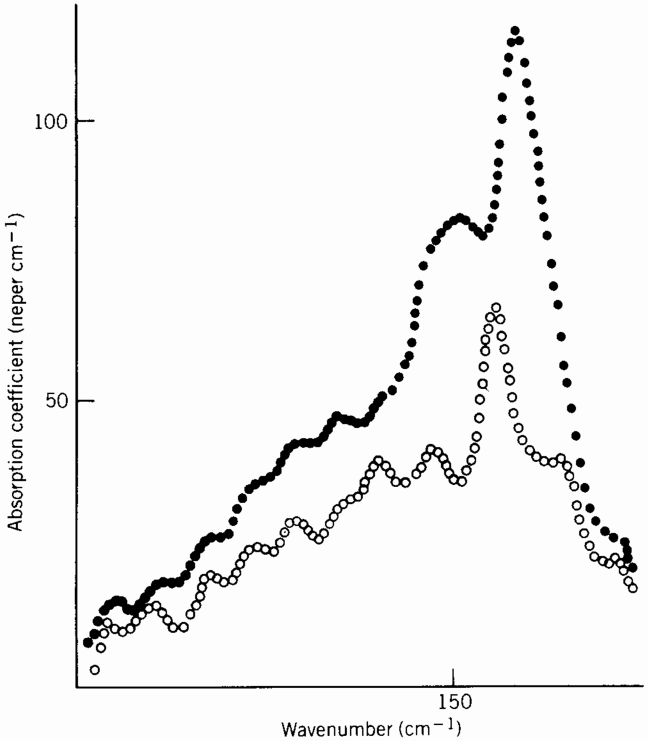

Figure 7. The far-infrared spectra of 4-cyano-4-*n*-octyl biphenyl as it is slowly cooled into the solid phase, with a field of 600 G applied throughout the cooling process: ●, 8 CB near the freezing point; ○, a single cyrstal of 8 CB. (Reproduced by permission from ref. 45.)

B. Isotropic Liquid Systems

What of isotropic, small-molecule molecular liquids? There is considerable evidence in the literature for some liquids that suggests that a significant local order exists extending to molecules that do not belong to the nearest-neighbor shell.[‡] For example, let us look at acetonitrile. It has a large dipole moment (3.9 D). Thermodynamic,[50] dielectric,[51] other spectroscopic,[52] and X-ray- and neutron-diffraction experiments[53] all reflect a strongly oriented structure in the pure liquid. For example, light scattering and nuclear magnetic[14] N relaxation probe the tumbling motion of the C_3 axis. In this

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[‡] A. R. Ubbelhode (*The Molten State of Matter*, Wiley-Interscience, New York, 1978) presents a dearth of other precise experimental methods for elucidating molecular texture in quasicrystalline assemblies such as the melt.

instance

$$\tau_{\mathrm{LS}} = g_{00}^{(2)} \tau_S$$

where τ_S is the single-particle orientational time and $g_{00}^{(2)}$ is the second-rank structure factor. If τ_{LS} and τ_S are studied in a solution of acetonitrile in a solvent that shows weak depolarized scattering and does not form complexes with acetonitrile, τ_{LS} and τ_S should become equal at infinite dilution, when pair correlations are negligible. It is observed[54] that the factor $g_{00}^{(2)}$ (from the ratio $\tau_{\mathrm{LS}}/\tau_S$) at lower concentrations is unity; that is, pair correlations vanish. In pure CH_3CN $g_{00}^{(2)}$ reaches a value of 1.4. This value of $g_{00}^{(2)}$ indicates that a more parallel or antiparallel configuration is favored (since $g_{00}^{(2)}$ is symmetrical with respect to 90°, it is impossible to distinguish between the two cases). Further information comes from the ordinary $g_{00}^{(1)}$ factor, which is 0.78 for acetonitrile at room temperature. This negative deviation of $g_{00}^{(1)}$ from unity suggests that antiparallel alignment is the most likely structure. That $g_{00}^{(2)}$ deviates more from unity than does $g_{00}^{(1)}$ can be understood if pair ordering extends to neighbors *that do not belong* to the first shell of reference particles. That is, there is a suggestion of a significant local order in CH_3CN arising from molecular-shape considerations, as discussed by Warner and Wulf, and from the strong intermolecular forces due to the large dipole moments.

Information about pair correlations, of course, may be obtained from diffraction experiments, results of which have been reported for acetonitrile. To obtain this information the maximum number of diffraction experiments must be carried out. Neutron experiments on different isotopes of the substance must be performed together with X-ray-diffraction analysis. For acetonitrile X-ray data are available, as are neutron-diffraction data for CD_3CN, $CH_3C^{14}N$, and $CD_3C^{15}N$. These data allow three coefficients of the molecular pair-correlation function to be calculated: $g_{00}^{(000)}$, the center–center correlation term; and the orientational correlation terms $g_{00}^{(101)}$ and $g_{00}^{(202)}$. For acetonitrile $g_{00}^{(000)}$ is composed of two fluctuations: one at 4.7 Å, corresponding to a first-nearest-neighbor peak; and a second at 8.5 Å, corresponding to a second-neighbor peak. The orientational correlation terms give information concerning the orientation of a molecule relative to the center–center system irrespective of the orientation of the partner molecules. For $0° \le \gamma \le 90°$, $g_{00}^{(101)}$ is negative, and for $90° \le \gamma \le 180°$, $g_{00}^{(101)}$ is positive. Also, for $0° \le \gamma \le 54.7°$ and $125.3° \le \beta \le 180°$, $g_{00}^{(202)}$ is positive, but for $54.7° \le \gamma \le 125.3°$ it is negative. Thus, below 4.4 Å preferred orientations of the dipole axis relative to the center–center line are found in the range $90° \le \beta \le 125.3°$, whereas from ca. 5.2 Å preferred orientations of $0° \le \beta \le 54.7°$ dominate. A second reversal is observed at 6.8 Å that restores the initial situation.

Another X-ray investigation[53(ii)] revealed a short-range structure consisting of a bundle of five molecules in which a central molecule is surrounded by four antiparallel neighbors. A pronounced correlation is observed between these five molecules. The cluster diameters are 11 Å. Each cluster has eight molecules occupying sites in an orthorhombic unit cell with 95% site occupancy. This is in good agreement with the cluster diameter D of 13 Å estimated using a theory of Loshe[55] based on dipolar interactions in liquids.

P. Ignacz[56] has proposed a new theory for the liquid state based on this postulate of a significant local structure in liquids. The fundamental hypothesis is that the physical behavior of liquids is determined by their molecular structure. Both electrostatic and steric processes participate in the formation of the structure. Ignacz suggests that during melting the solid crystal decomposes into uniform octahedral groups of molecules. These groups or elementary crystals he calls "liquid grains," and he shows that the cubic lattice of molecules built up by octahedral formations is complete without any lack or surplus of molecules. The grains, and within them the molecules and atoms, are in thermal motion. The six peripheral molecules of a grain are in vibration relative to the central molecule. If the value of the vibrational energy exceeds the bond energy, then the grain disintegrates. The thermal motion of grains can be described in terms of the laws of thermodynamics. At the boiling point a second *crystalline* change is assumed to occur during which all the grains decompose totally. Below the boiling point, distances between the peripheral molecules of neighboring grains are not essentially larger than distances within the grains; the ratio is about 1:1.3. These distances exceed those between molecules in a solid crystal by less than 10%. This is in accord with diffraction studies on liquids in which local structure and the distances of neighbors appear to remain approximately constant relative to those in the corresponding solids. Since the grains get close to one another in the liquids, their peripheral molecules have a mutual influence. This influence can be shown statistically to be attractive, which explains the cohesion of liquids.

Let us return to our discussion of acetonitrile. The existence of this pronounced local structure must complicate significantly any attempts to obtain single-particle properties (e.g., single-particle correlation times) using the various spectroscopies. In fact several types of relaxation can and do contribute to the decay of the correlations observed in the various experiments. Furthermore, these relaxations contribute differently to correlation functions determined from different experiments. The experimental situation is a complex one, and considerable uncertainty is still associated with the experinental measurements, with the reduction of the data to a form suitable for omparison with theory, and with the theories themselves, which are often versimplified. What we suggest now is a contribution of collective molecular motions to spectral profiles even in simple isotropic liquid systems.

Computer simulation (see the first article of this volume) shows that rotational motion is strongly coupled to translation in liquid CH_3CN. The moment of inertia of CH_3CN about the unique (C_{3V}) axis is about 18 times smaller than the other two (equal) principal moments of inertia. The anisotropy of rotational motion consequently is large and must involve simultaneous translation of the molecular center of mass. Mixed correlation functions with linear and angular momentum components exist in a moving frame of reference fixed in the molecule. For convenience this may be defined by the three principal moment of inertia axes. Vector quantities such **v** (the center of mass velocity), **J** (the angular momentum), **F** (force), and **Tq** (torque) may be defined in either the laboratory or the moving frame. We denote the components of **v**, for example, in the laboratory frame by v_x, v_y, and v_z; and in the moving frame by v_1, v_2, and v_3. If we define three unit vectors $\mathbf{e}_1$, $\mathbf{e}_2$, and $\mathbf{e}_3$ with respect to the frame (1,2,3), the velocity components are then related by

$$v_1 = v_x e_{1x} + v_y e_{1y} + v_z e_{1z}.$$

$$v_2 = v_x e_{2x} + v_y e_{2y} + v_z e_{2z}$$

$$v_3 = v_x e_{3x} + v_y e_{3y} + v_z e_{3z}$$

In symmetric top CH_3CN $|\mathbf{e}_1| = |\mathbf{e}_2|$, so that $v_1 = v_2$. In these relations e_{1x} is the x component of $\mathbf{e}_1$ in the laboratory frame and so on.

Having made the transformation into the moving frame for each vector $\mathbf{v}_1$, **J**, **F**, and **Tq**, we can simulate the various auto- and mixed correlation functions of interest, for example, the function $\langle \mathbf{v}(t)\mathbf{J}^T(0)\rangle / (\langle v_i^2(0)\rangle^{1/2} \langle J_i^2(0)\rangle^{1/2})$, where the angle brackets denote a running-time average over vector components defined with respect to the moving frame of reference (1,2,3). The functions describe in detail the interaction of rotation with translation in acetonitrile molecules in the liquid state. By symmetry, all the elements of $\langle \mathbf{v}(t)\mathbf{J}(0)^T\rangle / (\langle v_i^2(0)\rangle^{1/2} \langle J_i^2(0)\rangle^{1/2})$ vanish except the (1,2) and (2,1) elements. Figure 8 shows that these elements are mirror images of each other peaking at ±0.23 and vanishing by symmetry at $t = 0$.[57] The existence of these functions provides direct information on rototranslational and cooperative molecular motion. The molecular dynamics of a heteronuclear molecule such as CH_3CN in the condensed state *may not* be approximated by the customary, and still popular, theories based on rotational diffusion alone. Evans[58] and Ferrario[59] have recently developed the traditional Langevin and Fokker Planck equations so that they may be used with rototranslation. As Berne and Montgomery[60] say, "spectroscopic techniques rarely if ever determine the pure reorientational correlation functions

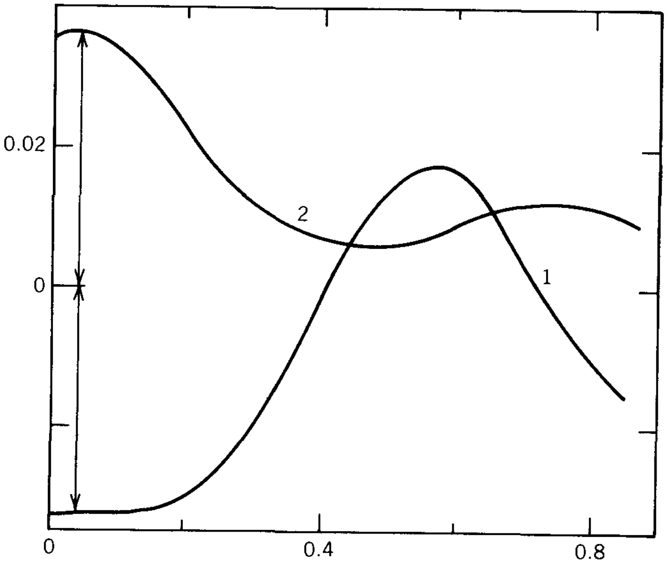


Figure 8. Pronounced rotation–translation coupling in CH_3CN as displayed by computer simulation, with $\langle \mathbf{v}(t)\mathbf{J}^T(o)\rangle$ in the moving frame. 1, (1,2) component; 2, (2,1) component. These functions provide directly information on rotation–translation coupling on the molecular scale. This coupling is the cause of cooperative molecular motions. (Reproduced by permission from ref. 57.)

$$C_\ell(t) \equiv \langle P_\ell(\mathbf{u}(0)\cdot\mathbf{u}(t))\rangle,$$

where $P_\ell(x)$ is the Legendre polynomial of order ℓ and **u** is a unit vector embedded in the molecule. Instead the correlation functions

$$C_\ell(\mathbf{k}, t) \equiv \langle P_\ell(\mathbf{u}(t)\cdot\mathbf{u}(0))\mathrm{exp}t[i\mathbf{k}\cdot\Delta\mathbf{r}(t)]\rangle$$

are determined where $\Delta\mathbf{r}(t) = \mathbf{r}(t) - \mathbf{r}(0)$ is the displacement of a molecule in a time t and **k** is the wave vector defining the scattering between the probing beam and the molecules of the fluid." Berne and Montgomery's calculations were based on a rough sphere model and did not take molecular shape implicitly into account. They add, therefore, that

> real molecules, unlike rough spheres, sweep out a volume larger than the molecular volume when they rotate. Thus in dense fluids volume fluctuations

> must occur if these molecules are to rotate in certain directions. This should lead to a much stronger coupling between rotational and translational motions in real molecular liquids than in rough sphere fluids. And, by establishing the importance of coupling in rough sphere fluids [which they did], it becomes all the more obvious that these effects should be heeded in real molecular liquids.

So, there exists a pronounced interaction of rotation with translation and a significant local molecular structure in acetonitrile. This structure may persist in solutions of 10% and lower concentration, may actually be increased, and varies with the solvent used. For example, the relaxation time in benzene (25% volume/volume) is 6.7 ps at 297 K, decreasing to 3.1 ps at 333 K. In CCl_4 under the same conditions the relaxation times are 7.6 and 4.5 ps, respectively. Care must be exercised in using solvents to eliminate correlation effects, as is customary in, for example, nuclear magnetic resonance (NMR) experiments. Solvents may actually increase the apparent molecular aggregation.[15(b)] As Michel and Lippert[36] have said, "the environment of a single acetonitrile molecule is lattice-like and even solutions are influenced by this structure...in solutions in organic solvents a lattice-like orientation with mainly axial effects is dominant. Small molecules like LiBr, HBr, Br_2 and water take the lattice place of one acetonitrile molecule." Acetonitrile behaves as a waterlike organic solvent. Its local structure is extremely stable and survives even if the local lattice is disturbed by the interaction of ions in the system. The local lattice is stabilized by the strong electrostatic interactions arising from the large dipole moments of the molecules, just as the structure of water is stabilized by the three-dimensional hydrogen-bonded network. The structure of water is so stable that at ambient temperature and pressure a saturated solution of cesium fluoride in water contains ions and water molecules in the ratio 1 : 1.2. This extraordinary stability arises, of course, because the two particles are isomorphous and can be interchanged in the local lattice structure.

The stability of the CH_3CN local structure in CCl_4 is displayed in Fig. 9. The plot remains linear up to 20% (volume/volume) acetonitrile in CCl_4. Only thereafter is a striking nonlinearity observed as the local structure is disrupted. The frequency of maximum absorption of the far-infrared spectra is denoted as $\bar{\nu}_{max}$. If such spectra could be analyzed with purely rotational models for the molecular motions then, as Reid[61] has discussed, this feature of the spectrum could be related in a simple way to intermolecular mean-square torques. However, as we have established, such absorptions are in fact rototranslational in origin and, in the absence of a suitable theoretical model for such motion, $\bar{\nu}_{max}$ presently has an unknown dynamical significance. But

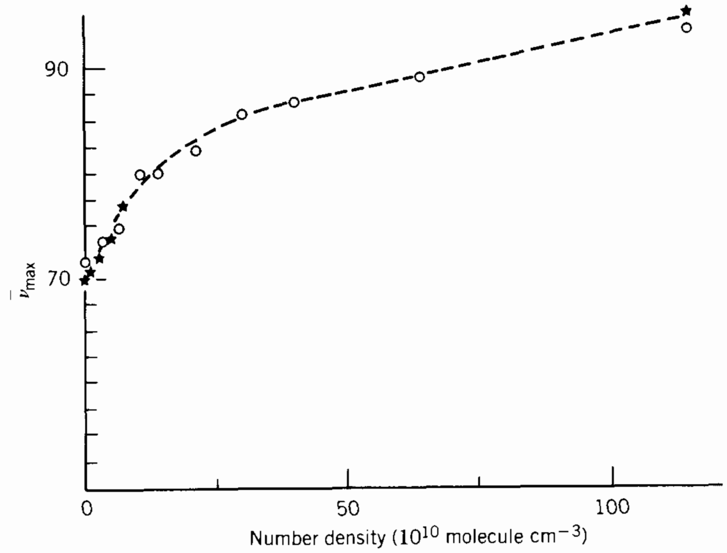


Figure 9. Variation of $\bar{\nu}_{max}$ with number density for CH_3CN in CCl_4: ●, data of Evans;[13] ○, data of Yarwood (personal communication). $\bar{\nu}_{max}$ is the frequency of maximum absorption of the far-infrared spectrum. The nonlinearity of the plot demonstrates the breakup of the liquid CH_3CN local structure in an approximately 20% solution. At this point CCl_4 molecules replace CH_3CN molecules at local lattice sites. (Reproduced by permission from ref. 13.)

we can be sure that it reflects in some way local changes in the intermolecular interactions, because the far-infrared frequency region is the energy range of intermolecular interactions and the time range of collisional and molecular relaxational processes.

