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A LATTICE MODEL OF IONIC CONDUCTIVITY IN THE ELASTOMER STATE

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Résumé. — On étudie par un modèle de réseau de l'état élastomère la conductivité ionique d'un polymère. Les résultats prédisent le comportement de la conductivité en fonction de la fréquence du champ appliqué et de la température.

Abstract. — A lattice model of the elastomer state allows the calculation of the electrical conductivity due to ions in a polymer matrix. The results predict the changes of conductivity with the frequency of the electric field and the temperature.

Depending upon temperature two amorphous states exist for linear polymers : the elastomer and the glassy states. When ionic salts are dissolved in elastomers, the system exhibits a relatively strong electrical conductivity, typically 10^{-5} to 1 Ω/m [1]. This conductivity has an Arrhenius behaviour as indicated in figure 1. The activation energies are different in the glassy and in the elastomer regions, suggesting different conductivity mechanisms.

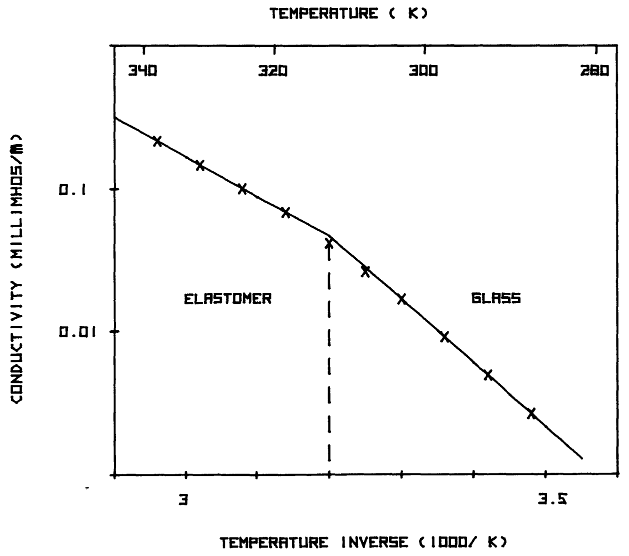

FIG. 1. — Arrhenius plot (log σ versus $1/T$) of the electrical conductivity of a nickel perchlorate-polyacrylonitrile system. The molar composition of the system is polyacrylonitrile 10 moles, $Ni(ClO_4)_2$, 6 H_2O 1 mole. This plot shows clearly the two different slopes corresponding to the elastomer state and to the glassy state.

The purpose of this letter is to describe a plausible mechanism for the electrical conductivity in the elastomer state, based on the lattice model of Flory [2].

In this model, space is divided into cells arranged in a periodic lattice. A cell can be occupied by a monomer unit or be empty. In the elastomer state the empty cells are numerous and mobile. They are responsible for the high compressibility of elastomers. In the glassy state their small number hinders movements of the chains.

When ions are added, they also occupy lattice sites. Because of its high activation energy in the glassy state, it is assumed that the electrical conductivity is due to ions moving between interstitials. On the other hand, we assume that in the elastomer state, ions substitute for monomers in the lattice cells. They can move only if at least one of the neighbouring cells is empty. From this assumption, we can already presume that, in the elastomer state only, the conductivity might show a frequency dependence, and that a characteristic frequency might be the characteristic frequency of the monomers movements.

The electric current can be written :

$$I = Ze \sum_{\substack{i \text{ ions} \\ \text{and } j \text{ neighbouring sites}}} t_{ij} H_{ij} \mathbf{r}_{ij}$$

where :

— H_{ij} is the probability that the jth cell is empty when there is an ion in ith cell ;

— t_{ij} is the transition probability per unit time for an ion to move from i to j ;

— $\mathbf{r}_{ij}$ is the space vector between the jth and the ith cell ;

— Ze is the charge of the ions.

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We evaluate t_{ij} according to Eyring's model [3]

$$t_{ij} = \frac{kT}{h} \exp\left(- \frac{\Delta E + U_j - U_i}{kT} \right)$$

where ΔE is an energy barrier and U_j and U_i the electrostatic potential energy on the two sites.

