# Displacement instabilities in classical Coulomb systems

V. N. Bondarev
*Scientific-Research Institute of Physics, I. I. Mechnikov University, Odessa*

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Relaxation transverse modes are found in the long-wave limit for conducting systems. In conductors lacking a symmetry center, these modes are unstable and give rise to displacement superstructures. This result helps explain the experimental data on several known superionic crystals.

Electrical phenomena in "poor" conductors (in the terminology of Ref. 1), e.g., liquid and solid electrolytes, are described on the basis of Maxwell's equations[1]

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$$\operatorname{rot}\mathbf{E} = 0, \tag{1}$$

$$\operatorname{div}\mathbf{D} = 0 \tag{2}$$

for the electric field $\mathbf{E}$ and the electric displacement $\mathbf{D}$. These phenomena can also be described by constitutive equations, which can be written in the following form in the simplest case of an isotropic conductor in the absence of a spatial dispersion:

$$\frac{\partial \mathbf{D}}{\partial t} = \epsilon_\infty \frac{\partial \mathbf{E}}{\partial t} + 4\pi \mathbf{j}, \tag{3}$$

$$\mathbf{j} = \sigma \mathbf{E}. \tag{4}$$

Equation (3) has a simple meaning. Substituting the expression for the conduction current $\mathbf{j}$ from Ohm's law (4) into (3), writing $\mathbf{D}$, $\mathbf{E} \sim \exp(-i\omega t)$, i.e., introducing the frequency $\omega$, and using the definition $\mathbf{D}(\omega) = \epsilon(\omega)\mathbf{E}(\omega)$, we find

$$\epsilon(\omega) = \epsilon_\infty + i\frac{4\pi\sigma}{\omega}. \tag{5}$$

At low frequencies $\omega$, Eq. (5) corresponds to the ordinary expression for the frequency-dependent dielectric constant of a poor conductor,[1] characterized by a conductivity $\sigma$ and a "high-frequency" dielectric constant $\epsilon_\infty$.

To take into account the spatial dispersion in an isotropic, centrally symmetric conductor, we should add to the right side of (4) the expression

$$-\frac{1}{4\pi}(\beta_1 \operatorname{grad}\operatorname{div}\mathbf{E} + \beta_2 \operatorname{rot}\operatorname{rot}\mathbf{D})$$

with parameter values $\beta_1 > 0$, $\beta_2 > 0$ (in the Debye-Hückel approximation we would have $\beta_1 = 4\pi\sigma R_D^2$, where $R_D$ is the screening radius). In a conductor without an inversion center (e.g., an electrolytic solution containing chiral molecules), we should also add a term[2]

$$-\gamma \operatorname{rot}\mathbf{D}, \tag{6}$$

where $\gamma$ is a parameter. In this case the dielectric tensor ($e_{ijm}$ is the Levi-Civita symbol)

$$\epsilon_{ij}(\mathbf{k},\omega) = \epsilon_T(\mathbf{k},\omega)\left(\delta_{ij} - \frac{k_i k_j}{k^2}\right) + \epsilon_L(\mathbf{k},\omega)\frac{k_i k_j}{k^2} + i\epsilon_G(\mathbf{k},\omega)e_{ijm}\frac{k_m}{k},$$

which appears in the relation

$$D_{i\mathbf{k}}(\omega) = \epsilon_{ij}(\mathbf{k},\omega)E_{j\mathbf{k}}(\omega),$$

has a longitudinal component[3]

$$\epsilon_L(\mathbf{k},\omega) = \epsilon_\infty \frac{i\omega - (4\pi\sigma + \beta_1 k^2)/\epsilon_\infty}{i\omega - \beta_1 k^2/\epsilon_\infty}, \tag{7}$$

a transverse component

$$\epsilon_T(\mathbf{k},\omega) = \epsilon_\infty(Q_+ + Q_-), \qquad Q_\pm = \frac{i\omega - 4\pi\sigma/\epsilon_\infty \pm \gamma k - \beta_2 k^2}{2(i\omega \pm \gamma k - \beta_2 k^2)}, \tag{8}$$

and a gyrotropic component $\epsilon_G = (\mathbf{k},\omega) = \epsilon_\infty (Q_+ - Q_-)$; here $k$ is the wave vector.

If retardation effects are ignored, the eigenmodes are determined by

$$\epsilon_L(\mathbf{k}, \omega_L) = 0, \quad \epsilon_T^{-1}(\mathbf{k}, \omega_T) = 0. \tag{9}$$

From (7) and (9) we find the overdamped longitudinal Coulomb mode[4] $\omega_L = -i(4\pi\sigma/\epsilon_\infty) \times (1 + R_D^2 k^2)$.

However, we see from (8) and (9) that in the presence of a gyrotropy one of the transverse modes (at $k$, this would be $\omega_T = i|\gamma|k$) is a growing mode. This circumstance ultimately leads to the appearance in a gyrotropic conductor of a displacement superstructure [the latter can be stabilized by adding nonlinear terms to (4) and (6)].

An analogous situation arises in conductors of cubic classes $O$ and $T$. The latter, however (and also the $T_d$ class in a cubic system), allows a piezoelectric effect, which leads at small $k$ to yet another instability, of a completely different kind. Omitting a detailed derivation (which will be given in a detailed paper), we note that in this case the dispersion relation for transverse modes which are propagating along, for example, a fourfold axis contains at small $k$ an unstable root

$$\omega_T \sim ik^{2/3}, \tag{10}$$

which ultimately gives rise to a displacement superstructure in conducting piezoelectric materials.

There are some experimental results which suggest the presence of displacement superstructures in ionic conductors lacking an inversion center (not only cubic conductors).

1) Superionic $\alpha$-$RbAg_4I_5$, class $O$. NMR data[5] indicate that the symmetry point group of Rb sites is lower than $C_3$. On the other hand, Geller *et al.*[6] have examined the possibility that the rubidium ions occupy the positions assigned to them by the $O$ group only on the average; they are actually displaced slightly from their ideal positions.

2) Superionic $\alpha$-$Ag_2HgI_4$, class $S_4$. According to x-ray data,[7] the actual positions of certain ions are not the positions assigned them by the symmetry. An analogy with the alloy $Cu_3Au$, in which a long-period superlattice is observed (Ref. 9, for example), was used in Refs. 7 and 8.

3) Superionic $\beta = LiAlSiO_4$ ($\beta$-eucryptite), class $D_6$. Neutron diffraction data[10] imply that even at the highest temperatures which have been reached (800 °C), there are long-period correlations in the arrangement of the mobile ions (the reciprocal wave vector along the hexagonal axis is $\sim$20 Li-Li distances).

4) $\beta$-AgI, class $C_{6v}$. In order to satisfactorily explain experiments on the Raman effect, it is necessary to assume[11] that some of the silver ions are displaced from their ideal positions.

This list could be continued.

There is some similarity between these phenomena and those observed in cholesteric liquid crystals (Ref. 2, for example), where again there is necessarily a "secondary" periodic structure. However, even though this structure stems from a term

which is similar to (6) in nature ($\sim$curl **n**,where **n** is the director), it has physically nothing in common with the structure discussed by us in this letter (it is sufficient to recall the condition[2] $\mathbf{n}^2 = 1$).

Finally, it is useful to note that in nature a metal without a symmetry center is a rarity indeed (alloys such as[12] $Ag_3Al$).

There is a need for experiments to directly identify these displacement superstructures in conductors lacking an inversion center.

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