Following the example of Lippert, it is revealing to compare the liquid and solid phases of CH_3CN. Two solid phases are known (α and β), though an additional γ-phase has been postulated. The α-phase is orthorhombic, with eight molecules per unit cell; the β-phase is probably a glassy phase. Comparisons of the α-phase and β-phase spectra indicate perturbations of the intermolecular symmetry. There is a loss of long-range order in the β-phase that reduces the degree of coupling of lattice vibrations. Lippert has calculated values for *inter*molecular vibrations for the α-, β-, and liquid phases. The intermolecular distances along two axes in the liquid are the same as those in the α-solid. In one perpendicular direction, however, the distance is significantly longer. Consequently, in this direction the frequency of the *inter*molecular vibration is reduced from 116 cm^{-1} in the α-solid phase to 87 cm^{-1} in the liquid. The frequencies corresponding to the two intermolecular distances that are approximately the same in the liquid and β-solid are the

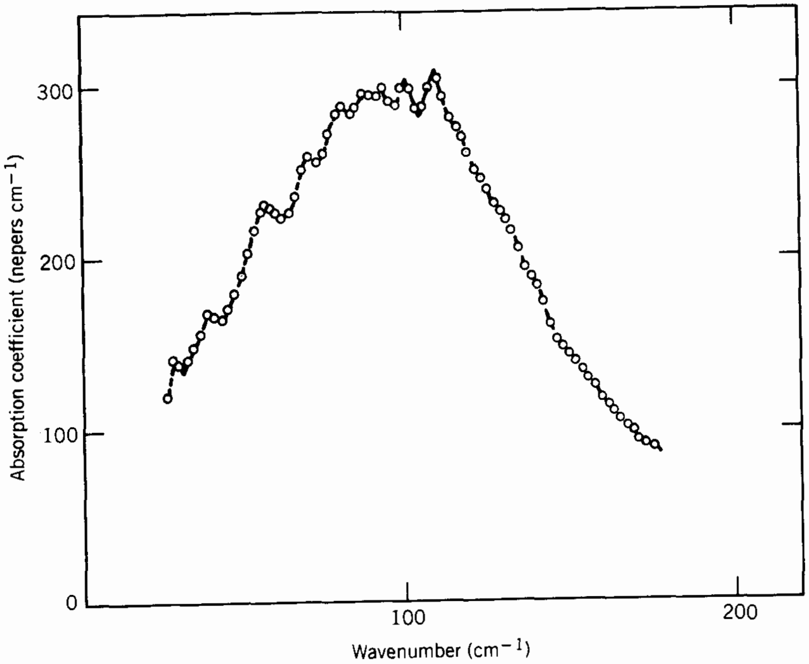


Figure 10. Absorption spectrum of CH_3CN (isotropic liquid state) at far-infrared frequencies. Features are resolved on the low-frequency side of the spectrum. (Reproduced by permission from ref. 62.)

same (50 cm^{-1}). Are such *inter*molecular vibrations resolved in spectra of the liquid? If they were they would provide directly information on the intermolecular forces in the liquid.

Evans[13] has rerecorded the far-infrared spectrum of CH_3CN neat and in solution. He suggests that spectral details are resolved on the low-frequency side of the overall spectral contour for the neat solution and in the region where they have been estimated (Lippert, above) (Fig. 10). These details disappear at sufficiently low concentrations (< 10% volume/volume) of CH_3CN in CCl_4 (Fig. 11), as one would anticipate. It is encouraging that Evans's spectrum for the neat liquid is similar to that of Yarwood when the same window materials are used, even though the measurements were recorded on different makes of spectrometer.[62] It is also encouraging that the decay of the contour at higher frequencies is very smooth, which gives some indication of the low noise level of the instrument. However, having said this, we must emphasize that acetonitrile is a strongly absorbing liquid, so we must work at the absolute limits of present-day instrumentation. Only higher-precision apparatus will confirm or refute these results.

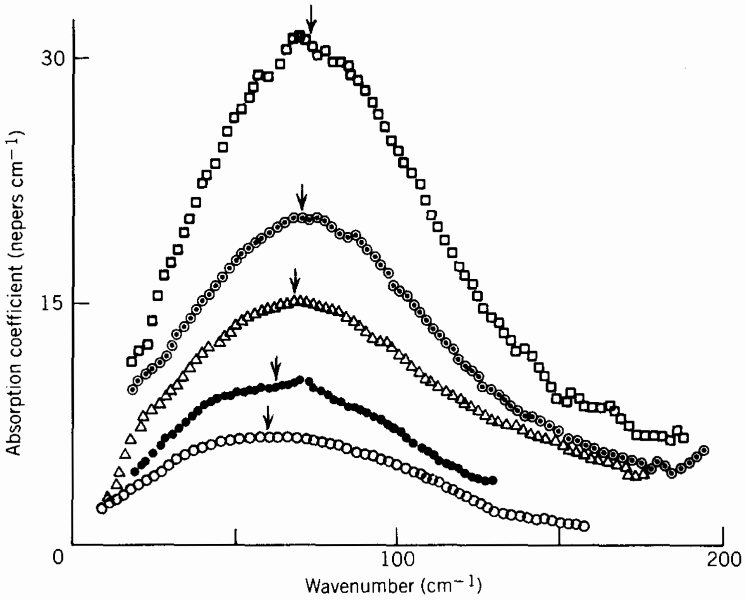


Figure 11. Far-infrared spectra of CH_3CN in CCl_4 at number densities between 7.2 and 0.6×10^{20} molecules cm^{-3}: ⌖, 7.2×10^{20}; ⊙, 4.9×10^{20}; △, 3.3×10^{20}, ●, 1.2×10^{20}; ○, 0.6×10^{20}. *Note:* The resonant modes at lower frequency disappear in dilute solution as the pronounced local structure is disrupted. (Reproduced by permission from ref. 13.)

Gerschel[63] is presently reporting "the existence of an unexpected resonant absorption in CH_3Cl at millimetre frequencies" (Fig. 12). CH_3Cl is, of course, another strongly polar molecular liquid. Gershel's results, obtained using a carcinotron source available in Warsaw, are of high precision and high resolution. He explains his resonant millimeter absorption in terms of a dynamical coupling effect that is basically the same physical process as that assumed responsible for the appearance of long time tails in velocity autocorrelation functions (Fig. 13). The usual exponential behavior of the angular-velocity autocorrelation function at long times is replaced by one that varies roughly as $t^{-5/2}$. It is observed in the computer simulation of Tresser[64] that the more elongated the rotary molecule is, the more pronounced is the deviation from logarithmic decay. Because a molecule's rotation is coupled to its translation, the effect of a molecular rotation must be to cause neighboring molecules to translate in a coherent fashion; that is, a vortex is set up in the surrounding ensemble in which there is a marked degree of correlation between the linear velocities of the molecular centers of mass. Using generalized hydrodynamics, Ailawadi and Berne[65] have shown the normalized angular-velocity correlation function $\langle\omega(t)\cdot\omega(o)\rangle/\langle\omega^2\rangle$ to decay

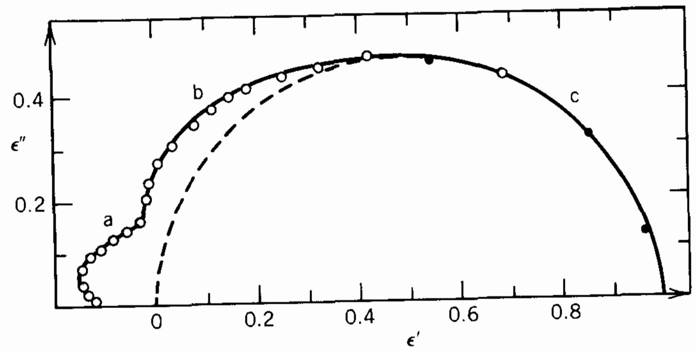


Figure 12. Normalized Cole–Cole plots of the complex permittivity for CH_3Cl at 273 K: —, experimental results; ---, predictions based on Debye's equation. Note the resolution of three absorptions, a, b, and c: a is the normal, far-infrared "Poley absorption"; b is a new resonant absorption in a polar liquid and is multimolecular in origin; and c is the Debye relaxational process. In terms of the normal absorption versus wavenumber spectra this resonant absorption peaks at $< 20\ \text{cm}^{-1}$. It is important to realize that the frequency regions 1–10 cm^{-1} and 10–100 cm^{-1} are *two decades* of frequency. It is common practice, however, to characterize this whole frequency span with about ten data points, as above. High-precision, high-resolution results on such liquids are still required.

asymptotically as

$$C\omega(t) = \frac{d\pi I}{2mn}\left[4\pi(D+\nu)\right]^{-(d+2)/2} t^{-(d+2)/2}$$

where I, m, n, ν, D, and d are, respectively, the molecular moment of inertia, molecular mass, number density, kinematic shear viscosity ($\nu = \eta/mn$), self-diffusion coefficient, and dimensionality of the system. For planar motion, $d = 2$, and in space, $d = 3$. It follows that the orientational correlation functions

$$C_\ell(t) \equiv \langle P_\ell[\mathbf{u}(t)\cdot u(0)]\rangle$$

also behave asymptotically as $t^{-(d+2)/2}$, *if the effect of molecular translation on rotation is accounted for*. This asymptotic behavior of $C_\ell(t)$ was calculated from the "hydrodynamic equations" used to describe a feature of depolarized light scattering called the "shear doublet" or "Rytov dip," observable at low frequency (Fig. 14). It is proposed that this dip originates from local strains, set up by transverse shear waves, that are relieved by collective reorientations—a macroscopic or collective translation–rotation coupling. This shear dip does not appear to be related to a specific microscopic structure and has been observed in a number of molecular liquids, including

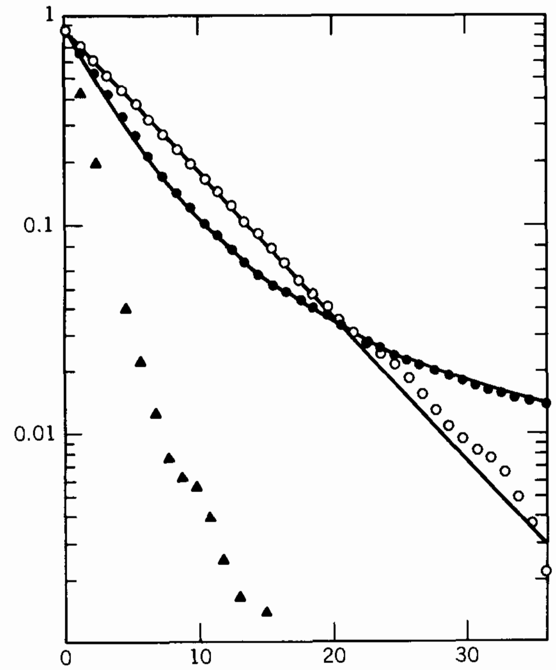


Figure 13. Semilogarithmic plots of the orientational autocorrelation function (▲), the velocity autocorrelation function (●), and the angular-velocity autocorrelation function (○) from a molecular-dynamics simulation of a two-dimensional system of 1600 diatomic molecules with periodic boundary conditions, atom–atom potential. (Reproduced by permission from ref. 64.)

polar and nondipolar liquids, and liquids containing planar and nonplanar molecules and both large and small molecules. It would be interesting to characterize the feature in terms of the symmetries of the molecules concerned and to discern whether in fact these observations have molecular origins. The shear waves are analogous to transverse phonons in a crystal.

Evans[62] reports that a *series* of absorptions appear on the low-frequency side of the far-infrared spectrum of CH_3CN. There also appear to be significant polarization effects. Such observations had been predicted by Ascarelli,[66] who pointed out that if a spectrum is composed of collective modes then there should be observable differences when different configurations of the polarized radiation are used. Also, a series of absorptions might be anticipated if the motions of aggregates of molecules are indeed contributing to the spectrum. A whole set of intermolecular vibrational transitions that may strongly but *incompletely* overlap is then possible. Michel and Lippert[36] propose the existence of collective modes in this liquid to explain the presolid state that exists just before freezing and does not depend on the

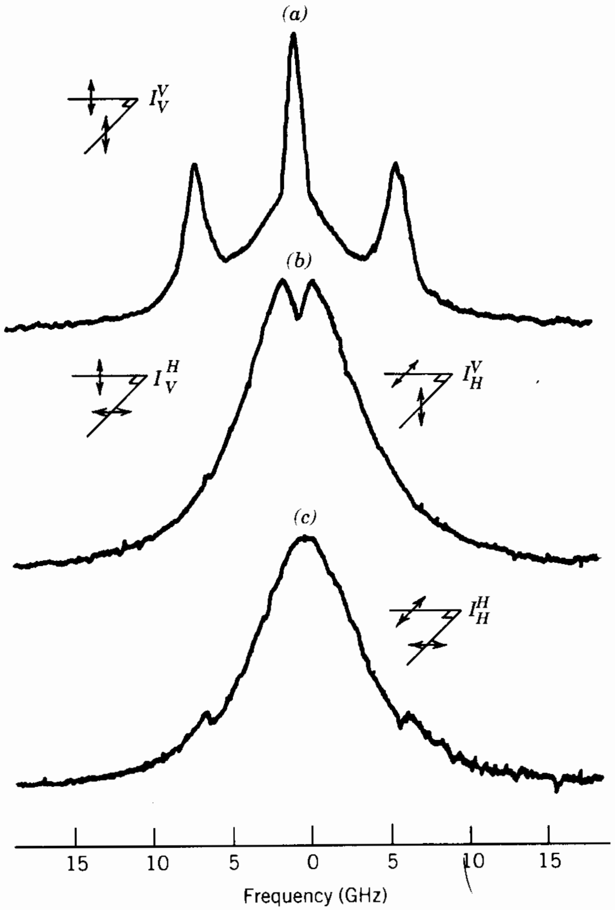


Figure 14. High-resolution polarized and depolarized spectra of quinoline showing (*c*) deviation from a simple Lorentzian and the emergence of (*b*) a "shear wave" or "Rytov dip" in VH and HV spectra. [Reproduced by permission from G.I.A. Stegeman et al., *Phys. Rev.*, **A7**, 1160 (1973).]

temperature of freezing. As we saw in the last section, the freezing point varies and a significant hysteresis occurs on heating and cooling the material through the melting point. A sudden increase of the maximum intensities of the normal infrared modes coupled with a sudden decrease of the combination modes occurs near the freezing point. Michel and Lippert postulate the existence of strong cooperative phenomena originating from a coupling of the molecular oscillations and state that "collective modes might be the basis of the cooperative phenomena. . . . the discussion of collective modes leads us to a model of waves in liquid acetonitrile. . . . different waves must interfere and because of this the waves themselves will fluctuate. The dimension of the dynamical order in the liquid can be described through the size of the region of the expansion of the phonon-like waves." Fini and Mirone,[67] using isotropic and anisotropic Raman scattering, have also identified cluster vibrations on the shoulders of the ν_2 and ν_4 fundamentals.

Lobo et al.[68] have presented a theory of collective molecular behavior in the liquid state that predicts the existence of collective modes. Starting from the dynamical extension of the Onasager theory developed by Nee and Zwanzig,[69] but generalizing it so as to be applicable at high, far-infrared frequencies, they studied the dynamical dielectric response of a condensed system of molecules with permanent electric-dipole moments. The dielectric function so obtained, and consequently the far-infrared absorption, contains a diversity of both collective and single-particle behaviors. This supports the conclusions that Knozinger et al.,[70] Evans,[13] and Gerschel[63] arrived at from experimental considerations. The first two propose that *the submillimeter band is composite in nature*, with contributions arising from single-particle motions, the motions of dimers, and the motions of higher aggregates of molecules. Evans et al. discuss the first in detail in their text *Molecular Dynamics*.[17] The existence of dimers of CH_3CN has been postulated *even in the vapor phase*. Rowlinson's[71] second-virial-coefficient calculations for ΔU locate the maximum value of the dipole–dipole energy interaction at 4640 cal mol^{-1}, *which is larger than even that for water*, 4440 cal mol^{-1}. Interestingly, vibrations of the dimeric water band have been isolated, and at far-infrared frequencies. Harries et al.,[72] in a study of the Earth's atmosphere using the sun as a source, reported an absorption feature between 7 and 9 cm^{-1}, which they attributed to the dimeric water species. Dimers and higher clusters of water molecules are known to exist in isolation in the Earth's atmosphere. Jakobsen and Brasch[73] have also proposed a contribution to the far-infrared profile in acetonitrile from dimers of molecules. Bulkin[74] tested their hypothesis by measuring five aliphatic nitriles. He found that if the spectra of dilute solutions of CH_3CN were measured in nonpolar solvents and concentrations were such that the product obtained by multiplying concentration by pathlength was kept constant, then it was not possible to measure a decrease in the intensity of the absorption band. He explained this observation in terms of a simple monomer-dimer equilibrium.

A contribution to the spectral profile from higher aggregates of molecules is established if, following Knozinger et al., one studies the temperature dependence of the spectra at higher concentrations, when aggregates are most likely to exist. Both total band intensity and frequency of maximum absorption are seen to decrease when the temperature is raised between 263 and 313 K. In addition there is an increase in the band intensity at 263 K and a decrease in the total band intensity at 313 K when one increases the concentration; at the same time, an increase of concentration shifts the band maximum to higher wavenumbers independently of the temperature applied. All of this can be explained only if *at least two* different types of aggregates are present. A *whole set* of intermolecular vibrational transitions are then possible. Intermolecular vibrations associated with vibrations of hydrogen bonds, in structures stabilized by hydrogen bonds, are well known. But the hydrogen bond is only one of the known intermolecular links. The acetonitrile structure is stabilized by strong dipolar interactions. It is easy to show, for example, that the large dipole moment associated with the molecule is actually necessary for the existence of the liquid at room temperature. So, should we not then have anticipated the existence of absorptions arising from fluctuations of this significant local molecular order? This order is so well established that dielectric experiments suggest that the relaxation times of CH_3CN in CCl_4 and benzene may actually be increased initially upon dilution[79]—the solvent apparently *encourages the association of solute molecules*. In much the same way, in the classic example of 2,6-lutidine in water, the lutidine molecules *increase* the water structure. Frank and Evans in 1945 compared this increase in structure with "the formation of an iceberg around a hydrophobic molecule."