We now have to calculate the ion-hole correlation function H_{ij}. Let us neglect in a first approximation ion-ion correlations [4]. This allows us to consider an ion placed at the origin of the lattice. In order to calculate H_{ij}, we now have to evaluate the probabilities of having a monomer or a hole at $\mathbf{r} = \mathbf{r}_{ij}$. This is done by solving the differential equations yielding these probabilities. When calculating the rates of variation of the probabilities, we take into account the fact that each time the ion moves, the origin of the lattice is also moved. What appears in the equations as probabilities, are in fact correlation functions. The rate of variation of M_r, the probability of having a monomer in r, can be written

$$\begin{aligned} \dot{M}_r = \sum q(H_r\, M_{r+\varepsilon} - M_r\, H_{r+\varepsilon}) + \\ + t_\varepsilon\, H_\varepsilon (H_r\, M_{r+\varepsilon} - M_r\, H_{r+\varepsilon}) \quad (1) \end{aligned}$$

where :

— q is the probability that a monomer moves into a neighbouring hole [5];

— H_r is the probability to have a hole in r;

— ε are the vectors joining to the neighbouring sites.

The origin of the two terms of the sum is the following :

$$- q[H_r\, M_{r+\varepsilon} - M_r\, H_{r+\varepsilon}]$$

is due to possible changes of site of a monomer unit from $r + \varepsilon$ to r or *vice versa.*

$$- t_\varepsilon\, H_\varepsilon [H_r\, M_{r+\varepsilon} - M_r\, H_{r+\varepsilon}]$$

comes from the fact that when the ion moves by ε with a probability $t_\varepsilon\, H_\varepsilon$, the lattice is translated and, after the translation, what was in the site $r + \varepsilon$ is in the site r.

The electrostatic potential distribution being given, it is then possible (at least in theory) to solve the non-linear differential system in M_r and to obtain the values of H_ε and the electric current.

We further simplify the differential system with the following approximations :

— We restrict ourselves to the linear response in electric field.

— We take the electric field $\mathbf{E}$ along the x axis and we neglect all the transverse correlations.

We have then a one dimensional system of equations :

$$\begin{aligned} M_n = qx(H_n\, M_0 - H_0\, M_n) + qH_n(M_{n+1} + M_{n-1}) - \\ - qM_n(H_{n+1} + H_{n-1}) + t_+\, H_1(M_{n+1}\, H_n - M_n\, H_{n+1}) \\ + t_-\, H_{-1}(M_{n-1}\, H_n - H_{n-1}\, M_n) \end{aligned}$$

where :

— n refers to the position of the cell,

— H_0 and M_0 are the equilibrium probabilities of having a vacancy or a monomer unit ($H_0 + M_0 = 1$),

— x refers to the number of transverse neighbours (4 for a cubic lattice),

— $t_\pm = t \pm s$.

t is the transition probability for the ion in the absence of electric field and s in the linear approximation is :

$$s = \frac{Zeat}{kT} E$$

a is the lattice parameter.

The equations of variation of the neighbours of the ion are different :

$$\begin{aligned} \dot{M}_1 &= qx(H_1\, M_0 - H_0\, M_1) + qH_1\, M_2 - \\ &\quad - qM_1\, H_2 + t_+\, H_1\, M_2 - t_-\, H_{-1}\, M_1 \\ \dot{M}_{-1} &= qx(H_{-1}\, M_0 - H_0\, M_{-1}) + qH_{-1}\, M_{-2} - \\ &\quad - qM_{-1}\, H_{-2} + t_-\, H_{-1}\, M_{-2} - t_+\, H_1\, M_{-1} . \end{aligned}$$

