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Stability Conditions for Polymer Dielectrics in Uniform Electric Field

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Summary

A classical model system consisting of the polymer molecules under the influence of a homogeneous external electric field is presented. A set of Lagrange equations of motion, characterized by only the nearest interactions of the atoms, are formulated. From them, the stability conditions for a polymer, defining a pre-breakdown phenomenon in the presence of an external homogeneous electric field, are derived.

Introduction

The very high resistivity of the common polymers makes them of great practical use as insulating materials. It is thus of enormous practical importance to understood the limitations in usefulness of these materials as insulators. In particular, there exists a critical voltage gradient across the material, above which the polymer no longer acts to insulate the electrical conductor (SCHULTZ, 1974). Interest in the physics of polymeric insulators centers about understanding the mechanism of the breakdown (MARČEK et al., 1981). Such understanding will presumably lead to an ability to tailor and control the insulating properties of polymers. It is generally agreed that breakdown must be somehow a property of the field - induced structural changes in the linear macromolecules. If the critical condition for the structural changes can be determined, the physics and physical chemistry of breakdown is fully understood. The instability may occur either directly through the breakdown of the binding forces or by generating heat suffi-

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cient to bring the material to its melting point.

It is well established fact that physical characteristics of molecules and ions in free-space approximation differ dramatically from those which characterize these systems under the influence of an external electric field (BECKEY, 1971). Otherwise, when an electric field is applied to a system, the electronic charge distribution, energy levels, and thus molecular geometries will be affected (BOUNDS et al., 1977, PANCÍŘ and ZAHRADNÍK, 1978). Thus, a breakdown of the bonding forces therefore occur from a polymer structure different to the field free one. When trying to analyse a behaviour of macromolecules in an external electric field it is of great importance to know what types of internal deformations can contribute to the changes in polymer chain molecule geometry under the influence of a progressively stronger electric field.

There are at least three types of internal deformation coordinates which are necessary for the complete definition of a polymer molecule distortions when the problem is defined in terms of the usual bond lengths and valence angles, and internal rotational angles.

In the present paper we formulate the stability conditions for a model system consisting of the linear macromolecules subjected to an homogeneous external electric field. We consider the case in which the uniform electric field $\vec{E}_{ext} \equiv \vec{E}$ is in the longitudinal direction, namely $\vec{E}_{ext} \equiv (0,0, \vec{E}_{||})$.

Dipole potential energy

Consider a linear macromolecule containing N skeletal bond numbered 1, 2, ..., N successively from one end to the other. The skeletal C-C bond lengths of linear vinylic molecule are represented by the bond length changes $r_1, r_2, \ldots, r_N$ and valence angle deformation $\phi_1, \phi_2, \ldots, \phi_{N-1}$. The internal rotational angles Θ_i about the i-th bond, measured from the trans position is assumed to be permitted to take N-2 discrete values by $\Theta_1, \Theta_2, \ldots, \Theta_{N-2}$. The bonds connecting the repeat units of a polymer chain are generally flexible enough to permit a degree of rotational freedom about the bonds. This freedom allows the molecule to assume any of a number of conformations. The limiting conformations are the random coil and the fully extended chain. The linear macromolecules subjected to an external field are deformed and the magnitude of the distance between chain ends increases with field intensity and the segments between the ends have fewer possible configurations.

The molecular charge distribution is approximated by an intrinsic permanent point dipole for each bond located at an arbitrary position (and pointing) along the bond. Induced dipoles are located as polarization centres at same positions as intrinsic dipoles. The magnitude and direction of each induced dipole is determined by a bond polarizability tensor and the electric field at its location. The sources of the field are all of the other intrinsic and induced moments in the molecule and mainly the uniform external electric field.

Let $\vec{\mu}_k^o$ and $\vec{\mu}_k^I$ be the intrinsic permanent moment and the induced moment, respectively, in the k th bond. The bond dipole moment may then be expressed as $\vec{\mu}_k = \vec{\mu}_k^o + \vec{\mu}_k^I$. The macromolecular dipole moment may then be computed as

$$\vec{\mu} = \sum_k (\vec{\mu}_k^o + \vec{\mu}_k^I) \tag{1}$$

where the induced $\vec{\mu}_k^I$ dipole moment k is given by

$$\vec{\mu}_k^I = \alpha(k)\vec{E}(k) \tag{2}$$

Here $\alpha(k)$ is a 3x3 matrix (bond polarizability tensor) and $\vec{E}(k)$ is the electric field at bond k. Using Gribov's formulation (GRIBOV, 1964) of the so called "valence optical theory":