The contribution of collective modes to far-infrared spectra implies that the wavevector **k** remains finite at these frequencies, as Berne and Montgomery[60] have proposed. Following Lobo et al.,[68] if we deal with a Kirkwood correlation sphere containing a large number of molecules and do not restrict the cavity region to the volume around only one molecule, the relevant O-THz correlation function is

$$\frac{1}{k^2\mu^2}\left\langle \mathbf{k}\cdot\boldsymbol{\mu}_i(t)e^{i\mathbf{k}\cdot\mathbf{r}_i(t)}\sum_j \mathbf{k}\cdot\boldsymbol{\mu}_j(0)e^{-i\mathbf{k}\cdot\mathbf{r}_j(0)}\right\rangle$$

where the sums run over all the molecules within the Kirkwood sphere centered on $\mathbf{r}_i(0)$ and $\boldsymbol{\mu}_i(t)$ and $\mathbf{r}_i(t)$ are Heisenberg picture quantities. The $\mathbf{k}\cdot\boldsymbol{\mu}$ terms appear because it is the polarization charge density that now responds to our scalar probe *and not* the polarization, as tacitly assumed in more simplistic approaches. For $\mathbf{k}\to 0$ we are left with a *time-dependent Kirkwood correlation factor*

$$\left(\frac{1}{3\mu^2}\right)\left\langle \boldsymbol{\mu}_i(t)\cdot\sum_j \boldsymbol{\mu}_j(0)\right\rangle$$

This may be evaluated only by computer molecular dynamics. The familiar Kirkwood static correlation factor

$$\left(\frac{1}{\mu^2}\right)\left\langle \boldsymbol{\mu}_i(0)\cdot\sum_j \boldsymbol{\mu}_j(0)\right\rangle$$

is recovered only at $\mathbf{k}=\mathbf{0}$. This gives us *no information concerning the dynamics*. As Lobo et al. say for H_2O, "symmetric orientation about the tetrahedral directions, by whatever mechanism and however slow, would suffice to give the Kirkwood value of the static correlation factor, which accordingly implies very little about the dynamics."

Consider a fluid made of ions. Here we may define a charge density (in c.g.s. units) via the Poisson equation

$$\nabla\cdot\mathbf{E} = 4\pi q\delta p$$

where q is the particle charge and $\mathbf{E}$ an external applied field. A term proportional to $\mathbf{E}(\mathbf{r},t)$ must be applied to the Navier–Stokes equation. When solved, this leads directly to a plasma frequency

$$\omega_p^2 = \frac{4\pi pq^2}{M}$$

where M is the particle mass. The frequency of collective oscillations does not vanish as $|\mathbf{k}|\to 0$ in this case, but approaches ω_p. This collective oscillation in the ionic fluid is called the plasmon and may be simulated by computer molecular dynamics. In some molten salts it is possible to separate and identify the fluctuations in density and those in charge density. The former determine sound-wave propagation; the latter determine the plasmons and are the liquid-state analogues of the acoustic and optic longitudinal phonons in an ionic crystal. These show up in the far infrared for ionic crystals and have been identified, for example, by Wegdam and van der Elsken.[75]

There is a great similarity between ionic melts and molecular liquids. The dominant interaction in the ionic melt is the Coulomb interaction between the charged particles, which is attractive for unlike charges and repulsive for like charges. The induction effects must be larger than in an organic molecular liquid, because the dipole induced by a charge is larger than that induced by a dipole. Even in a dilute gas the ions are associated with dipoles, quadrupoles, or higher multipoles. It is because the interaction between the multipole associates dies off rapidly with distance that ionic melts and molecular liquids are so similar.

By similar analogy, therefore, if we consider a molecular liquid and substitute for the charge density the polarization charge density, as proposed above, then the plasmon frequency of polarization-charge-density fluctuations in the molecular liquid is the liquid-state analogue of the longitudinal optical phonon mode that may be observed in the far-infrared spectrum of a molecular crystal. Molecular crystal phonon modes are classifiable into those of translational and those of rotational origin.

The predicted frequencies of Lobo's longitudinal (ω_p) and transverse collective (ω_t) modes are

$$\omega_p^2 = \omega_t^2 + \omega_0^2$$

where

$$\omega_0^2 = 4\pi\left(\frac{N}{V}\right)\left(\frac{\mu_v^2}{I^*}\right)\frac{(\varepsilon_\infty + 2)^2}{9\varepsilon_\infty} \qquad \text{(I)}$$

and

$$\omega_t^2 = \left(\frac{k_B T}{I^*}\right)\left(1 + \frac{2\tau_0}{\tau}\right) \qquad \text{(II)}$$

where N/V is the number density of dipoles, μ_v is the value of the dipole moment in a vacuum, $(I^*)^{-1} = (I_1^{-1} + I_2^{-1})$ is the average moment of inertia for rotations of the dipolar molecule around an axis perpendicular to the dipole moment, and ε_∞ is the high-frequency dielectric constant of the liquid surrounding the dipole.

Ascarelli[66] studied nitromethane as a characteristic dipolar liquid with a large dipole moment (3.4 D) in which he anticipated collective modes might be isolated. The prerequisites laid down by Lobo et al. for the existence of collective modes were "physical systems composed of neutral molecules with large permanent dipole moments (~ 1D). They should also have small moments of inertia and large $\varepsilon_0/\varepsilon_\infty$." Ascarelli's results for the power reflection spectra of different solutions of nitromethane in CCl_4 are shown in Fig. 15. That the structure assigned to ω_p is collective was demonstrated by inserting a Mylar electret into the sample. The observed value of ω_p shifted from ca. 30 to 60 cm^{-1}, the Mylar electret producing a further aggregation of dipoles. Also, this feature completely disappeared when the light was polarized perpendicular to the plane of incidence, confirming its longitudinal oscillation assignment. The structure assigned to ω_t was present in all polarizations and was in excellent agreement with the absorption measured by Kroon and van der Elsken in a 0.7% solution of nitromethane in *n*-heptane by transmission methods. Insertion of the measured values of ω_p and ω_t for pure nitromethane into Eq. (1) gave a value for ω_0 that was in excel-

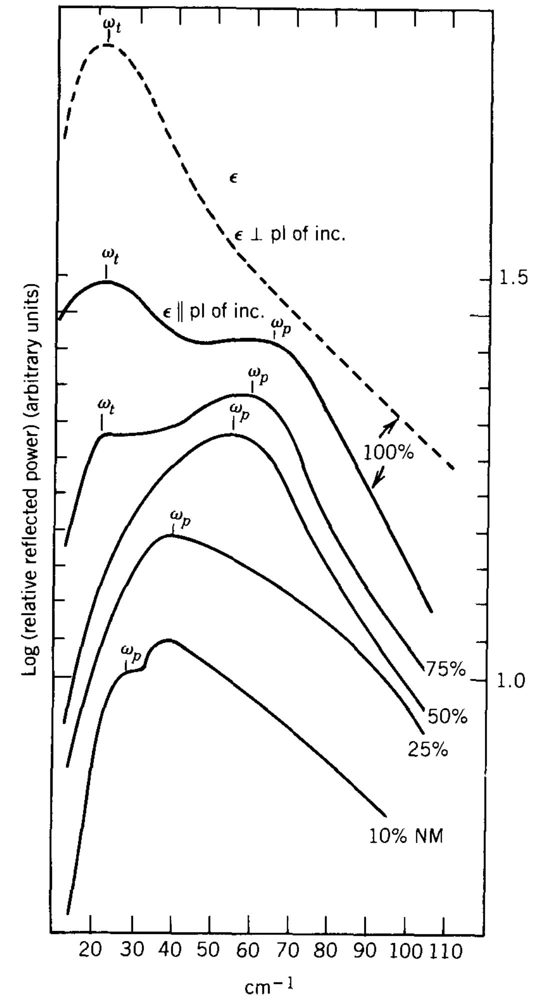


Figure 15. Power reflection spectra of different solutions of nitromethane in CCl_4. Polarization is either in the plane of incidence (∥) or perpendicular to the plane of incidence (⊥). The scale on the right side of the figure refers only to the spectrum of pure nitromethane with light polarized in the plane of incidence. Different spectra are displaced vertically for clarity. Note that ω_p shifts to lower frequency with dilution. ω_t remains approximately constant and in agreement with absorption measurements. (Reproduced by permission from ref. 66.)

lent agreement with the value calculated using independently measured parameters.

Two features of Ascarelli's measurements were not in accord with the theory of Lobo et al. First, the theory predicts sharp lines, whereas the observed spectra were much broader than this. Second, the spectra frequently showed extra structure that was not predicted by theory, in much the same way that Evans's spectra for CH_3CN showed a series of absorptions. It is important to recall, therefore, the assumptions used in Lobo's theory: "In any system, however strong the interactions, the 'elementary constituents' will evolve dynamically like free particles over some initial interval following an arbitrary zero of time. By elementary constituent we mean a physical entity whose internal structure is, or is treated as if it were, *fixed* and *constant*. In our present model, these elementary constituents are *rigid, non-polarizable* molecules and this initial motion is free translation and free rotation." That is, flexibility of the molecules, the coupling of rotation and translation, and the polarizability of the molecules are not allowed for. Density fluctuations and the existence of intramolecular motions would certainly contribute to a broadening of the spectrum beyond the calculated value.

Before leaving this section, we must mention that several important new areas of research that may give information on these topics are now receiving considerable attention. The first is microcluster physics. Microclusters are defined as aggregates existing in appreciable proportions, where the aggregates may be atoms, ions, molecules, and so on that have lifetimes longer than the characteristic inverse frequencies for internal motions. This field is already causing a shift of interest in, for example, the very economically important field of catalysis from the study of surfaces as general adsorbing substrates with locally important electronic properties to the study of definite few atom features of cluster type known to be present on the surfaces of many active preparations. And insights are being gained into the nucleation process on an atomic level rather than through the more conventional and restricted continuum approach.

Microclusters composed of no more than a few molecules can now be prepared. As a consequence it is emerging that the thresholds for the onset of effectively "macroscopic" properties may, somewhat against our preconceptions, actually be in the microcluster size region. Melting transitions are surprisingly well-defined at the $N = 100$ level, and superconductivity and ferromagnetism have been shown to set in at cluster sizes that are surprisingly small to exhibit phenomena of long-range order. Wegener and coworkers[76] have carried out Rayleigh scattering measurements in controlled expansions of H_2O and observed that nucleation starts with a critical nucleus undoubtedly in the $N < 100$ range. It is interesting that helium clusters are the only species so far known unequivocally to be liquidlike under the conditions of nozzle expansion. (The clusters are made with high-velocity expanding jets. It is possible to produce selectively quite high concentrations of bound clusters from the dimer to the $N = 100$ range.) The result for helium is perhaps not so surprising if we recall from an earlier part of this review that it remains liquid down to 0 K and may be solidified only under considerable external pressure at this absolute temperature. Farges et al.[77] have produced argon clusters with size range below $N = 100$ and have determined a pentagonal symmetry giving way to a normal fcc structure at the level of some 1000 atoms.

The appearance of bulk properties on such microscopic scales is good news, of course, for the computer simulator, who, because of computer size and speed, is presently restricted to studying small ensembles of molecules. It is bad news for the hydrodynamicist, who does not consider the detailed structure of the medium, let alone the structure of molecules. Continuum theories *cannot* project short-range effects.

The second important new technique is the use of electrons as microscopic probes of the fluid.[78] The molecular structure in the fluid is reorganized only slightly to accommodate the electrons. It appears that even in condensed gases and supercritical vapors the electrons may be solvated and stabilized. On injection of the electrons, a cavity is created and the dipoles making up the inner walls of the cluster line themselves up in the field of the electron. Countereffects from repulsive dipole–dipole interaction also contribute to determining optimum cavity size, and the continuum, defined as the fluid outside the coordination shell, is polarized in response to this field of the electron. Thus, electrons residing in clusters can be viewed as microscopic probes of both the local structure and the molecular dynamics of the liquid. This enables us to study the evolution of the system from a single particle to a collective state. Trapped electrons in liquids exhibit far-infrared absorptions. Kenney-Wallace[78] says that "the evidence from solvated electron studies points toward a molecular model in which a delocalized electron is initially trapped within small molecular clusters, whose configuration relaxes under the influence of the electronic charge while the molecular structure grows. The excess charge may be distributed over a cluster of 4–12 molecules"—a conclusion in accord with many of the inferences we have made throughout this section. Kenney-Wallace also points out that "there is a symbiotic relationship between the excess electron and its supporting fluid, one which demands an understanding of the local structure prior to the addition of the electron. Not so surprisingly, such molecular details are seldom anticipated through a knowledge of only the bulk properties of the liquid."

In the presence of the solvated electron, inner molecules remain locked in their configuration for the lifetime of this electron, which at 295 K ranges from 10^{-9} to 10^{-4} s for most liquids—an indication of the lifetime of the local structure in a liquid. There is a characteristic vibration peaking from ca. 500 cm^{-1} upwards associated with the cluster as a whole. As an example of the results that may be obtained, the spectra and dynamics of a solvated electron in alcohol–alkene systems apparently remain unperturbed for dilutions $\chi_{\text{ROH}} < 0.15$, indicating that the structural integrity of the cluster is maintained. All absorptions undergo a shift to lower frequency with increasing temperature, consistent with the idea that the structure is loosened as the thermal energy is increased. When subjected to pressures on the order of kilobars, the solvated electron exhibits a shift to higher frequencies, implying a compression of the trap.

III. THE INTERACTION OF EXTERNAL ELECTRIC FIELDS WITH LIQUIDS

A. A New Crystal-Growing Technique and the Thermodielectric Effect

Nothing could be simpler, it would seem, than the description of an electric field between two large, identical, flat-ended, parallel metal electrodes separated by a highly insulating liquid and having different potentials. Conventional electrostatic theory leads us to expect a uniform field in such a situation. In reality, this ideal is but a fleeting transient condition, lasting perhaps a few nanoseconds. The field rapidly warps to a high degree of inhomogeneity in microseconds. This was shown by the workers at Grenoble[79] by using the Kerr effect on chlorobenzene. Pohl[80] emphasizes that at present, "experiment overshadows theory in the study of the behavior of real matter in the presence of real but non-uniform fields." We will discuss some instances of this in the following section, which is intended to catalyze interest in an exciting field still in its early stages of development. Quoting Pohl again:

> Non-uniform electrical fields produce unique, useful and frequently mystifying effects on matter—even on neutral matter. With non-uniform fields, for example, it is possible to classify and separate minerals, pump liquids or powders, produce images (xerography), provide an 'artificial gravity' useful in 'zero-g' conditions, clean up suspensions, classify microorganisms, and even separate live and dead cells. And this just starts the list. Applications in biophysics and cell physiology to studies of normal and abnormal cells are at an early but exciting phase. In colloid science the new technique is helping to resolve surface properties. At the molecular level, non-uniform field effects are seeing renewed use in determinations of molecular polarizabilities, in maser operations and in laser control.

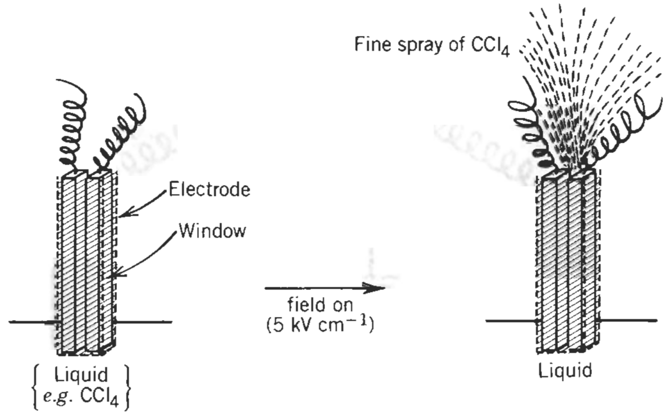


Figure 16. A simple laboratory experiment demonstrating how a liquid may be suspended against gravity or even pumped rapidly against gravity (as illustrated for CCl_4) in the presence of strong electric fields. Two brass electrodes are sealed with two insulating polymeric windows. (Reproduced by permission from ref. 13.)

Here we shall confine our discussions mostly to the author's own observations. We shall see that some of the phenomena we report may be explained in terms of ideas introduced in preceding sections of this review. We will confine ourselves to electric field effects but point out some similarities with magnetic field effects on magnetic fluids.

Figure 16 shows a simple electrode configuration that was used to suspend dipolar molecular liquids against gravity.[73] The two parallel brass electrodes were sealed with two insulating windows; the ends remained open. One end of this cell was immersed in a neat liquid and a static electric field (~ 5 kV cm^{-1}) was applied. Liquid was drawn up into the contained gap. For example, 11 cm of aniline was suspended in this way. For some nondipolar liquids (e.g., CCl_4) the effect is so strong that fine droplets of liquid are expelled very rapidly through the top of the two electrodes some 13 cm long. A liquid can be pumped against gravity in this way.

Insulating dielectric liquids are attracted from regions of lower to regions of higher electric field intensity *even in the absence of free electric charge.* This may be observed with a simple setup such as that shown in Fig. 17. In the presence of a field, liquid is drawn into the stronger-field region between the electrodes that are closest to each other. Jones et al.[81] have suggested that this effect occurs because of polarization charges. These authors demonstrated how the effect may be used to produce a dielectric syphon (Fig. 18). At large enough voltages, parametric surface instabilities set in. These are the electric analogue, in dielectric systems, of the surface instabilities of magnetic liquids in magnetic fields normal to the surface.[82] A destabilizing effect

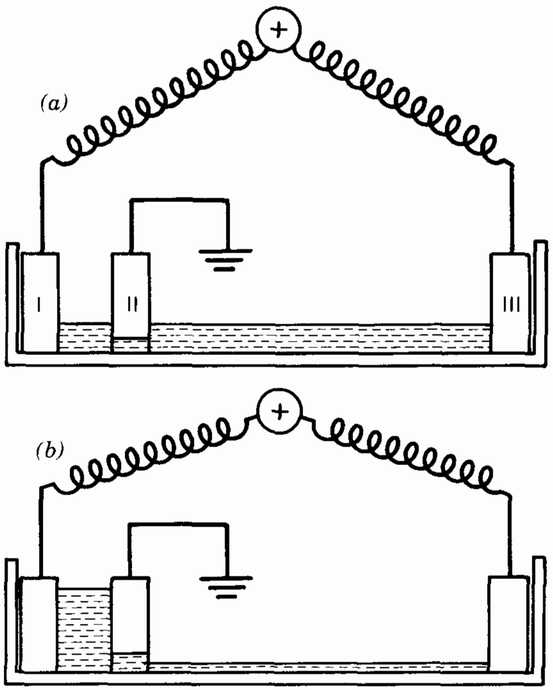


Figure 17. An insulating liquid moves from a region of weaker to a region of stronger field strength. This may be demonstrated with a simple laboratory experiment. (*a*) Three brass electrodes (I, II, and III) are set in an insulating block of material. Electrodes I and III are fixed permanently in a rectangular hole machined in the block. Electrode II has a hole drilled in its base and may be moved between the two fixed electrodes. (*b*) When a field is applied, liquid fills the gap between the two electrodes in closest proximity to each other, where the field intensity is greatest.

is produced that results in the appearance of a periodic structure of liquid spikes.