The system is linearized by writting

$$m_n = M_0 + m_n$$

and by keeping in the equations the terms linear in m_n and s. Taking into account the translational invariance of the equation in $\dot{M}_n$ (except near the origin), we look for a solution of the type :

$$m_n = m \exp i(\omega t + kn)$$

where ω is 2π times the frequency of the applied electric field. The linearized equation in m_n gives a dispersion relation :

$$i\omega = - qx + (q + tH_0)(\mathrm{e}^{ik} + \mathrm{e}^{-ik} - 2)$$

writting $z = \mathrm{e}^{ik}$ we obtain a second degree equation in z

$$z + \frac{1}{z} = 2 + \frac{i\omega + qx}{tH_0 + q} .$$

In each half space, we take as the physical z the solution such that m_n decreases when $|n|$ goes to infinity. For $n > 0$, we take the root smaller than 1 and for $n < 0$, the one larger than 1.

Knowing the values of k for $n > 0$ and for $n < 0$, the following linear system in m_1 and m_{-1} can be solved

$$\begin{aligned} i\omega m_1 &= [- qx + (z - 1)(q + tH_0) - tM_0]\, m_1 + \\ &\quad + tM_0\, m_{-1} + 2\, sH_0\, M_0 \\ i\omega m_{-1} &= [- qx + (z - 1)(q + tH_0) - tM_0] \times \\ &\quad \times m_{-1} + tM_0\, m_1 - 2\, sH_0\, M_0 \end{aligned}$$

where

$$z = 1 + \frac{\alpha}{2} - \sqrt{\alpha + \frac{\alpha}{4}}$$

and

$$\alpha = \frac{i\omega + qx}{q + tH_0}.$$

The linearized electric current is :

$$I = Zea[2\,sH_0 + t(m_{-1} - m_1)]\,.$$

We thus obtain :

$$I = I_\infty \left[1 - \frac{2\,tM_0}{i\omega + qx + (q + tH_0)(1 - z) + 2\,tM_0}\right].$$

When the infinite frequency current is

$$I_\infty = 2\left(\frac{Zea}{h}\right)^2 H_0 \exp\left(-\frac{\Delta E}{kT}\right) E\,,$$

it corresponds to a zero ion-hole correlation function.

On the other hand, at low frequency, the current is reduced simply by the fact that when an ion moves it leaves behind it a vacancy, thus increasing the probability of the reverse current. Of course if the frequency of the field is very high as compared to the transition probability of the ion, the correlation does not reduce the conductivity.

Typical conductivity behaviour is plotted on figure 2.

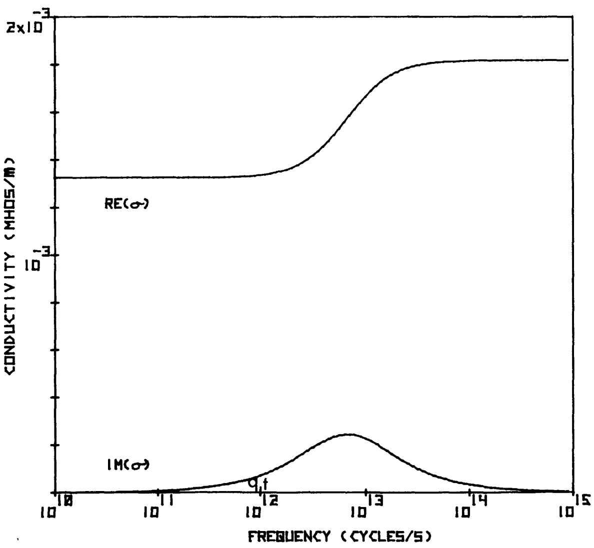

FIG. 2. — Plot of the real and imaginary part of conductivity versus frequency, for the following values of the parameters defined in the text $q = t = 10^{12}$ Hz, $H_0 = 0.1$, $M_0 = 0{,}9$, $x = 4$ (cubic lattice).

We have tested the validity of the assumption on the absence of transverse correlation, by computing a numerical solution of system (1). The computation is done on a 9 × 9 cells lattice and the differential system is solved by a fourth order Runge-Kutta method [6]. Figure 3 shows the comparison of the two methods for 2 transverse neighbours (the two dimensional case). There exists a slight difference in the obtained currents, especially at low frequency, where correlations are most important.