$$\vec{\mu} = \sum_k \mu_k \vec{e}_k \tag{3}$$

where μ_k is the magnitude of $\vec{\mu}_k$ and $\vec{e}_k$ a unit direction vector along bond k. Clearly, external electric field must change the magnitudes of bond dipoles. Then, associating r_k with $\vec{e}_k$ and noting that atoms i and j in the polymer chain define bond k, one can write

$$\vec{e}_j r_k q_k = (\vec{z}_i - \vec{z}_j) q_k = \vec{z}_i q_k^i - \vec{z}_j q_k^j \qquad (4)$$

since $\vec{e}_k$ is the unit vector along r_k and q_k is the charge associated with bond k, and r_k is the k th bond distance in the presence of an external homogeneous electric field. The major assumption used in this equation was that the bond moments μ_k could be approximated by two charges, $+q_k$ and $-q_k$, separated by a distance r_k.

Thus, the total dipole of a macromolecule $\vec{\mu}$ is written as a sum of i , j point dipoles of the neighbour bonds

$$\vec{\mu} = \sum_k (\vec{z}_i q_k^i - \vec{z}_j q_k^j) = \sum_{i,j} \vec{\mu}_{ij} \qquad (5)$$

Then, the potential energy of the dipole in an uniform external electric field $\vec{E}$ can be written as

$$V^{(el)} = \sum_{i,j} \vec{E}.\vec{\mu}_{ij} \qquad (6)$$

Stability conditions

The predictions of molecular geometries, energies, vibrations, and thermal properties of organic molecules has been greatly facilitated by conformational energy (or "molecular mechanics") calculations (BOYD et al., 1973). The basic idea is that for polymer molecules the Born-Oppenheimer energy surface can be simulated by an empirical valence force field. This field is assembled from energy functions for bond stretching, bending, and twisting that are transferable between molecules containing the same kind of bonds. In addition, nonbonded functions are used to represent the steric or van der Waals interactions of more distant atoms. The stable molecular conformations and geometries are those of local minima in the total energy function.

Consider a Lagrangian in the general from

$$L = \sum_{i,j} (T_{ij} - V_{ij} + F_{ij} + \vec{E}.\vec{\mu}_{ij}) \qquad (7)$$

where T_{ij}, V_{ij}, F_{ij} and $\vec{E}.\vec{\mu}_{ij}$ are the kinetic energy, the dissipation function, and the mechanical and dipole moment, respectively, potential energy

$$T_{ij} = m_{ij}\dot{R}_i\dot{R}_j/2 \qquad (8)$$

$$F_{ij} = \gamma_{ij}\dot{R}_i\dot{R}_j/2 \qquad (9)$$

the mass coefficient m_{ij} and the dissipation factor γ_{ij} are in general functions of the R_i internal coordinates.

A conventional conformational energy model can be summarized by saying that the mechanical energy of a macromolecule, for example, can be represented by

$$\begin{aligned} V_{ij} = {} & V_{ij}(\text{stretching}) + V_{ij}(\text{bending}) + V_{ij}(\text{torsion}) + \\ & + V_{ij}(\text{nonbonded}) \end{aligned} \qquad (10)$$

where

$$\left.\begin{aligned} V_{ij}(\text{stretching}) &= D_{ij}\ \{\exp\{-2\alpha_{ij}(|\vec{r}_i - \vec{r}_j| - r_o)\} \\ &\quad - 2\exp\{-\alpha_{ij}(|\vec{r}_i - \vec{r}_j| - r_o)\}\} \\ V_{ij}(\text{bending}) &= k_{ijk}(\phi_{ijk} - \phi^o_{ijk})/2 \\ V_{ij}(\text{torsion}) &= V^o_{ijk}(1 + \cos 3\Theta_{ijk})/2 \\ V_{ij}(\text{nonbonded}) &= A_{ij}\exp(-B_{ij}r_{ij}) - C_{ij}/r^6_{ij} \end{aligned}\right\} \qquad (11)$$

Here r, ϕ, and Θ are coordinates representing bond lengths, interatomic distances, valence angles, and bond torsion, respectively. D_{ij}, A_{ij}, B_{ij}, C_{ij} and α_{ij} are parameters characteristic of given macromolecule. The superscript o values are parameters that represent "relaxed" or "natural" values of these coordinates.