Another well-known effect in magnetic liquids is fluid magnetic levitation. Consider the Bernoulli equation to which a magnetic energy term is added

$$p + \frac{pv^2}{2} + \rho g h - \mu_0 \int_0^H M\,dH = \text{constant}$$

where p is the pressure energy (work done by the liquid), $pv^2/2$ is the kinetic energy, $\rho g h$ is the potential energy, and the last term is the magnetic energy. Consider now the pressure term in conjunction with the magnetic term. The equation predicts that the greater the applied magnetic field is, the greater is the pressure produced within the liquid. If a body is immersed in a magnetic liquid, it sinks or floats, depending on its density with respect to the liquid. Let us suppose it is more dense and sinks. If a magnetic field is now applied normal to the surface of the liquid and gradually increased, a gradually increasing field gradient is introduced, and at a strong enough field the body floats and eventually sits on the surface of the liquid, where the lowest pressure is found.

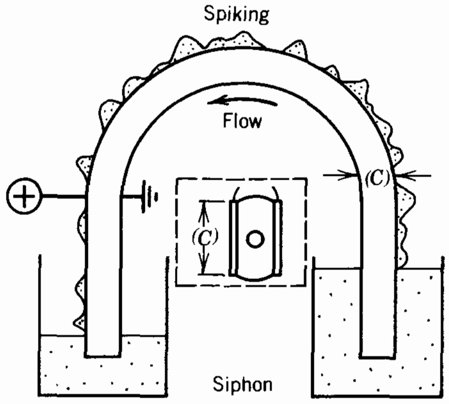


Figure 18. The dielectric siphon. The liquid flows in the direction shown. As it flows, the surface of the liquid exhibits parametric instability. The electrode arrangement is shown in inset (*c*). For photographs of the siphon in operation see ref. 81.

Evans[83] has used the electric analogue of these two effects, spiking and levitation, to induce the nucleation process. Consider the electrode arrangement schematically depicted in Fig. 19. For a liquid of nonzero conductivity, an electric field causes a current flow and, in our case, an accumulation of negative charge at the liquid surface. In addition, of course, polarized molecules travel to the surface of the liquid and reorient themselves in accordance with the direction of the field. As the electric field is increased, a force is exerted on the surface of the liquid. If the surface charge density is $\rho_s C/m^2$, this force is given simply by

$$F_s = \rho_s E$$

The force tries to pull the charges out of the surface; in a strong enough field, surface disruption occurs and, as illustrated in the figure, spikes appear.

If a saturated solution of a polarizable solid substance, for example, camphor, is prepared in nonpolar CCl_4 and an external electric field is applied using the electrode arrangement described above, the following occurs. The camphor molecules, or groups of molecules, are polarized and reoriented, and acquire, in effect, a negative charge on the side facing the upper positive electrode. The field is nonuniform, diverging across the individual (or groups of) particle and producing unequal forces on the two ends of the molecule(s).

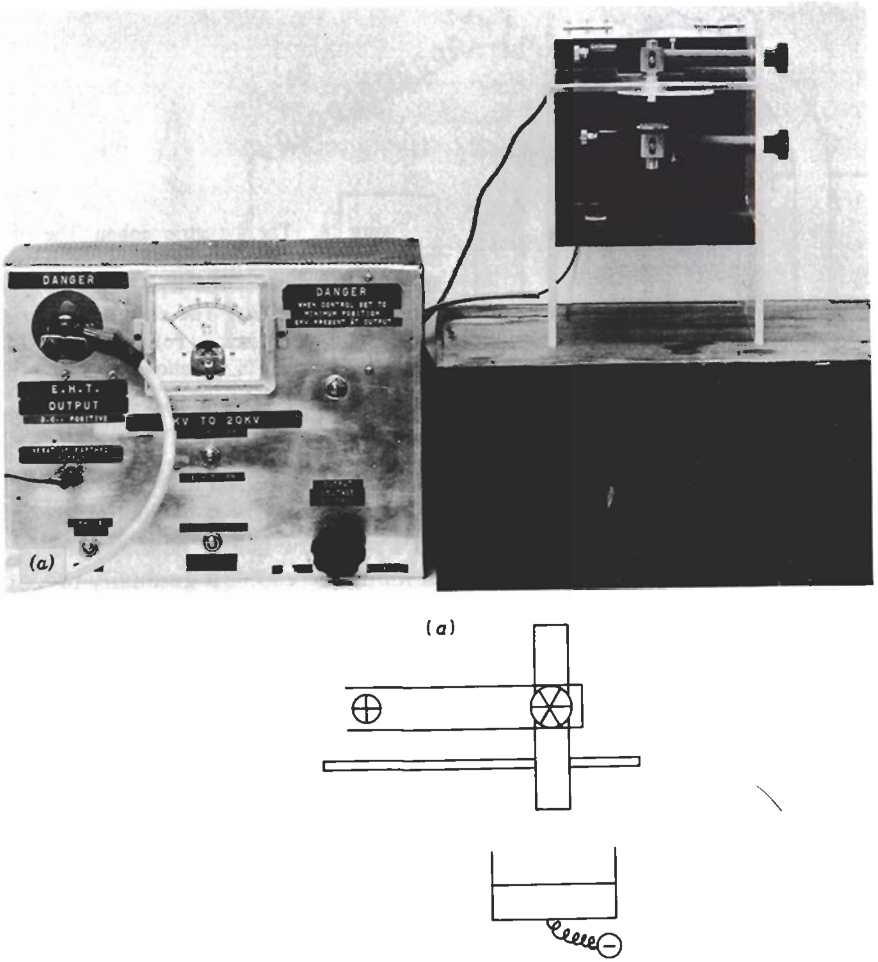


Figure 19. A new crystal-growing technique, as used for the growth of crystals of camphor. (*a*) The setup with no field. (*b*) A field is applied and a "spike" appears. Note that the PTFE rod used to induce this spiking acquires surface charge in the presence of the field. (*c*) The crystal growing. It may be drawn out of the solution or grown by steadily increasing the field. The maximum size of the crystal that may be grown depends on the size of and the distances between the electrodes.

The force on a small neutral body is given by[80]

$$\mathbf{F} = (\mathbf{P}\cdot\nabla)\varepsilon_e$$

where **F** is the net electric force on the body, **P** is the (constant) dipole vector, ∇ is the del operator, and ε_e is the external field. Assuming that the dielectric body is linearly, homogeneously, and isotropically polarizable, that is, that

$$\mathbf{P} = \alpha v \varepsilon_e$$

where α is the polarizability (the dipole moment per unit volume in a unit

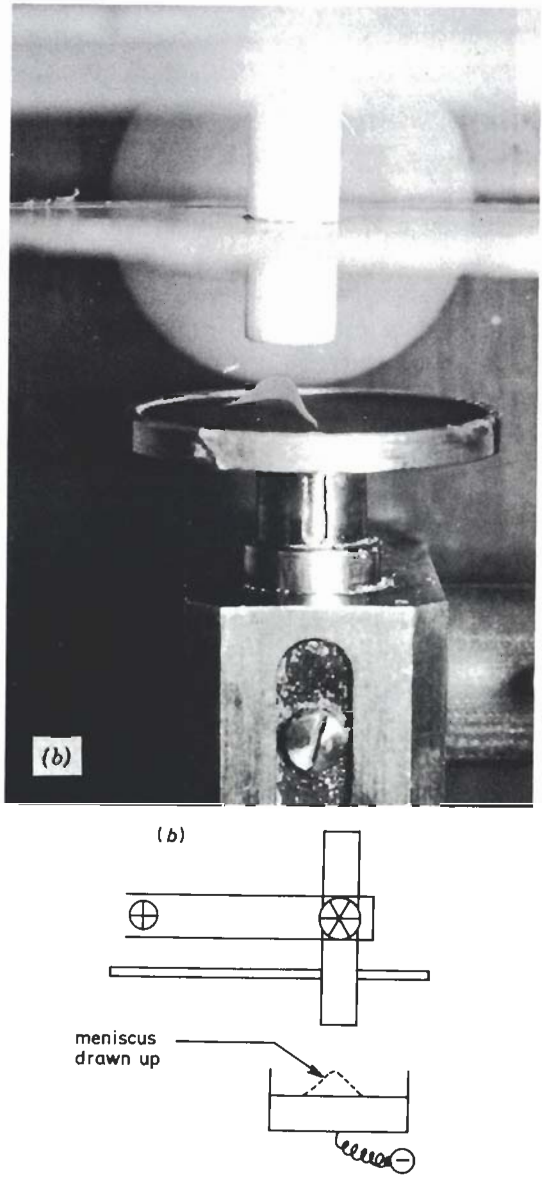
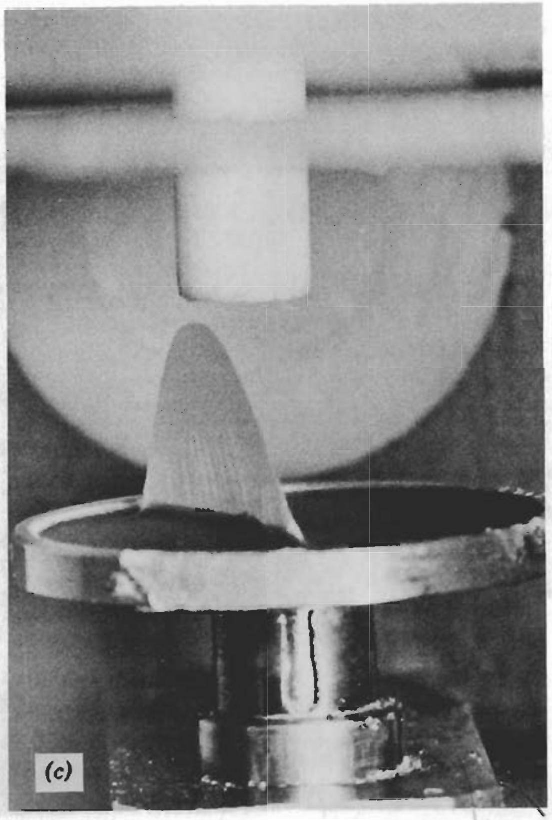


Figure 19. (*Continued*)



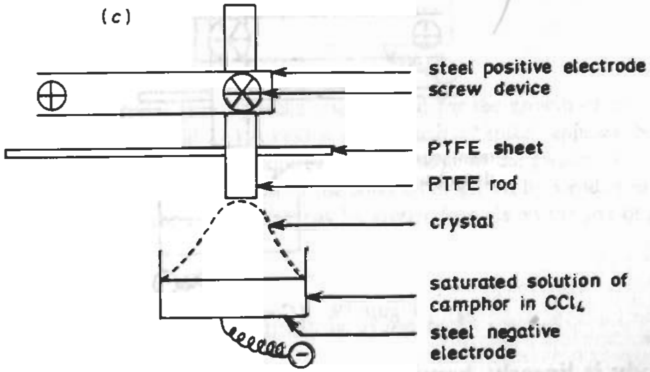


Figure 19. *(Continued)*

field) and ν is the volume of the body, we can write

$$\mathbf{F}=\alpha\nu(\varepsilon_e\cdot\nabla)\varepsilon_e=\tfrac{1}{2}\nu\alpha\nabla|\varepsilon_e|^2$$

In a conservative (i.e., friction-free) field the force on the body is the negative of the gradient of its potential energy. Since $\boldsymbol{P}$ is a constant vector, and $\nabla\times x\varepsilon_e$ is zero in a static field, we have

$$\mathbf{F}=(\mathbf{P}\cdot\nabla)\varepsilon_e=\nabla(\mathbf{P}\cdot\varepsilon_e)$$

For an anisotropic body, of course, the polarizability $\boldsymbol{\alpha}$ is a tensor and the calculation is more involved. However, for present purposes, this equation suffices to illustrate that a force exists impelling the particle into a region of stronger field.

Let us consider our saturated solution of solid camphor in the nonpolar solvent CCl_4. (The latter is chosen because of its strong response to an electric field, as already discussed.) The saturated solution is placed in a lower, cylindrical electrode made of stainless steel. The top electrode, also made of stainless steel, is isolated from the bottom one with an insulating sheet of PTFE (or similar material), (see photographs in Fig. 19). An insulating rod of the same material projects below this surface and is used as the source that induces the nucleation (Fig. 19); this rod acquires a surface charge. When the field is switched on (and gradually increased), particles of camphor may be seen floating on the surface of the solution—the electric levitation effect. Under strong enough fields a spike of the solution is drawn upward toward the PTFE rod. As the field is further increased, the spike grows, the CCl_4 is ejected out of the field region (just as it was in the first experiment discussed in this section), and a thin, uniform crystal of camphor remains. The samples are grown straightforwardly in a continuous manner using this technique. The crystals grow instantaneously when the field is increased, and instantaneously stop growing when it is removed. One therefore has great control over the growth of the crystal. There is a great potential for growing such samples *in situ* in many experiments.

If the drawn-up spike is allowed to touch the PTFE rod, the crystal may even be grown by keeping the field constant and raising the PTFE rod using a simple screw device. A crystal of required length may then be drawn out. The method resembles at this stage the Langmuir trough technique, developed by Irving Langmuir and Katharine Blodgett between the World Wars and now used to deposit monolayer films. This method has great potential in the field of electronics, where it is anticipated that new semiconducting materials can be developed to supplement the ubiquitous silicon. Some have speculated that our new crystal-growing technique may be used for such thin-film production.

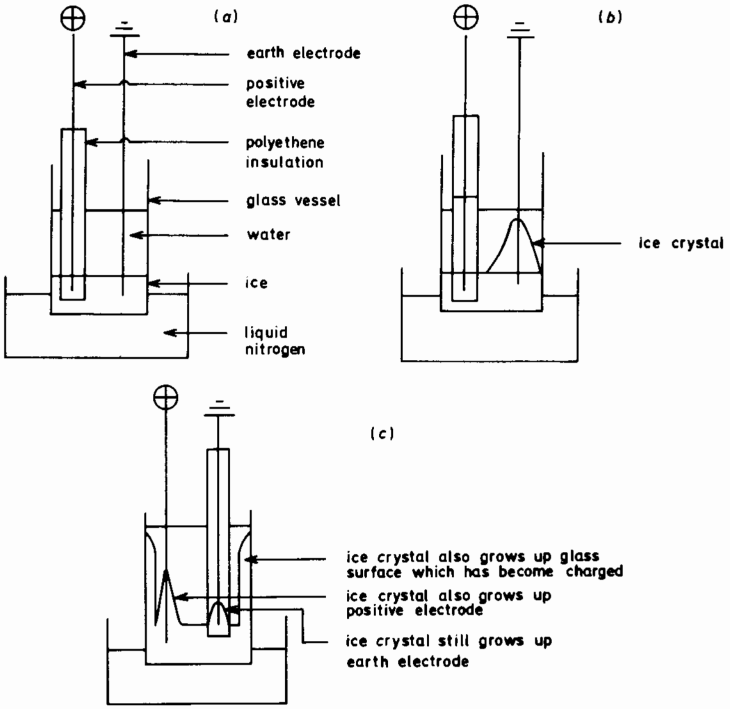


Figure 20. Ice grows preferentially in the region of a strong field. (*a*) The setup with no field. A layer of ice is allowed to grow at the bottom of the glass vessel to seal the open end of the polyethylene insulation tube around the one electrode (thereby eliminating conduction processes) and to provide a liquid–solid interface before application of the field. (*b*) With a field applied and the positive electrode insulated, ice grows up the earth electrode. (*c*) With a field applied and the earth electrode insulated, ice grows up *both* electrodes and up the surface of the glass vessel, which must also become charged. [Reproduced by permission from G. J. Evans, *J. Chem. Soc., Faraday I*, **80**, 2343 (1984).

It was found necessary, at least for camphor, to insulate the top electrode from the bottom in the way described, because the crystals are easily broken and splinter if the fields are too strong. Evans[83] has even observed that ice crystals grow preferentially in a field region and around an immersed electrode (Fig. 20) if water is cooled too close to its freezing point in the presence of a field. And Rajeshwar[84] et al.[84] report that it is possible to "tune or even alter the thermal decomposition behavior of solid materials by imposition of electric fields across the heated samples." They found that the decomposition temperatures could be lowered by as much as ~100°C in the presence of the field. This is an important observation because of the significance of thermal decomposition of solid materials used in, for example, rocket propellants. Rajeshwar et al. report other observations:

> Electric field effects have been implicated in various thermophysical and thermochemical phenomena in solids and in solid–gas or liquid interfaces. It has been reported that an electric field accelerates the rate of growth of $BaMoO_4$ crystals in silica gel media. A change in the sublimation pattern of KCl crystals has been observed in the presence of an electric field. The lower dielectric strengths observed for ionic metal azides relative to other more thermally stable materials have been attributed to 'electrocatalytic' effects induced by the presence of highly conducting metal nuclei. Selective phase formation at sample–electrode interfaces has been observed in a study of the effect of electric fields on the transformation of γ- to α-Al_2O_3. An electric field enhancement of dehydroxylation rates in magnesium and aluminum hydroxides, has also been reported.

Rajeshwar et al.'s differential scanning calorimetry (DSC) results for $KMnO_4$ in the presence and absence of dc fields are illustrated in Fig. 21. Note the drastic increase in the exothermicity of the autooxidation peak and the lowering (by ~65°C) of the peak temperature for the sample exposed to the electric field relative to that for the control sample. It is suggested that the efficacy of the external field in lowering the extrapolated onset temperature of the DSC peak is related to the extent to which charge transfer plays a rate-determining role in the very early stages of the decomposition, but this has not been proved.

Mechanisms for charging particles during the nucleation process have been proposed. For example, Workhom and Reynolds[86] found large potential differences of up to 230 V between the ice and water phases during the freezing of water. Costa Ribeiro[85] reports similarly that "in a condenser whose dielectric is partly in the solid and partly in the liquid state, one of the plates being in contact exclusively with the solid and the other with the liquid phase, if a phase change takes place at the boundary between the two phases, so that solidification or melting occurs at the interface, an electric current is produced as a consequence of the phase change." Costa Ribeiro asserts that electric charges always appear on the interface between the liquid and solid phases in a dielectric; he named this effect the thermodielectric effect. His results have similarities with those of Stephen Gray,[87] the discoverer of electrical conduction, who reported in 1732 that dielectrics acquire charge purely by melting and solidification.