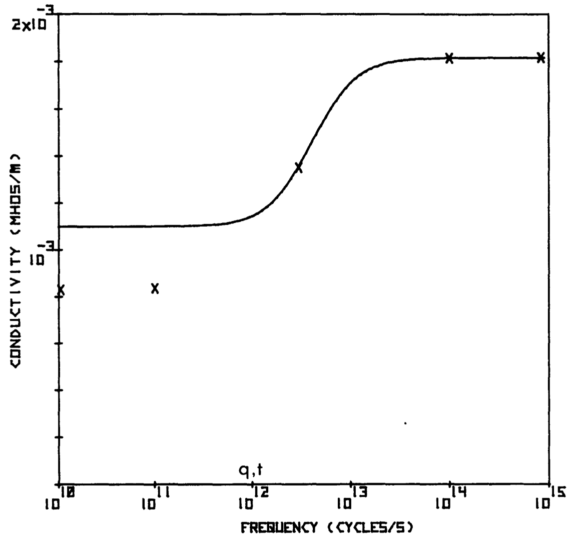

FIG. 3. — Comparison of the values obtained from the analytic expression of the current (full line), with those obtained from a computer simulation of equation (1) for a 9 × 9 square lattice (Crosses). Parameters are the same as for figure 2, except that $x = 2$. The ordinate is the magnitude of the conductivity.

In conclusion, from these calculations we should expect the following behaviour for the electrical conductivity.

— The conductivity should increase with *frequency* when the frequency is of the order of q or t. q is typically an inverse relaxation time for rotation of monomers and is expected to be in the microwave region. t is frequency of transition of the ion between adjacent sites and should be in the same frequency region. The change in conductivity and in permittivity due to the ions should be sought in the microwave region, unfortunately also the region for dipole relaxation phenomena. Nevertheless, one can play with the ion concentration parameter to distinguish the predicted effects from these parasitic phenomena.

— The low frequency conductivity is expected to vary with *temperature* according to an Arrhenius behaviour. When reasonable assumptions are made on q, t, M_0 and H_0 ($q = t = 10^{12}$, H_0 = a few percents), we expect an activation energy of the conductivity which is the sum of ΔE, the activation energy of t, frequency of transition for the ions, plus E_h the activation energy for hole creation since in the elastomer region, H_0 is given by

$$H_0 = C\exp(-E_h/kT)\,.$$

Since E_h can be known from free volume measurements, conductivity activation energy could be used to measure the activation energy of t.

On the other hand, the lattice model can be extended to treat other transport problems, like, for instance, ionic conductivities in solutions or molten salts. The general philosophy of the model is that the ion movement creates a perturbation from the equilibrium probabilities of occupation of the site left by this ion, and that this perturbation interacts strongly with the ion movement. This picture is reminiscent of the quasi-particle description, used for instance in the theory of Fermi liquids [7].

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Cros, A., *Conductivité ionique dans le polyacrylonitrile.* Thèse 3^{e} cycle Marseille (1974) unpublished.

[2] Flory, P. J., *Proc. R. Soc. London A* **234** (1956) 60.

[3] Eyring, *J. Chem. Phys.* **3** (1935) 107.

[4] Ion-Ion correlations could be taken into account by a Debye-Huckel expression, in which the zero concentration limit ion mobility is taken from our calculation.

[5] Writing that the probability for a monomer in r to go in $r + \varepsilon$ is independent of the covalent bonds existing with two of its neighbours, is indeed a strong simplification. It is consistent with the fact that the static statistical properties, for instance the concentration of holes, do not depend of these correlations in the elastomer state.

[6] See, for instance, Mineur, H., *Techniques de calcul numérique* (Dunod) 1966.

[7] Pines, D. and Nozières, P., *Theory of quantum liquids* (Benjamin) 1966.