The corresponding equations of motion of our dissipative system are given by (LANDAU and LIFSHITZ, 1960)

$$\frac{d}{dt}\frac{\partial L}{\partial R_i} = \frac{\partial L}{\partial R_i} - \frac{\partial F_{ij}}{\partial R_i}\,, \qquad i,\ j \quad 1,\ 2,\ \ldots, \tag{12}$$

from which if only the nearest interactions are considered, it follows

$$m_s\ddot{R}_j = \frac{\partial\{V_{j-1,j}\ (R_{j-1},R_j) - \vec{E}.\vec{\mu}_{j-1,j}\ (R_{j-1},R_j)\}}{\partial R_j} - \frac{\partial\{V_{j,j+1}\ (R_j,R_{j+1}) - \vec{E}.\vec{\mu}_{j,j+1}\ (R_j,R_{j+1})\}}{\partial R_j} - m_s\gamma_j\dot{R}_j \tag{13}$$

$j = 1,\ 2,\ \ldots\ \Omega$ degrees of freedom, where terms $m_s\gamma_j\dot{R}_j$ are included to take into account the lateral interactions of the chain with those of another. The damping factors γ_j of the polymer solid atoms simulate the effect of the bulk of the lattice in presenting the free translational motion of the one-dimensional linear chain.

If mechanical equilibrium is characterized only by $\dot{R}_j = 0$ $(j = 1,\ 2,\ \ldots,\ \Omega)$, then from the last equation follows stability theorem for a model system consisting of the linear macromolecules subjected to an external homogeneous field $\vec{E}$

$$\frac{\partial\{V_{j-1,j}\ (R_{j-1},R_j) - \vec{E}.\vec{\mu}_{j-1,j}\ (R_{j-1},R_j)\}}{\partial R_j} = - \frac{\partial\{V_{j,j+1}\ (R_j,R_{j+1}) - \vec{E}.\vec{\mu}_{j,j+1}\ (R_j,R_{j+1})\}}{\partial R_j} \tag{14}$$

$j = 1,\ 2,\ \ldots,\ \Omega$, which is fulfilled only if the second differential of the total potential energy

$$d^2V(\mathrm{mechanical+dipole}) = \sum_{i,j} \left(\frac{\partial^2 V}{\partial R_i\, \partial R_j}\right)_{(R_i^o,R_j^o)} R_i R_j$$

$$- \sum_{i,j} \vec{E}.\left(\frac{\partial^2 \vec{\mu}}{\partial R_i\, \partial R_j}\right)_{(R_i^o,R_j^o)} R_i R_j, \qquad i,j = 1,\ 2,\ \ldots, \qquad (15)$$

or

$$d^2V(\mathrm{mechanical+dipole}) = \tilde{R}FR - \tilde{R}\Lambda R \qquad (15')$$

where

$$F_{ij} = (\partial^2 V/\partial R_i \partial R_j)_{(R_i^o,R_j^o)}, \quad \Lambda_{ij} = (\partial^2 \vec{E}.\vec{\mu}/\partial R_i \partial R_j)_{(R_i^o,R_j^o)},$$

R is a column vector of the internal coordinates and $\tilde{R}$ its transpose form, is positive definite quadratic form. Otherwise the eigenvalues λ_1, λ_2, ..., of matrices $F-\Lambda$, are all real and positive. If the stability conditions or voltage life (14), in some local volume of the polymer are unfulfilled, then a breakdown of the polymer dielectrics proceeds.

Here presented model system of polymer dielectrics, based on a classical Lagrangian, where the masses and the driving forces are defined in terms of the real atomic coordinates, provides more details of the physical picture of a real system (e.g., how the active modes and the associated generalized force may be generated and singled out from the bath modes), which may not be readily available in a quantum formulation.

The development of efficient computer algorithms for minimizing the conformational energy and determining the stability conditions will have practical and routine application of the method to a variety of problems.

Conclusions

From the formulated stability-criterion it results that breakdown strength of the polymer dielectrics subjected to a strong external homogeneous electric field, depends on the amount and type of abnormalities built in the chains and on the field-induced changes in their structure. Presented model enables to evaluate the insulating properties of the solid dielectrics and moreover to estimate the effect of additives on their stability.

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