Costa Ribeiro also claims that his thermodielectric effect may be observed not only in melting and solidification, but also in other changes of physical state in which one phase is a solid (e.g., similar potentials are produced in sublimation, as confirmed by the work of Rajeshwar et al. discussed above,

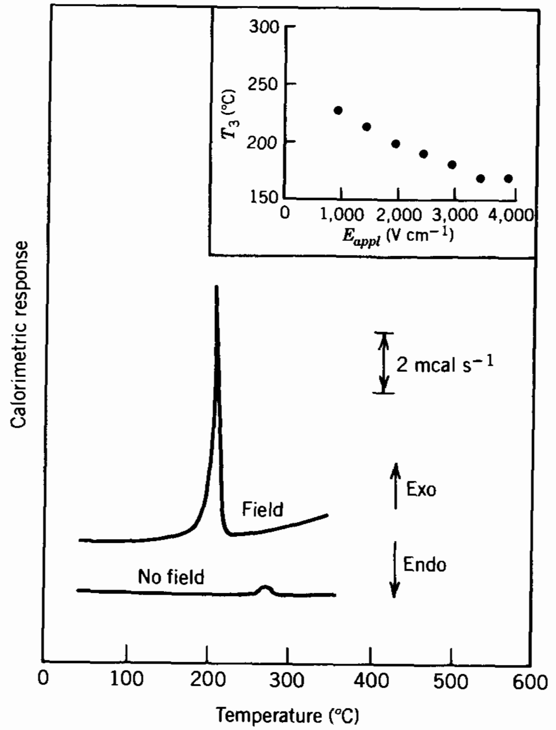


Figure 21. Electric field effects on the differential scanning calorimetry (DSC) results for $KMnO_4$. This is another example of the reciprocal effect of the thermodielectric effect of Costa Ribeiro.[85] The field applied was 2 kV cm^{-1}. The inset shows the dependence of the DSC peak extrapolated onset temperature, T_3, on the applied field, E_{appl}, for $KMnO_4$. (Reproduced by permission from ref. 84.)

and in the precipitation of substrates from saturated solutions, as in Evans's camphor–CCl_4 solution). Evans was unaware of Costa Ribeiro's experiments when reporting his induced nucleation effect.[83] However, Costa Ribeiro reported in his remarkable paper that "we have tried, but without success, to detect the reciprocal of the thermo-dielectric effect, that is: the production of melting or solidification, in a solid–liquid dielectric system, by application of a potential difference across the interface." This, the inverse of the thermodielectric effect, is precisely what Evans has now reported—the induction of solidification from a saturated solution by the application of strong external fields.

It is remarkable that Costa Ribeiro's work has not received the attention, scrutiny, and acclaim it deserves. His observations are of fundamental importance, yet little reference to his work is made in currently popular texts

on liquids, solutions, and interfaces, or in the discussion of nucleation, where it is obviously of most importance. It is well known, however, that in crystal growth the structure at an interface has a major effect on the growth.[88] As Melcher et al.[89(a)] point out, an external field E "influences a liquid at an interface where the permittivity ε undergoes an abrupt change, and therefore $\Delta\varepsilon$ is not zero, as in the bulk. In some cases it is fruitful to think in terms of an analogy between dielectrophoretic forces (the force on a non-charged but polarizable molecule) and surface tension forces because, in a homogeneous liquid, the electric field produces only a surface force."

Costa Ribeiro proposed two laws concerning the thermodielectric effect and even postulates the existence of a new specific physical constant. His laws read thus:

1. *Law of Intensities*: "In isothermal melting or solidification, occurring at a constant rate, in a thermo-dielectric cell, the intensity of the current produced is proportional to the time rate of the phase change."
2. *Law of Charges*: "If a dielectric system passes from one state of equilibrium to another state of equilibrium, the total electric charge associated with the change of mass of one of the phases is proportional to this change of mass."

Costa Ribeiro proposes an internal, molecular mechanism for the phenomenon in terms of the Helmholtz double-layer hypothesis. When solid particles (e.g., camphor in Evans's experiment) are immersed in an insulating liquid (e.g., CCl_4), they may, because of the existence of a contact potential, become charged (if the conductivity of the liquid is nonzero) or polarized by selective adsorption of ions from the liquid or because of the adsorption of dipoles on the surfaces of the particles. Normally both processes are anticipated to contribute. When a particle has somehow acquired a charge or a dipole on its surface, ions or polarized molecules of the opposite sign will be attracted to the vicinity of the particle, but will be present in a diffuse layer around the particle. These two layers, a very thin, tightly bound primary layer and a loose secondary layer, together form the well-known Helmholtz double layer, which Helmholtz suggested is always formed at the surface between two phases of material. Ribeiro points out that a displacement of this double layer as a consequence of the phase change might account for the electric potentials observed during the phase change. As Ribeiro says, "there may be a difference in the electronic densities (cubic density of electrons loosely bound to the atoms) in the solid and liquid phases... this should permit a theoretical treatment of the subject similar to the method used in discussing cohesion of solids by means of the collective electron model of Bloch."

An excellent review on current approaches in applied quantum mechanics that adopt single-particle density as a basic variable, namely, density-functional theory, quantum fluid dynamics, and the study of the properties of a system through the study of "local" quantities in three-dimensional space, has recently appeared.[89(b)] The authors of this review write that

> in recent years electron density has attracted a great deal of attention in connection with its use as a basic variable in applied quantum mechanics. The appeal of this quantity as an attractive alternative to the quantum mechanical wave function is basically threefold:
>
> Firstly, it describes the 3D [three-dimensional] distribution of electrons in a system and hence is a function of only three coordinates irrespective of the number of electrons present. Thus density-based formulations offer a tremendous simplification over the usual wave function approach where the difficulty in solving the Schrodinger equation increases very rapidly with the number of electrons.
>
> Secondly, it is a fundamental physical observable and can be determined experimentally.[90] Thus the accuracy of quantum chemical calculations and approximations can be tested directly.
>
> Finally, being a function in 3D space it enables one to build up various interpretive models thus providing a 'classical' picture of quantum phenomena. The density plays a very important role[91] in many chemical and physical applications from both interpretational and computational points of view. Its vital significance has been emphasized by the statement:[92] 'A theory of chemistry and the chemical bond is primarily a theory of electron density.'

The interested reader is referred to this review for further details.

Because Costa Ribeiro observed electric charges in crystals formed by sublimation or by precipitation from a saturated solution, he was careful to emphasize that the thermodielectric effect occurs not only in processes of melting or solidification, but also *in other types of phase changes in which one of the phases is a solid*. He was unable to observe similar effects in changes of state not involving the solid state, such as vaporization or liquefaction, and so concluded that his effect must be related to the passage of the dielectric from a state of ordered structure, the crystalline state, to one of greater disorder, the liquid or gaseous state, or vice versa.

For some years after its appearance, no reference to Costa Ribeiro's work could be found in the literature. However, the effect reappears in the literature of the late 1960s. In brief, Dang Tran Quan[93] reported the existence of thermodielectric voltages and variations in the dielectric constants of some organic compounds near transition points when one of the states involved a solid. He observed that during cooling or heating at temperatures corresponding to transition points, radiofrequency measurements revealed abnormal variations of the dielectric constant. For 1-butanol and 1-bromobutane peaks corresponding to crystallization were observed at 134 and 127 K and peaks corresponding to melting at 183 and 162 K, respectively. For cyclopentanol and cyclohexanone, peaks were observed at 205 and 222 K, respectively, corresponding to solid-state molecular vibration–rotation transitions, and at 224 and 223 K, respectively, corresponding to solid–liquid transitions.

Cassettari and Salvetti[94] reported the design of an experimental setup that improves the study of the thermodielectric effect, and Mascarenhas[95] studied charge and polarization storage in solids over a wide range of phenomena and materials. Included was a study of the Costa Ribeiro effect, which he described as "charge storage during a phase transition."

Dias Tavares[96] provided experimental proof of production of the double space charge in dielectric and organic semiconductors due to the Costa Ribeiro effect and tested a theory of the distribution of such charges with two zero-field planes. He accomplished this by the liberation of charges inside the crystal using a focused beam of light that crossed thin layers of the crystal. The current produced changed sign twice when the beam swept over the thickness of the crystal, showing the existence of the two zero-field planes. Rozental and Chetin[97] showed that a reorientation of polar molecules determines the interfacial potentials and redistribution of ions in a two-phase system. The potentials detected by molecular polarization reached 10^5 V cm^{-1} for polar substances. Kapustin et al.[98] observed thermodielectric effects when nematic *p*-azoxyanisole crystallized. The space charge increased with the cooling rate, in accordance with Costa Ribeiro's conclusions, to a limit of 4×10^{-8} coulombs g^{-1}. And Garcio Francisco[99] reported use of the effect for solar-energy conversion. It is a fascinating thought that water, the most abundant of liquids, may yet contribute significantly to solving our world's energy problems. An efficient method for the sunlight-assisted electrolysis of water using a p-InP photocathode is already available. It uses 10.2 mW cm^{-2} of the incident 84.7 mW cm^{-2} sunlight for the production of hydrogen. The resulting engineering efficiency of 12% is the largest ever obtained for any scheme for conversion of sunlight to fuel. Green plants are able to convert 1–3% of the incident sunlight to combustible fuels. There is great interest in this area; the race is already underway to provide a scientific basis for a new large-scale energy resource option. The thermodielectric effect may make significant contributions to this race.

Eyerer[100] has reviewed the Costa Ribeiro and Workhom–Reynolds effects. He discusses experimental results, theoretical considerations, and potential applications of the thermodielectric effect, and reviews the Workhom–Reynolds effect in the water–ice system.

We will leave the last words on this particular effect to Costa Ribeiro himself: "From the standpoint of chemical-physics, the new possibility of associating a specific electric charge with changes of state of aggregation is certainly interesting... the existence of an electric double-layer in solid–liquid interfaces suggests also the possibility of investigating the correlation between the thermo-dielectric effect and other electrochemical phenomena of interfaces."

Colloidal solutions represent another interesting and important class of systems in which large electric field effects can be expected and from which crystals or films may be grown. Hauer and LeBeau[101] investigated the properties of films formed by the gradual extraction of water from benzonite solutions containing very small and uniform particles. They observed that a concentration was reached at which Brownian motion ceased and the particles tended to align themselves. On further removal of the water, the particles appeared to snap into position and form "crystallites" of highly anisometric shape. It would be interesting to carry out field experiments at various points of such an extraction procedure. Of course, colloidal particles are believed to be prevented from coagulating by potential barriers between them originating from their electrical charges—each particle is surrounded by an electric double layer that keeps the system as a whole electrically neutral. As Grisdale[102] says, "small amounts of ionic material, many times no more than are adventitiously present, suffice to create the double layers essential to long time stability of colloidal systems (*and also have profound influences on crystal growth*)."

Many biomolecular processes are consequences of high electric field effects. This follows from the role of the surface (the interface) in all cell structures, membranes, capillaries, and so on. Davies[103] writes that "such surfaces almost invariably carry, adsorbed, an excess of ions of one charge type: this could produce a field in excess of 10^6 V cm^{-1} at a distance of 5 Å from the surface." The molecular consequences can be considerable. Gregson and Krupkowski[104] studied lecithin, an important constituent of mammalian brain, of egg yolk, and of many other tissues. Its zwitterionic structure and long chains lead to its forming small inverted micelles in nonhydroxylic solvents. They found an interesting sequence of changes when the lecithin solution was subjected to a pattern of rectangular voltage pulses of width ca. 3×10^{-3} s and of amplitude varying up to 10^5 V cm^{-1}. Two differing perturbations of permittivity were observed. A small low-field perturbation was interpreted as a field-induced distortion of the quasispherical micelle whose polarity was so increased. The higher fields induced partial disruption, that is, fragmentation of the almost nonpolar micelle. These observations suggest a value for the effective field within the micelles (ca. 10^4 V cm^{-1}), offer the possibility of monitoring the kinetics of micelle formation, and illustrate the type of molecular-kinetic features that can be profitably explored by high-field methods.

Hirano[105] investigated crystal formation in a supersaturated electrolytic solution and analyzed the electrical behavior of the crystal–solution interface. Ubbelohde[106] has already postulated that charged microcrystals act as crystallization nuclei in such solutions and Hirano reported observations that appeared to support this view. Hirano reported the growth of crystals from a saturated solution of sodium nitrate (in water) that was electrolyzed between two platinum electrodes for 10 h in a field of 0.4–0.5 V cm^{-1}. He then charged a glass surface negatively and observed the "creeping phenomena."[107] He emphasized that silica glass, which has no ionic structure, failed to show the creeping. Note the analogies with the water-crystal growth in the presence of a field reported earlier (fig. 20). Crystals of ice grow up the sides of a glass vessel whose surface becomes charged by the high fields. Hirano also observed that crystallization occurred more rapidly in fields of high frequency, which seems to support the idea that charged nuclei exist in the solution and determine the crystal-growth process. The collision rate between such nuclei should be increased by an alternating field.

Ubbelohde[106] pointed out how important this mechanism for migration of nuclei may be in the deposition of crystalline masses at controlled places in animal systems. For example, it is possible that the deposition of crystals associated with certain diseases and the formation of teeth and bones are controlled by this phenomenon. That such a phenomenon is not confined to electrolytic solutions but also applies to organic molecular systems may have wide-ranging implications for plant and animal biology. It is interesting, for example, that citrus orchards have been protected[108] from low temperatures, which destroy unprotected control plants, by placement of high-frequency electric fields at the ends of the leaves so that high-frequency currents flow on the sensitive surface layers of the plants. A pronounced effect of electric fields on the growth of barley has been reported,[109] and it is well established that the common method of inhaling uncharged aerosols for the treatment of bronchial asthma, nasal and sinus conditions, bronchitis, emphysema, and other ailments of the respiratory tract is markedly enhanced by first charging the aerosols.[110]

External fields influence themselves most strongly at those interfacial regions in a liquid where the permittivity undergoes an abrupt change. However, electric field effects may also be observed in ordinary isotropic liquid systems, where interfacial effects would not be expected to be so pronounced. We have already considered some spectroscopic consequences of the interaction of external electric (and magnetic) fields on nematic liquids. Intensity changes occur, and at far-infrared frequencies, collective modes are resolved. But what of spectroscopic effects of electric fields in isotropic, small-molecule molecular liquids? In 1980 Evans and Evans[111] reported electric-field-induced intensity changes in the far-infrared spectrum of an isotropic liquid, aniline (Fig. 22). The effects are surprisingly large. And Michel and Lippert[36] reported that the π-electrons of the nitrile bond (in CH_3CN) may be polarized by electric fields in axial and perpendicular di-

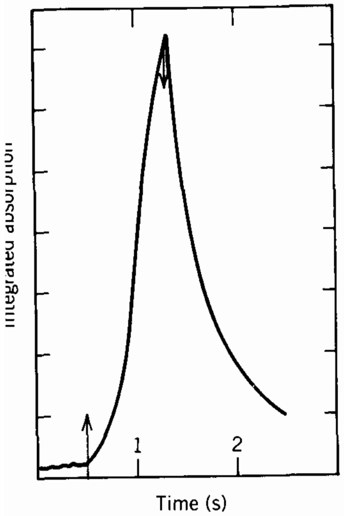


Figure 22. The spectroscopic (far infrared) effect of an electric field on the transmission properties of liquid aniline. The transmission was monitored as the field was applied (first arrow) and removed (second arrow). Note that the effects were instantaneous and large. (Reproduced by permission from ref. 111.)

rections. The polarization is very sensitive and affects the intensity of the CN mode. Although the axial polarizability is higher than the perpendicular one, the CN intensity is more sensitive to perpendicular fields. Whereas axial fields increase the CN intensity, perpendicular fields decrease it. Michel and-Lippert studied the polarization in static fields of up to 5×10^5 V cm^{-1}. With an increase in the electric field, a rapid decrease of the CN intensity was observed (Fig. 23). They suggested that the field effect points to a perpendicular excitation of the π-electrons.

Under the influence of applied external electric fields, matter may become electrified internally throughout its volume. This electrification or polarization may occur at the atomic, molecular, or bulk level, and particularly at an interface, which may be solid–liquid or solid–gas, as we have seen, or solid–solid and so on. Such interfaces are sites of natural transfer of electric charge. Solid–solid interfaces are well studied, of course, because of their importance in semiconductor devices. It is surprising that interfacial polarization effects between other surfaces have not been studied in such detail, and that the development of our understanding of polarization phenomena in such systems has not parallelled the rapid developments in solid state physics.

We can discern four basic types of polarization at the atomic or molecular level, all of which may occur to some extent in our molecular systems. The coexistence of all four types is particularly likely if charged carriers or impurities are also present in appreciable quantity. These types are as follows:

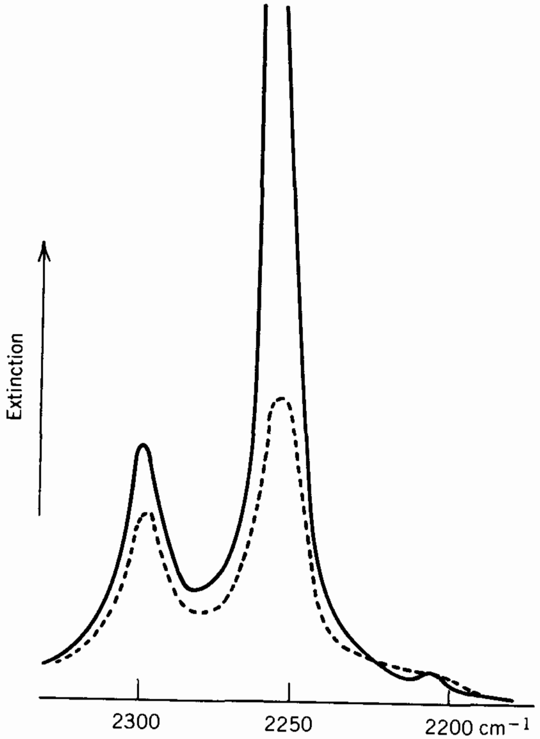


Figure 23. This spectrum depicts similar effects on CH_3CN to those on aniline shown in Fig. 22 but at infrared frequencies. ---, No field; —, with a field of 5×10^5 V cm^{-1} applied. (Reproduced by permission from ref. 36.)

1. Electronic polarization: When an atom is placed in an external electric field, the electron cloud and positive nucleus shift in opposite directions and an electric dipole (which may be additional to an existing dipole) or "induced polarization" appears. Note that the effect involves the shift of the center of electrical interaction with respect to the center of mass, so we may predict a change in magnitude of rotation–translation coupling. This electronic shift (ca. 10^{-8} Å) is usually not large with respect to the nucleus and results in dielectric constants of 2–4 in organic solids and up to 20 in some inorganic solids.

2. Ionic or atomic polarization: Ionic polarization occurs because if ions are present, the ions of different signs will be pulled apart by external electric fields. This effect, though most prominent in ionic dielectrics, may also occur in organic molecular systems if appreciable amounts of charged carriers or impurities are present. Even so, it is only expected to be 15–20% as large as the effect due to electronic polarization in such systems. It can be

very large in some solids; for example, it results in barium titanate having a dielectric constant of ca. 4000.

3. Orientation polarization: This occurs if the molecules have a permanent dipole. Under the influence of the electric field, all dipoles that are not lined up with the field experience a torque that tends to orient them in the direction of the field. This effect can be large, as, for example, in water, which has a dielectric constant of 80 at low frequencies and room temperature. It must be significant to some extent in all liquids, because even liquids composed of molecules with symmetrical charge distributions become distorted in a liquid environment and have temporary dipoles associated with them. Thus even "nonpolar" CCl_4, for example, has a rototranslation absorption at submillimeter frequencies.

4. Hyperelectronic polarization: This type of polarization occurs in large molecular domains, particularly domains that are elongated, as, for example, along polymeric chains, where long-range molecular orbital delocalization can occur. The electronic shift can then be 100–1000 Å, which is enormous in comparison with electronic polarization effects on atoms alone. Some polymers have dielectric constants of up to 300,000 because of this effect.

But polarization may also occur at multimolecular or bulk levels. One type of bulk polarization, flexoelectric polarization, results from distortions in the bulk of insulating nematic materials induced by external electric fields. Conversely, a splay or bending distortion can create a polarization. Schmidt et al.[113] observed that the long-range alignment does indeed become distorted in an electric field in a study on nematic MBBA.

The most well-known bulk polarization is interfacial polarization. This occurs more often than is generally realized. The crystal-growing procedure reported above and a phenomenon discussed in the following section, bubbling (the precursor to complete dielectric breakdown), both display elements of this polarization effect.

Interfacial polarization arises from the migration of charge carriers through the dielectric over some distance in the presence of a field and the appearance of "space charges" in the medium. Charge carriers may become trapped at impurity centers, at interfaces, or at electrodes if they are not freely discharged or replaced at the electrode. Pohl[80] reports the phenomenon of insulator-induced conduction, in which the current flow increases many-fold through a layer of highly purified dielectric liquid if one of the electrodes is covered with a thick layer of insulator particles, thus promoting the production of space charges that distort the macroscopic field. Interfacial polarization can become large at higher field strengths. Living matter and soils or earths consisting of conductive regions interleaved with barrier layers can appear to have enormous dielectric constants (10,000 or so). The technological applications and implications of different combinations of solid, liquid, and gas interfaces are widespread and varied.

It is not easy to separate all of these polarization mechanisms in a real system, nor to assign an observation to a particular polarization mechanism. The total induced polarization almost certainly arises from a number of contributory and competing factors. The spectroscopic effects on isotropic liquids alluded to above are interesting and need to be carefully analyzed. Ascarelli[66] also observed the pronounced effect of an electric field on the collective mode he resolved in nitromethane. The collective mode shifted considerably to higher frequencies when the sample was in contact with an electret (a permanently electrified body).

Interfacial polarization is certainly of vital importance in the nucleation process. Approaches to nucleation have emerged as a result of studies of interfacial problems.[116] In classical models interfacial energetics have been treated in terms of atomic bond-breaking and -making at the interface. This consideration conveniently leads us to another phenomenon of the liquid state—"bubbling" and dielectric breakdown. In this phenomenon bond-breaking is induced at the interface between solidlike and gaslike molecules in the liquid environment by strong electric fields. Bubbling always occurs before complete dielectric breakdown and demonstrates rather well the importance of interfacial phenomena even in isotropic "simple" molecular liquids.

B. Bubbling in Liquids in Strong External Electric Fields and Liquid Structure

Ignacz[56] discusses bubbling in detail in his new text. His central hypothesis is that the physical behavior and dielectric breakdown properties of liquids are determined by their structure, and that microbubbles and bubbles are produced and stabilized by external electric fields. Ignacz proposes the existence of a local "crystalline structure" in liquids. "Crystal defects," he says, "lead to the generation of unattached gas-like molecules prior to complete dielectric breakdown." The thermal motions of aggregates of molecules lead to the formation of cavities in the liquids and the appearance of solid–gas interfaces. These cavities grow into bubbles in the presence of the external electric fields. Gassing, of course, is even known to occur (to a lesser extent) in solids. The author has observed bubbling in liquid acetonitrile under fields as small as 1 kV cm^{-1}.

Let us consider this phenomenon in some detail. According to Ignacz, bubbling occurs under both uniform and nonuniform electric fields in strongly stressed regions (interfaces) of nonpolar and polar liquids and at the interfaces with the metal electrodes. The bubbles become ionized by the external fields, and atomic bond-breaking occurs at the interface. Quoting Ignacz:

> The mean free path of electrons is 10^3 times longer in gases than in liquids, consequently, they can gain 1000 times more energy from a field in the gas. Becoming free, the electrons accelerate inside the bubble and they can break out into the parts of the liquid between the bubbles. Here, thin channels are formed by the kinetic energy of electrons and by several additional processes, e.g. electron multiplication, photo ionization etc. These channels connect the neighboring bubbles, thus preparing the total breakdown spark, which bridges the two electrodes. This spark does not form a continuous channel, it remains a chain of separate ionized bubbles connected by thinner channel parts.

Ignacz discusses the role of impurities and points out that their presence distorts the externally applied field: Locally the field becomes strongly nonuniform. If there is a great difference between the permittivities of the impurity and of the medium, then the local field intensity in the medium at the interface can be 20 to 50 times that of the original field. Bubbling occurs most easily in liquids containing impurities. Compare this situation with that in a solid. The microphysical influence of an impurity on the crystalline order in a solid is of very great importance, since the total physical equilibrium responsible for the strong bond between molecules can be ensured only by a perfect order. Every impurity, or boundary, disturbs this order and causes a decrease in the original polarization of the boundary molecules. So the possibility of bubbling (gassing) exists also in the solid. If there is a defect in the structure of a crystal, and some of the neighbors of a given molecule are missing, then the polarization of that molecule will decrease to a few percent of its original value or the bond may no longer exist. If the number of missing neighbors is as high as four the bond almost certainly will break. An externally applied electric field can easily break the bond for even fewer absent neighbors. When this happens the boundary molecule breaks out of the lattice and becomes free, entering into a gaslike state. The role of impurities and the defects they cause is as crucial in determining liquid-state properties as it is in determining solid-state properties. Recall the situation in colloidal systems, which may be stable over long periods only because of the presence of ionic material. As we have said, the amount of such material need be no more than is adventitiously present to create the double layers necessary for this stability.

Note how the phenomenon of bubbling requires a short range structure and demonstrates the role of interfacial phenomena in determining properties of the medium, which are made more pronounced by the presence of impurities. Let us consider the first aspect for nonpolar molecules, again following Ignacz's description. The nonpolar crystalline solid is stabilized by

van der Waals forces. The field at a lattice point j generated by the molecules at other points of the lattice is

$$E_j = \sum_k C_{jk} \frac{\alpha}{r_{jk}^3} E_k \qquad (2)$$

where r_{jk} denotes the distances between the points of the lattice, the factors C_{jk} depend on the angles between the directions of the radius vectors and that of Z, α is the polarizability, and E_k is the resultant field in the molecule at lattice point k. Calculations show that the moments and internal fields of the molecules along a given Z-line all have the same direction P or A, where in type P E_k and M_k (the dipole moment of the molecule) are parallel to Z and in type A both are antiparallel to Z. Along a line perpendicular to Z there are alternating P- and A-type moments. The moments pointing in the same direction in a Z-line attract each other, as do two moments of opposite directions in a line perpendicular to Z. "In fact, *only the above arrangement can give a cohesive structure*."[56] The intermolecular bond energy of a chosen molecule is given by

$$V_j = -\alpha E_j^2$$

In the presence of an external field this becomes

$$V_j = -\alpha E_j (E_j - E)$$

A cubic or parallelepiped-based (if the molecules are elongated) lattice is identical to a lattice consisting of regular or irregular octahedrons. There is a molecule, c, in the center of each octahedron and its "nearest neighbors" are the molecules at the six vertices—two of P type and four of A type.

Thus, Ignacz proposes that during melting the solid crystal decomposes into uniform octahedral groups (liquid grains, the building blocks of condensed-state matter). The cubic lattice of molecules built up by octahedral groups is complete, with no lack or surplus of molecules. The system of equations (2), considered exclusively for the molecules of an octahedron, proves to be a stable formation in itself. As we have seen, the distances between molecules in the liquid, in some directions at least, are smaller than in the solid state. These can be calculated as for the solid crystalline state, with the important difference that we cannot assume that all of the local fields at a lattice point have the same absolute value. Formally the intermolecular bond energies are then the same in the liquid as in the solid state.

At the boiling point a second crystalline change occurs during which all of the grains totally decompose. The grains, and within them the molecules and atoms, are in thermal motion. The six peripheral molecules of a grain are in vibration relative to the central molecule. If the vibrational energy exceeds the bond energy, the grain disintegrates. This must occur at various places from time to time, producing gaslike molecules (it is an accepted fact that a liquid always contains a certain percentage of gas molecules). Gassing is produced within the bulk liquid itself by natural thermal motions and the subtleties of the intermolecular interactions. Ignacz calculates that "at room temperature about 10% of the molecules are unattached, and at a temperature somewhat below the boiling point this becomes about 25%." Hence, "there will always exist cavities in a liquid... a cavity which, for some reason, has survived for some time and exceeds a given size, shows a tendency to grow into a bubble."

An electric field contributes to the formation of cavities and their subsequent growth into bubbles. Recombination of unattached gaslike molecules to liquid grains is rendered difficult because they become polarized in the direction of the P-type molecules by the external field. Their dipole moments have the same direction as those of the grain fragments, contrary to the antiparallel direction that would be required for their recombination. We have already discussed the role of the external fields in breaking intermolecular bonds in cavity regions. The field may be able to detach A-type molecules of a complete grain. The accelerating effect of the field on ions and electrons causes the microbubbles to become charged and grow to macroscopic size. The fields must again have their most pronounced effects at interfacial regions where the change in permittivity is most significant, that is, across a solidlike–gaslike surface of a grain fragment. The electron distribution and its distortion at an interface is of paramount importance.

C. The Induced Translation of Liquids in External Electric Fields

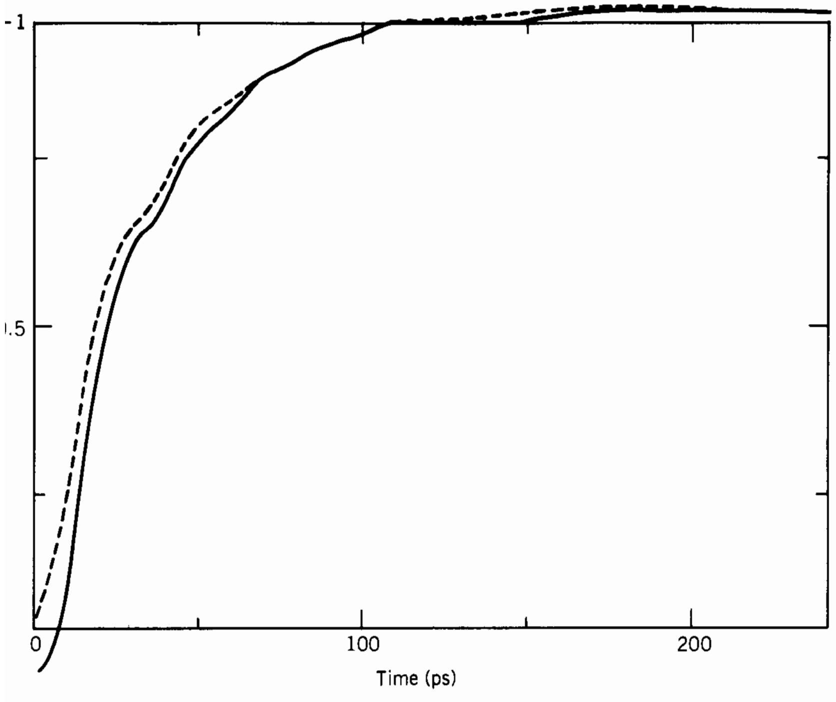
From the foregoing it is apparent that the intermolecular forces in the liquid state, like those of chemical bonding itself, are expressions of the electrical nature of matter and the distribution of electrons in the system. As Faraday taught us, magnetic aspects are also directly involved. These electronic distributions may be modified by external electric fields, particularly at interfacial regions in the medium. Quoting Davies:[103] "All our understanding of the behaviour of molecular systems, including biological systems, rests on our ability to represent interactions in an electric field, as there is, in these systems at the molecular level, nothing known to science other than atoms composed of localized positive and distributed negative charges."

Evans[13] has reported the observation of induced translation in *insulating* molecular liquids. Liquids may be suspended and, in some instances, even pumped rapidly against gravity. Induced translation occurs in both polar and nondipolar molecular liquids; the phenomenon is a general one. We have explained it in terms of nonuniform electric field effects on matter and dielectrophoretic forces. In one of our experiments the electric field between two parallel brass electrodes warps and rapidly becomes nonuniform in the region of the liquid–air interface (Fig. 16) and also within the bulk liquid itself.[79] The molecules become polarized, acquiring a negative charge on the side nearest the positive electrode and a positive charge on the side nearest the negative electrode. Because the field is nonuniform, it diverges across the molecules and produces unequal forces on the two effective ends of the molecules. The net effect, even on nonpolar molecules, is an overall force that results in the molecule being impelled into the region of stronger field. Ours is a paraelectric effect resulting from a two-step process, namely, polarization followed by the action of the nonuniform field on the polarized molecule producing a dielectrophoretic force toward the region of higher field intensity. Note that the effect of the first stage of this process at the molecular level may, therefore, increase the influence of rotation on translation, and vice versa.

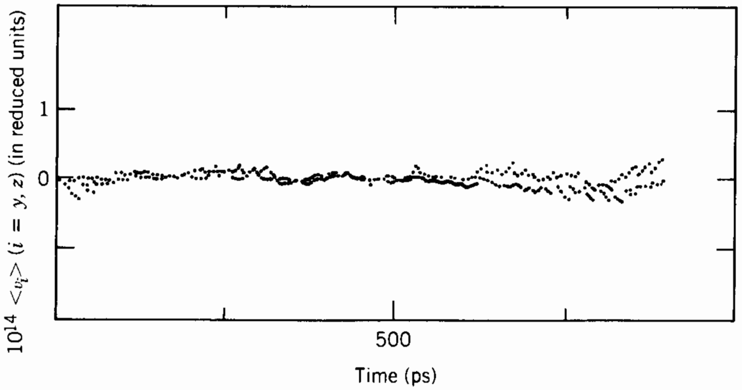
As we have seen, we can study this influence with a molecular-dynamics computer simulation. In a simulation of 108 CHBrClF molecules, the application of a strong external electric field was seen to produce a net translation of the sample even though the direct effect of such a field on an isolated molecule is purely rotational. Computer simulation shows that on the molecular level, a redistribution of rotational to translational energy occurs in the presence of an external electric field. The statistical correlation between the rotational motion of a chiral molecule and its center-of-mass translation may therefore be used to separate, for example, the enantiomers of a racemic mixture by irradiation with an external field of force—a conclusion first arrived at by Baranova and Zeldovich[115] using hydrodynamic arguments based on the propeller effect in molecules that are left or right handed. The induced translation of one enantiomer, by symmetry-mirror images, must be opposite in direction to that of the other.

In the computer simulation[116] an electric field effective in the z-direction of the laboratory frame was applied[66] to the sample. The effect of the field was programmed into the algorithm in a variety of ways. The simplest was to take the net molecular dipole as the arm of the torque imposed on each molecule by the field of force $E_z \equiv |\boldsymbol{E}|$. A second method was to decompose the electrostatic characteristics of each molecule into point charges located at each atomic site and to simulate the torque via the net force $\sum_i e_i E_z$, where e_i is the fractional charge on each atom of each of the (S)-CHBrClF molecules. To emphasize the translation effect, a field strength E_z was chosen sufficient to saturate the system, producing an orientation rise transient as illustrated in Fig. 24. The mean molecular center-of-mass velocities $\langle v_x \rangle$, $\langle v_y \rangle$, and $\langle v_z \rangle$ were monitored in the presence of the field over some thousands of time steps using the methods of conventional constant-volume computer simulation.[117]

The effect of saturating the molecular ensemble with the strong field E_z is to force each and every one of the 108 molecules to rotate in the same direction against their natural thermal motions. An appropriate orientational



igure 24. The rise transient $\langle e_{3z} \rangle$, where e_3 is a unit vector in the 3-axis of the principal ent-of-inertia frame of (3)-CHBrClF. The angle brackets denote averaging over the num-f molecules in the ensemble at each time step. (Reproduced by permission from ref. 118.)



e 25. The behavior of $\langle v_z \rangle$ (straight line) and $\langle v_y \rangle$ (dotted line) in the absence of an applied field. (Reproduced by permission from ref. 118.)

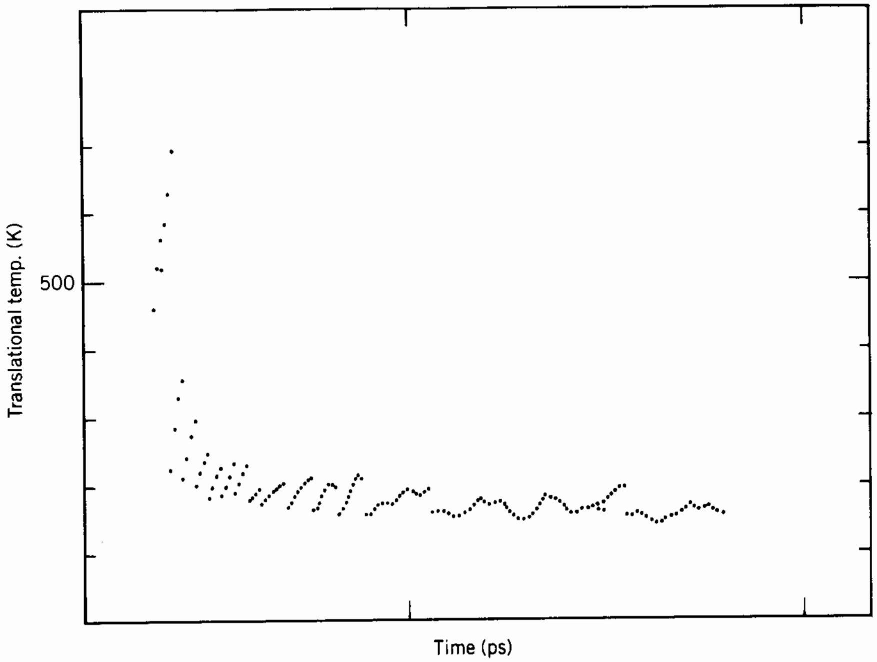


Figure 26. The effect of the thermostat on the translational temperature. (Reproduced by permission from ref. 118.)

average such as $\langle e_{3z} \rangle$ then evolves as in Fig. 25; (that is, it rises from near 0 to near 1 in a finite interval of time—the rise transient. In our case this is about 0.6 ps from the instant the field is applied. Before application of the field, the system is in equilibrium with $\langle v_x \rangle = \langle v_y \rangle = \langle v_z \rangle \doteqdot 0$ (Fig. 25) and with a translational temperature of about 158 ± 25K. The sample is thermostatted by the conventional method of temperature rescaling. Figure 26 illustrates the work the thermostat does in restoring the translational temperature to 158 ± 25K after the sudden input of energy from the field E_z at $t = 0$. Immediately after $t = 0$, during the initial lifetime of the rise transient (about 0.07 ps), the translational temperature is very high, despite the fact that the effect of E_z on an isolated molecule would be purely rotational. After about 0.07 ps, the thermostat has effectively reduced the temperature once more to the required 158 ± 25K. The important point to note about Fig. 26 is that in the interval from about 0.07 ps to 5 ps the temperature is roughly constant at the same level as prior to the application of the field E_z.

In the interval from 0.07 ps after the field is applied the behavior of $\langle v_x \rangle$, $\langle v_y \rangle$, and $\langle v_z \rangle$ is illustrated in Fig. 27. It is clear that all three components of the mean molecular center-of-mass translational velocity of the 108 molecules gradually increase in magnitude over an interval of time much longer

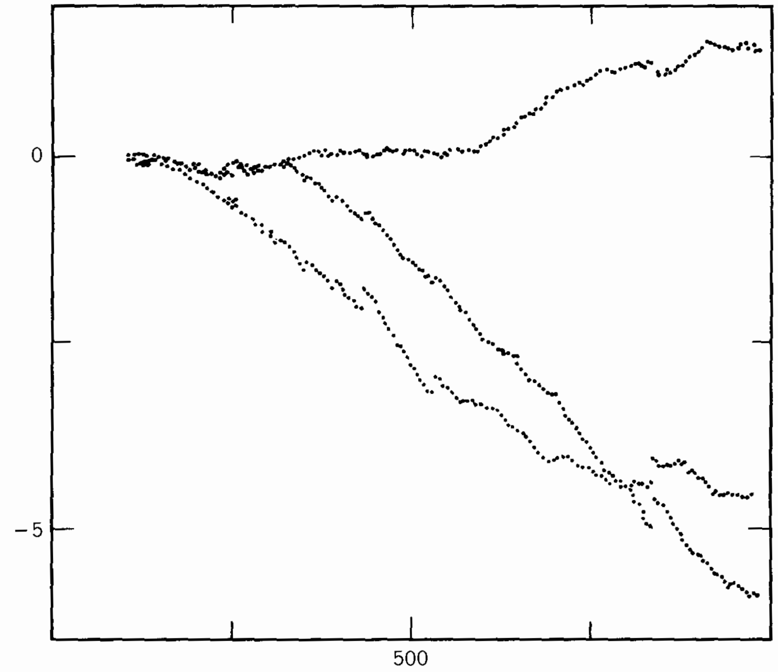


Figure 27. The behavior of (1) $\langle v_z \rangle$, (2) $\langle v_y \rangle$, and (3) $\langle v_x \rangle$ in the presence of a strong unidirectional field E_z. In contrast to the situation in Fig. 25, the averages are considerably different from zero. (Reproduced by permission from ref. 118.)

than that of the orientational rise transient. If the direction of E_z is reversed (i.e., $E_z \to -E_z$), the orientational rise transient is unaffected, but the drift $\langle \mathbf{v} \rangle$ is reversed.

These results can be explained only if rotational and translational motions are mutually coupled.[112] In simple terms, the field E_z forces the 108 molecules to rotate in the same way. Rotational freedom, at least in one direction, is restricted and there occurs a redistribution of the total thermal energy into other modes of motion. These may be translational modes—producing the observed translational motion. Because the induced translational motion for all the molecules is necessarily in the same direction (because of the unidirectional external field), the whole bulk sample must translate.

In their paper Baranova and Zeldovich[115] used the electric component of a circularly polarized electromagnetic field of force and showed that this type of field produces a translational effect similar to that illustrated above. Note that the orientational variable $\langle e_{3z} \rangle$ responds much more quickly to the field than does the translational variable $\mathbf{v}$. The extreme importance of

rotation–translation interaction is established. So too vibration and rotation translation may be coupled. Van Woerkom et al.[118] were perhaps the first to question the separation of vibrational and reorientational functions in analysis of infrared and anisotropic Raman profiles for details of molecular dynamics. Lynden-Bell,[119] in reexamining the problem, showed theoretically that in many instances the line has a Lorentzian shape with a width equal to the sum of the vibrational and reorientational parts. Sometimes, however, these components become coupled to give complex, non-Lorentzian line shapes that are sometimes broader than expected, sometimes narrower, and on occasions showing a central dip. She also found that the linewidth sometimes varied with ℓ, that is, with the particular experiment. The coupling between *inter*molecular vibrations and other modes of motion must be significantly more pronounced.

IV. SOME CONCLUDING REMARKS—A CLASSICAL OR QUANTUM-MECHANICAL PROBLEM?

Some of the phenomena we have discussed are not predicted by and may not be explained using classical laws. Classical theories represent ensembles of molecules, as in a liquid, for example, as a system of particles or, at best, rigid bodies, and do not consider the detailed electrical nature of matter. When a body is considered as a particle, it is implicitly assumed that the mass is concentrated at a point and that all external forces *act through the same point*. As we have seen, in general, in heteronuclear molecules the electrical center (which is also the center of interaction) is displaced from the center of mass, which leads to the coupling of rotational and translational motions. Halfman[120] sums up the situation thus: "The particle approximation cannot serve even as a rough approximation in many situations. For example, it can give no information concerning the rotational motion of rigid or flexible bodies and by itself is useless in an attempt to study the dynamics of a fluid." Halfman discusses the analogies between fluid fields and electromagnetic fields and at the same time, by considering two charged particles in relative motion, provides some insight into the difficulties of applying classical Newtonian mechanics to the motion of charged particles. And Goldstein[121] warns that theorems derived for a system of particles should "be applied with due care to the electromagnetic forces between moving particles." Electromagnetic forces between moving particles do not generally obey Newtonian mechanics;[121] the third law is violated and the conservation of angular momentum, even in the absence of applied torques, is not valid. Internal forces of electromagnetic origin do not ordinarily have the convenient property of occurring in pairs that are collinear, equal, and opposite.

Molecules in a liquid are held together without being chemically bonded in the strictest sense. We say that residual forces hold them together—forces hat must be electromagnetic in origin. The molecules and groups of mole-ules are polarizable; the repulsive forces change with the orientation of the nolecule and are time-varying quantities; the centers of electrical interacion may not coincide with the center of mass and may be shifted with re-pect to this center by external electric fields; the distances between the atoms f the molecule are not constant because of intramolecular vibration; and he total potential energy of an ensemble of such molecules may not be ap-roximated by the sum of interactions of all possible pairs.

Quoting Planck:[122]

> Hitherto it has been believed that the only kind of causality with which any system of physics could operate was one in which all the events of the physical world might be explained as being composed of local events taking place in a number of individual and infinitely small parts of space. It was completely determined by a set of laws without respect to other events; and was determined exclusively by the local events in its immediate temporal and spatial vicinity. Let us take a concrete instance of sufficiently general application. We will assume that the physical system under consideration consists of a system of particles, moving in a conservative field of force of constant total energy. Then according to classical physics each individual particle at any time is in a definite state; that is, it has a definite position and a definite velocity, and its movement can be calculated with perfect exactness from its initial state and from the local properties of the field of force in those parts of the space through which the particle passes in the course of its movement. If these data are known, we need know nothing else about the remaining properties of the system of particles under consideration.
>
> In modern mechanics matters are wholly different. According to modern mechanics, merely local relations are no more sufficient for the formulation of the laws of motion than would be the microscopic investigation of the different parts of a picture in order to make clear its meaning. On the contrary, it is impossible to obtain an adequate version of the laws for which we are looking, unless the physical system is regarded as a whole. According to modern mechanics, each individual particle of the system, in a certain sense, at any one time, exists simultaneously in every part of the space occupied by the system. This simultaneous existence applies not merely to the field of force with which it is surrounded, but also to its mass and charge.
>
> Thus we see that nothing less is at stake here than the concept of a particle —the most elementary concept of classical mechanics. We are compelled to give up the earlier essential meaning of this idea; only in a number of borderline cases can we retain it.

We have tried to retain the concept of a particle in our treatments of quid-state matter, with limited success. Our molecular theories are still not redictive; we still cannot calculate with any degree of precision seemingly mpler phenomena such as the solubility of one substrate in another. In this

review I have presented experimental evidence that even requires that the concepts of collective molecular motions and distributed electric charge be introduced into our theories of liquid systems. Such concepts could certainly be used to explain some of the spectroscopic and electrical properties of liquids that have been presented.

Fortunately, to this end, it has recently been shown how the span between classical physics and quantum physics may be bridged using a mechanism derived only from classical physics. Piekara[123] considers the phenomenon of self-trapping (of, for example, a powerful laser beam in a liquid such as water), *a classical phenomenon based on the nonlinearity of the classical Maxwell equations.* As Piekara reminds us, "Maxwell's equations are essentially macroscopic, and are generally used in the linear approximation. However, these equations, with a change of name, 'microscopic Maxwell equations,'[124] are applied in the same linear form [incorrectly, Piekara believes] to isolated atoms and charges in any small volume." The main conclusion of Piekara's paper is that the quantum structure of waves is due to the nonlinearity of the wave equation. The nonlinear terms result in the self-trapping of waves, as, for example, in the liquid environment, and the production of photons. He provides us for the first time with a classical understanding of the energy quantum.

We have already made reference to the way in which the use of electron density as a basic variable in applied quantum mechanics may make possible the simplification of the usual wavefunction approach, the experimental determination of the physical variables, and the construction of various interpretive models, and thus may ultimately provide a "classical" picture of what are essentially quantum phenomena. We reiterate that the theory of chemistry and the chemical bond, whether intra- or intermolecular, permanent or temporary, is primarily a theory of electron density. The crystal-growing procedure and the thermodielectric effect certainly seem to be subtle consequences of electron redistribution across two phases of matter.

APPENDIX A: SOME POSSIBLE CONSEQUENCES OF THE THERMODIELECTRIC AND RECIPROCAL EFFECTS

As we have seen, the new crystal-growing technique reported in Section III.A is the reciprocal[125] of the little-known thermodielectric effect of Costa Ribeiro. Costa Ribeiro asserted that electric charges are always produced at the interface between the liquid and solid phases in a dielectric and may be observed not only in melting and solidification, but also in other changes of physical state in which one phase is a solid, such as sublimation and the precipitation of substrates from saturated solutions. These two effects demonstrate that mechanisms involving charge migration are involved in the nucleation process. Workhom and Reynolds[86] found potentials of greater than 200 V between ice and water phases *when a phase change was occurring.*

These two effects may explain many natural phenomena. For example, "before a thunderstorm, fair weather clouds suddenly grow dramatically in size and begin to exhibit *strong electric fields and precipitation*... almost without exception thunderclouds are characterized by convective instability with *strong up-drafts and down-drafts*... in a matter of less than 10^3 sec an innocuous cumulus cloud can suddenly change into a thundercloud producing both *heavy precipitation and lightning charges.*[126] These observations may now be explained because electric charges are always produced in changes of state involving a solid, including precipitation (the thermodielectric effect). Conversely, as the author has shown, electric fields may be used to induce phase changes at *an interface* between two states of matter when one of the states is a solid. Thus, in meteorological studies, "recent years have brought increasing evidence that electric fields can exert a pronounced effect on *the rate of growth of ice crystals in supercooled clouds*; indeed, it appears that under certain conditions *electric fields are responsible for ice nucleation phenomena* similar to those produced by cloud seeding techniques. Evidence is rapidly accumulating that electrostatic effects, far from being an incidental by-product of processes taking place in a thunderstorm, may be vitally important in determining the behaviour of the cloud."[126] The growth of ice crystals in field regions at an ice–water interface, reported by the present author, seems to substantiate this important hypothesis. Ice crystals may be grown from the melt in the laboratory in a simple manner using nonuniform electric fields.

It is known that in thunderstorms the intensity of electrical activity, as indicated by the number and repetition rate of lightning discharges, is closely related to the intensity of the convective activity. The existence of electrical forces in the atmosphere creates drafts of air, and it is estimated that in the strong electric fields in a thunderstorm the accelerations experienced by air might be equivalent to those resulting from temperature differences of as much as 5°C. Even so, movements of air in thunderstorms are for the most part the results of atmospheric temperature differences, which may be as large as 50°C.

Costa Ribeiro deduced that:

1. The current that flows in a thermodielectric cell on isothermal fusion or solidification occurring at a constant rate is proportional to the rate of migration of the phase boundary.
2. The total quantity of electric charge separated during the migration of the phase boundary in a two-phase dielectric system is proportional to the change of mass of one of the phases.

Considering these two laws in relation to thunderstorm activity, it is apparent that the convective activity resulting from temperature differences of as much as 50°C is so intense that the ice–water equilibrium in the atmosphere is continually and rapidly fluctuating. Law 1 tells us that large currents are consequently produced. In any natural phenomenon such as a thunderstorm, vast masses of ice and water are involved, and the changes of mass brought about by this convective activity are thus large. Very large electric charges are consequently produced (law 2), resulting in electrical breakdown of the atmosphere (lightning). Vonnegut[127] has estimated that "in the severe thunderstorms that produce tornadoes, lightning flashes at the rate of 10 or 20 per second may be capable of supplying power of the order of 10^8 kW" and has suggested that "if a column of air were heated by electrical discharges it might be capable of producing an updraft sufficient to cause a tornado."

There must also be biological consequences of these effects. Heinmets[128] pointed out the similarities between the Costa Ribeiro effect and electrical effects in biological systems. Many of the voltage curves recorded during the freezing of ice water, for example, resemble nervous impulses. We have already discussed other possible biological consequences in the text.

APPENDIX B: CRYSTAL GROWTH IN MAGNETIC FIELDS

Since writing this review, the author has observed the effects of magnetic fields[129] on the crystallization of 4*n*-octyl biphenyl from benzene solutions. 4*n*-Octyl biphenyl was specifically chosen for the experiment because of the existence in it of the magnetic moments associated with the π-electron clouds that are considered necessary for the observation of the effect. The author has not been able to observe similar effects of magnetic fields on the crystal growth of, for example, camphor from CCl_4 solution, as used in the electric field experiment described in Section III.A. It is important to realize that *n*-octyl biphenyl is not a liquid crystal in the melt (it is a solid at room temperature). However, 4-cyano-4*n*-octyl biphenyl forms both nematic and smectic phases. The effect of magnetic fields on the crystallization of the former is therefore all the more surprising.

Figures 28–30 show the effects of magnetic fields on the crystallization of 4-*n*-octyl biphenyl from a saturated solution in benzene. The magnetic field *induces a bulk translation of the sample — solution is expelled from the field region when a field is applied.* The author believes this is the first report of bulk translation in an isotropic liquid induced by an external magnetic field.

Figure 28 shows the crystals of *n*-octyl biphenyl grown from solution in benzene by evaporation in a darkened room. Note the random arrangement of crystalline masses. Figure 29 shows crystals of *n*-octyl biphenyl grown in

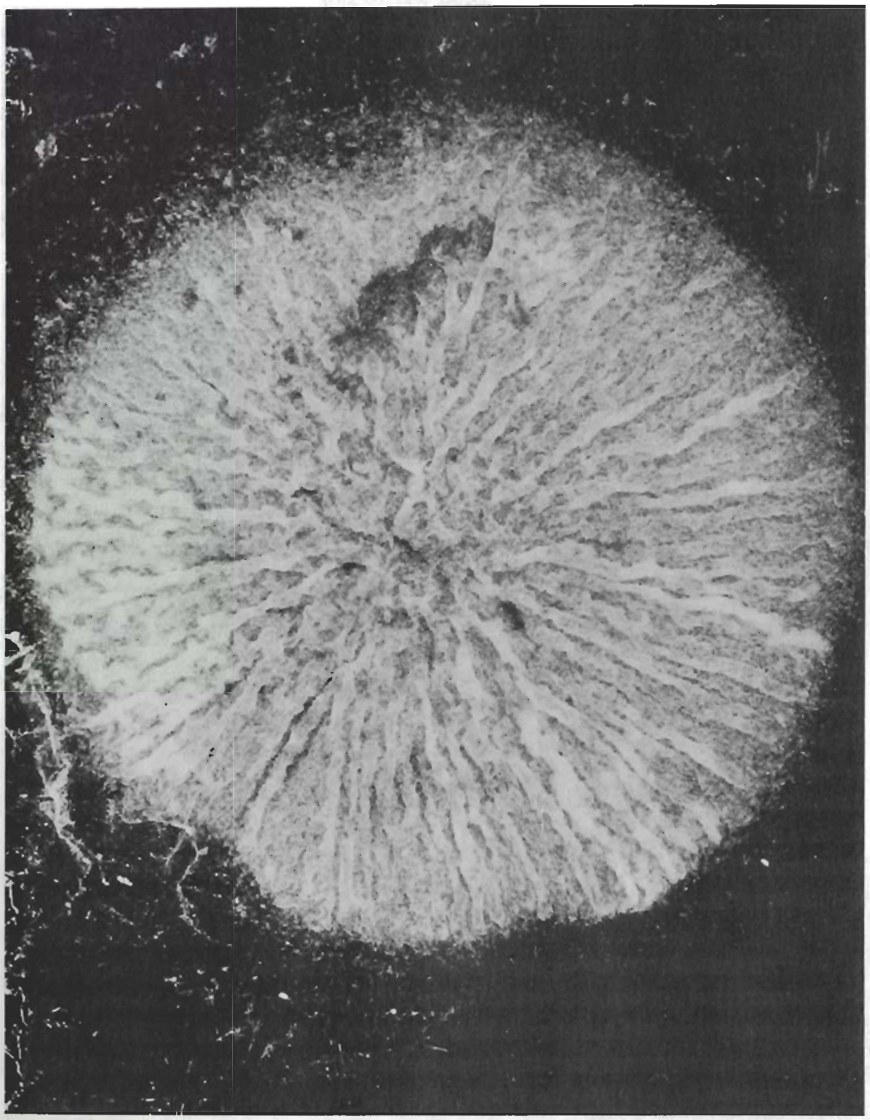


Figure 29.

a magnetic field of medium intensity (~ 5000 G) on a watch glass that retains the solution in the region of the field. Note the distinct veins following the magnetic lines of force running from the center to the perimeter. Single crystals, however, are not grown in this medium-intensity field. Figure 30 shows a single crystal of 4-*n*-octyl biphenyl grown in a strong magnetic field (> 1000 G). Arrows indicate the perimeter of the crystal (photographed on a darkened background), which is transparent in most regions.

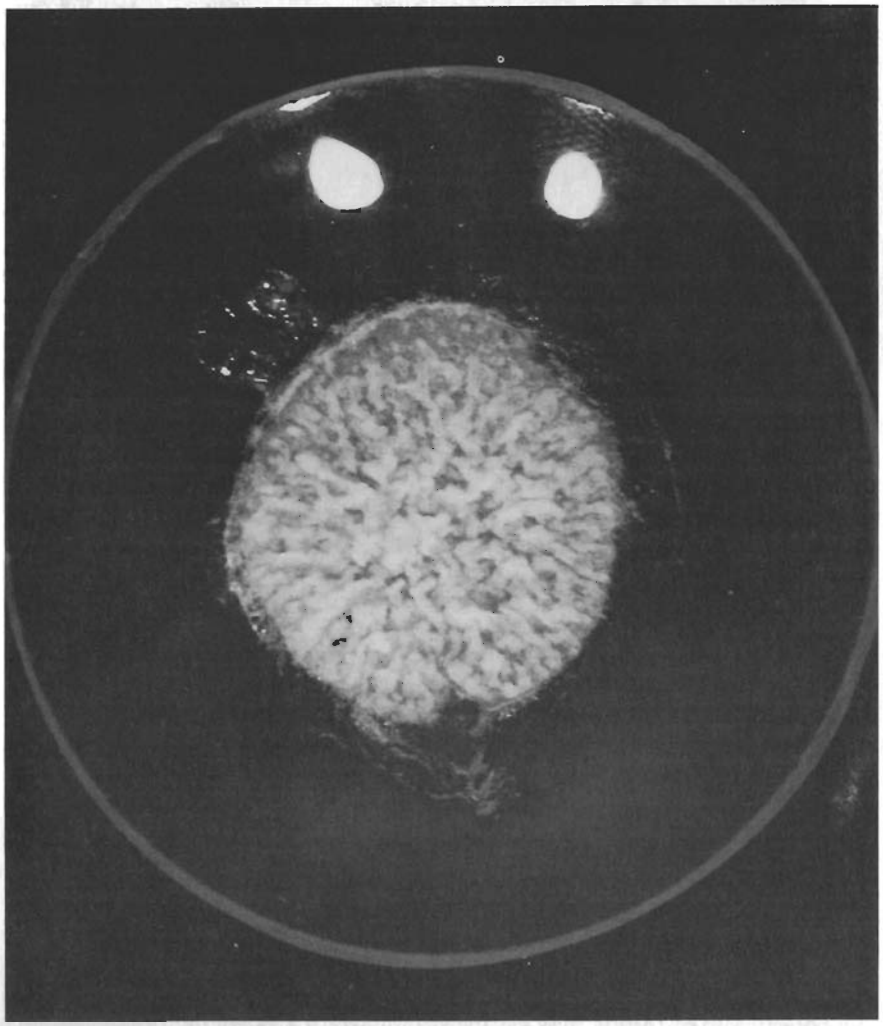


Figure 31.

It is interesting that in electric fields (Section III.A) crystals grow normal to the surface, whereas in magnetic fields the crystals grow parallel to the surface, at least at the field strengths currently used. However, crystals of azobenzene have recently been "pulled" out of solution in benzene by this author using similarly small magnetic fields. Note that the reciprocal, using magnetic fields, of the crystal-growing technique reported here may also exist, that is, the magnetic analogue of the thermodielectric effect of Costa Ribeiro.

It is important not to pretreat in any way the glass or plastic surfaces used to grow these crystals in magnetic fields. Even surfaces that are repeatedly used for crystallization may become charged. The author has successfully grown single crystals on charged glass and plastic surfaces. Also, it is essential to grow the crystals in darkened rooms, away from direct sunlight. The author believes that electromagnetic fields have similar influences on the crystallization of 4-*n*-octyl biphenyl. Figure 31 shows crystals of 4-*n*-octyl biphenyl grown in a darkened room under thermostatted temperature conditions. Note the random arrangement of crystalline masses, as in Fig. 28. Figure 32 shows crystals of *n*-octyl biphenyl grown in direct sunlight. The same solution (and same volume of solution) was used for Figs. 31 and 32. The crystals took significantly longer to grow in direct sunlight, even though the temperature was slightly higher and one would expect the evaporation rate to have been increased. In the crystals that grew in direct sunlight, distinct veins appear to follow the direction of incidence of the sunlight (indicated by an arrow). It would be desirable to repeat such experiments using electromagnetic fields under conditions controlled precisely using laser/light sources and careful temperature control.

Living matter, of course, grows in electromagnetic fields. Plant life grows toward the light source itself, with growth originating at sensitive *surface regions*. As Calvin[130] says, in relation to the study of photosynthesis,

> we are now in the midst of trying to determine precisely what happens after chlorophyll has absorbed the quantum and has become an excited chlorophyll molecule, a problem that involves the physicist and physical chemist, as well as the organic and biochemists. The determination of the next stage in the energy-conversion process is one of our immediate concerns. Either it is *an electron transfer process*, and thus comes close in its further stages to the electron transfer processes which are being explored in mitochondria, or it is some independent non-redox method of energy conversion. This remains for the future to decide.

Present observations may be providing vital clues to the details of such processes. Studies should be extended gradually to more ordered liquid crystalline phases and then to biological materials themselves. Certainly it is

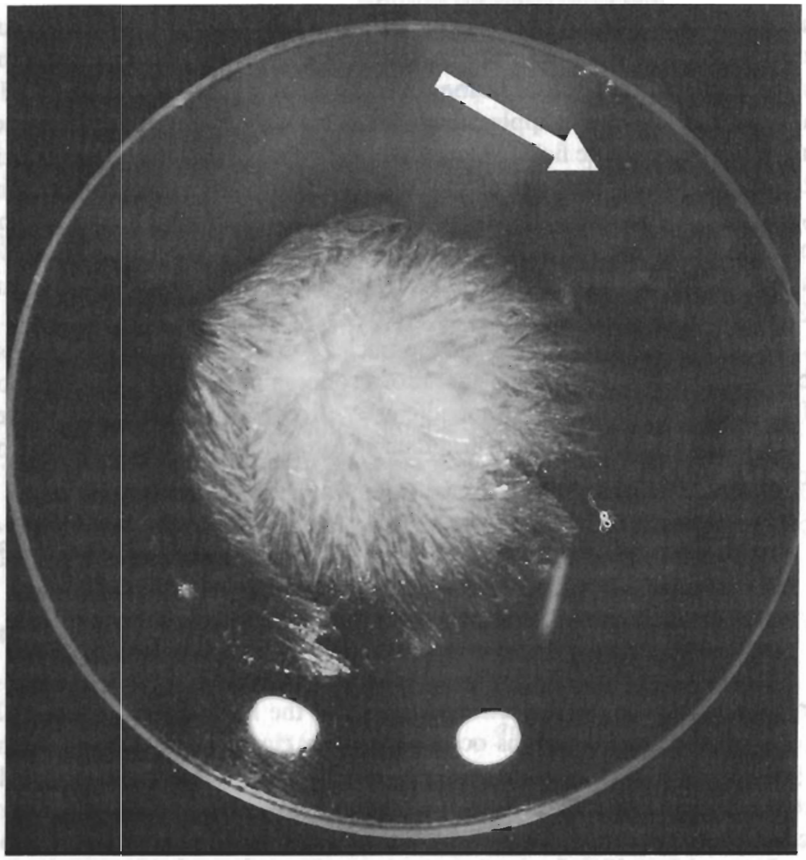


Figure 32.

now established that a specific electric charge is associated with a change of state or aggregation of matter, that is, with an order–disorder (or vice-versa) phase change (including a liquid crystalline-to-solid phase transition[98]). And it is established that external fields may influence and even cause such phase changes. A theory predicting such influences is abstracted in the Appendix C.

APPENDIX C: THE INFLUENCE OF ELECTRIC AND MAGNETIC FIELDS ON NUCLEATION KINETICS—THEORETICAL CONSIDERATIONS

Kashchiev[131] presents a theory explaining the effects of externally applied uniform electric fields on homogeneous nucleation as well as on nucleation on foreign completely wettable particles. He shows by means of a suitably defined effective supersaturation that if the dielectric permittivity of the new phase is smaller than that of the old phase, the electric field stimulates the nucleation, whereas in the reverse case it inhibits the process. He points out that his results apply equally to nucleation taking place in an external uniform magnetic field. Shablakh et al.[132] have observed in an investigation of the phase structures of the four cycloalcohols from cyclopentanol to cyclooctanol that time-dependent transformations occurred between some of these phases, and that at least one of these transformations was sensitive to the application of an electric field. They discuss their observations in terms of Kashchiev's theory.

Kashchiev derives equations for the nucleation rate and the time lag on the basis of thermodynamic considerations concerning the work required for the formation of a spherically shaped cluster. According to electrostatic theory, the free energies of the electric field before and after the formation of the cluster are given respectively by

$$W_1 = \frac{\varepsilon_m}{8\pi}\int_{\Omega_m} E^2\,dv \tag{3}$$

$$W_2 = \frac{\varepsilon_c}{8\pi}\int_{\Omega_c} E_c^2\,dv + \frac{\varepsilon_m}{8\pi}\int_{\Omega_m - \Omega_c} E_m^2\,dv \tag{4}$$

where ε_c and ε_m are the dielectric constants of the new and old phases; Ω_c and Ω_m are the spatial regions occupied by the cluster and by the system; $E = |\mathbf{E}|$, $E_c = |\mathbf{E_c}|$, $E_m = |\mathbf{E_m}|$ and $\mathbf{E_c}$ and $\mathbf{E_m}$ are the electric fields inside and outside the cluster.

Assuming a spherically shaped cluster, and considering that the system too is a sphere with radius R obeying the inequality $R^3 \gg r_c^3$, where r_c is the radius of the cluster, then in spherical coordinates r, θ, ϕ,

$$\begin{aligned} E_c,\ r &= \frac{3\varepsilon_m}{\varepsilon_c + 2\varepsilon_m} E\cos\theta \qquad 0 \le r < r_c \\ E_c,\ \theta &= -\frac{3\varepsilon_m}{\varepsilon_c + 2\varepsilon_m} E\sin\theta \qquad 0 \le \theta < \pi \\ E_c,\ \phi &= 0 \qquad 0 \le \phi < 2\pi \end{aligned} \tag{5}$$

and

$$\begin{aligned} E_m,\ r &= \left[2\frac{\varepsilon_c - \varepsilon_m}{\varepsilon_c + 2\varepsilon_m}\left(\frac{r_c}{r}\right)^3 + 1\right] E\cos\theta \qquad r_c \le r < R \\ E_m,\ \theta &= \left[\frac{\varepsilon_c - \varepsilon_m}{\varepsilon_c + 2\varepsilon_m}\left(\frac{r_c}{r}\right)^3 - 1\right] E\sin\theta \qquad 0 \le \theta < \pi \\ E_m,\ \phi &= 0 \qquad 0 \le \phi < 2\pi \end{aligned} \tag{6}$$

where the center of the cluster is chosen as the origin of the coordinates and the polar axis has the direction of the applied electric field.

With a little mathematics, using the inequality $r_c^3 \le R^3$ we find that the free-energy change due to the field is given by

$$\Delta W_E = W_2 - W_1 = -\frac{\varepsilon_m}{8\pi} f(\lambda)\nu_c E^2 x \tag{7}$$

where

$$\begin{aligned} f(\lambda) &= \frac{1-\lambda}{2+\lambda} \\ \lambda &= \frac{\varepsilon_c}{\varepsilon_m} \qquad 0 < \lambda < \infty \end{aligned} \tag{8}$$

so that for $\varepsilon_c < \varepsilon_m$ the electric field stimulates cluster formation, whereas for $\varepsilon_c > \varepsilon_m$ the field inhibits it.

Using Eq. (7) and the expression of Volmer[133] for $\Delta G_0(x)$, the isothermal reversible work required for the formation of a cluster of x atoms (or molecules) in the absence of a field,

$$\Delta G_0(x) = -kTS_0 x + \frac{a\sigma x^2}{3} \tag{9}$$

we obtain

$$\Delta G(x) = -kTSx + \frac{a\sigma x^2}{3} \tag{10}$$

where $\Delta G(x)$ is the work expended in the presence of a field, $S_0 = \ln(P/P_e)$ and is the supersaturation, P_e is the equilibrium pressure, k is the Boltzmann constant, σ is the specific surface energy, $a = (4\pi)^{1/3}(3\nu_c)^{2/3}$ is a constant, and $\Delta G(x) = \Delta G_0(x) + \Delta W_E(x)$. Hence, the effective supersaturation at which cluster formation occurs is given by

$$S = S_0 + S_E \tag{11}$$

and the influence of the electric field on the process is taken into account through the additional term

$$S_E = cE^2$$

in which $c = \varepsilon_m f(\lambda)\nu_c / 8\pi kT$ is a constant.

The steady-state nucleation rate is given by

$$J_{ST} = \left(\frac{\Delta G_k}{3\pi kTx_k^2}\right)^{1/2} D_k N \exp\left(\frac{-\Delta G_k}{kT}\right) \tag{12}$$

where N is the total number of atoms in the system and $D_k = \alpha a x_k^{2/3}$ is the probability per unit time of an atom joining to the nucleus.

Assuming that the dependence of the frequency factor α on the electric field strength is weaker than an exponential one, then, following Volmer,[135] we can write

$$J_{ST} = A\exp\left[\frac{-B}{\left(S_0 + cE^2\right)^2}\right] \tag{13}$$

where $B = 4(a\sigma/3kT)^3$. A is also a constant. Thus, for $c > 0$ ($\varepsilon_c < \varepsilon_m$) the electric field stimulates nucleation, and for $c < 0$ ($\varepsilon_c > \varepsilon_m$) the field inhibits the process.

For $S_0 = 0$, $c > 0$, the system is saturated before application of the field and

$$J_{ST} = A\exp\left(\frac{-B}{c^2E^4}\right)$$

that is, the field stimulates nucleation.

For $S_0 > 0$, $|S_E| < 0.1S_0$, the system is supersaturated and the supersaturation is either enhanced or reduced by the field within the limits indicated.

From Eq. (13) it follows that E_{cr}^2 is a linear function of S_0.

Kashchiev also considers nucleation on a foreign particle. In obtaining these relations he assumes a spherically shaped cluster, but "in principle, the more realistic case of ellipsoidal or polyhedral shape may be treated in the same way, but then serious mathematical difficulties have to be overcome."[131] However, he concludes that "when a uniform electric field is externally applied to a nucleating system the initial supersaturation S_0 in it will be effectively either enhanced or reduced, depending on the sign of the constant multiplying E^2x."

Kashchiev estimates that a field of $< 6.14 \times 10^3$ kV cm^{-1} is necessary to *inhibit* the formation of a water droplet. Such a field is orders of magnitude larger than the fields used by the present author for his camphor CCl_4 crystal-growth system, which are, in any case, nonuniform. The growth of camphor crystals from a saturated solution of camphor in CCl_4, for example, is observed in fields of only volts per centimeter. Crystals of camphor may also be grown away from a field region.[83] All of this seems to suggest that the phenomenon is an electrostatic one, involving charge migration as proposed by Costa Ribeiro.[85] Kashchiev points out that the results obtained in his paper "might be very useful in understanding some condensation phenomena occurring in the Earth's atmosphere in the presence of strong electric fields" (see Appendix A) and that "all results obtained hold good also when nucleation takes place in an externally applied uniform magnetic field" (see Appendix B).

Shablakh et al.[132] used their experiments on the cycloalcohols to examine the detailed predictions of Kashchiev's model, and in particular a square law dependence of some functions on the applied field. They observed that for such functions "the field power lies in the range 1.2 (cyclo-octanol) to 1.7 (cycloheptanol)." They propose that the discrepancies in the field power may have arisen because Kashchiev's calculation is based on the nucleation of a spherical droplet, a geometry which would be inappropriate to the solid–solid transition they examined. In cyclopentanol they observed a change in the field power exponent from 2.4 to 14 when the applied field was $> 5 \times 10^4$ kV cm^{-1}.

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A REVIEW AND COMPUTER SIMULATION OF THE MOLECULAR DYNAMICS OF A SERIES OF SPECIFIC MOLECULAR LIQUIDS‡

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‡ Dedicated to the South Wales Area of the National Union of Mineworkers.