Effective ion mass in a liquid crystal

E. D. Belotskiĭ, B. I. Lev, and P. M. Tomchuk
Institute of Physics, Academy of Sciences of the Ukrainian SSR

(Submitted 14 March 1980)
Pis'ma Zh. Eksp. Teor. Fiz. **31**, No. 10, 573–576 (20 May 1980)

The effective mass of an ion in a nematic liquid crystal, which is dependent on the orientational "coat" of the director produced by the field of an ion and moving together with it, was determined theoretically. An allowance for ion loading can eliminate the divergence between the theoretical estimates and the experimental data for mobility.

PACS numbers: 61.30. – v

The estimates of ion mobility in the nematic phase of a liquid crystal, which were obtained for a molecular-size Stokes sphere, give substantially higher values compared with those observed experimentally. One of the possible reasons for such divergence can be the "loading" of an ion due to formation of a polarization coat that moves along with the ion.[1]

According to current ideas,[2,3] the molecule moves in the liquid under the influence of random thrusts in a limited volume $r_T \sim r_0(kT/ms^2)^{1/2}$ (r_0 is the radius of the molecule, m is its mass, s is the velocity of sound, and T is the temperature) and performs fast chaotic motions in this region. A slow drift of the ion together with its "coat" (produced by the strong electric field of the latter) occurs as a unified whole against a background of fast oscillations of the ion within the mentioned volume. This volume occupies a small part of the total volume of the deformation coat. Taking into account the factors mentioned above, we can consider the motion of an ion (slow drift) with the velocity v as the motion of a particle in a rapidly oscillating field of frequency Ω,[4] which satisfies the condition $\Omega \gg 1/\tau_d$ (where τ_d is the diffusion time along the deformation coat). The particle motion, averaged over the oscillations, occurs in the field whose "effective potential energy" is determined by

$$U_{\text{eff}} = U + \frac{\overline{f^2}}{2m\Omega}, \tag{1}$$

where U is a constant field and $\bar{f}$ is an oscillating field with the frequency Ω, which influences the particle, and m is the particle mass.

The force f acting on an ion from the direction of the liquid crystal, is determined from the Franck free energy. A variation of the elastic energy of the medium due to reorientation of the director by the oscillating ion field leads to the appearance of a term in Eq. (1) proportional to v^2, which takes into account the additional change in the mass of the moving ion. This works is devoted to determination of the renormalized ion mass. The solvation effect was disregarded in determining the effective mass, since we are particularly interested in the liquid-crystal properties of this renormalization.

The free Franck energy, associated with the change in distribution of the director $n(r,t)$ in the presence of an electric field, can be written as follows[1]:

$$\mathcal{F} = \frac{1}{2} \int \{ K_{11} (\operatorname{div} \mathbf{n})^2 + K_{22} (\mathbf{n} \operatorname{rot} \mathbf{n})^2 + K_{33} [\mathbf{n} \times \operatorname{rot} \mathbf{n}]^2 - \frac{\rho_a}{4\pi} (\mathbf{n}\mathbf{D})^2 \} d\mathbf{r}, \tag{2}$$

where K_{ii} are the elastic Franck contacts, $\rho_a = (1/\epsilon_\parallel) - (1/\epsilon_\perp)$, $\epsilon_\parallel$ and $\epsilon_\perp$ are the longitudinal and transverse components of the dielectric-constant tensor, and D is the electric-induction vector.

The Euler dynamic equation for the director distribution has the form[5]

$$J \frac{d}{dt} \left[\mathbf{n} \times \frac{d\mathbf{n}}{dt} \right] = [\mathbf{n} \times \mathbf{h}] - \vec{\Gamma}, \tag{3}$$

where J is the moment of inertia of a unit volume, $\mathbf{h}$ is the molecular field determined from the condition $\mathbf{h} = -\delta\mathcal{F}/\delta\mathbf{n}$, and $\vec{\Gamma}$ is the moment of frictional force. In the single-contact approximation $K_{ii} = K$, and if the orientational influence of the velocity gradient (absence of solvation effect) is ignored, we can write in the coordinate system of a moving ion:

$$J \left(\frac{\partial}{\partial t} + \mathbf{v}\nabla \right) \mathbf{n} - K \nabla^2 \mathbf{n} + \gamma \left(\frac{\partial}{\partial t} + \mathbf{v}\nabla \right) \mathbf{n} - \frac{\rho_a}{4\pi} (\mathbf{n}\mathbf{D})\mathbf{D} = 0. \tag{4}$$

We shall represent the director in the form $\mathbf{n} = \mathbf{n}_0 + \delta\mathbf{n}$, where $\mathbf{n}_0$ is the distribution of the director around a fixed ion and $\delta\mathbf{n}$ corresponds to its variation due to the induced strength of the field of an oscillating ion which drifts slowly with a certain velocity $\mathbf{v}$.

The distribution of the director around a fixed ion can be determined from the following considerations.

The strong field around an ion lines up the director in a "hedgehog" configuration. If there were no disordering influence of the external field, of the boundaries, of the thermal fluctuations, etc., then the "hedgehog" would be located a large distance from the ion. The distance at which the orienting influence of an ion field is significant is

$$R = \min(R_1 R_2); \quad R_1 \approx \frac{(Ze)^2}{\epsilon_\perp kT}; \quad R_2 \approx \left(\frac{4\pi K r_0^4}{\rho_a Z^2 e^2} \right)^{1/2}. \tag{5}$$

The value of R_1 can be determined[1] from the condition of equality of the ion field energy $(Ze)^2/\epsilon_\perp R_1$ and from the thermal kT. The second correlation radius R_2 is attributable to the fact that there is no advantage in having the hedgehog located far from an ion because of the sharp increase of the elastic energy. The expression for R_2 can be easily obtained from the minimum of the free energy by substituting in it a trail distribution of the director in the form[1])

$$\mathbf{n}_0 = \frac{\mathbf{D}_{\text{eff}} + \mathbf{D}_0}{D_{\text{eff}} + D_0}, \quad \mathbf{D}_{\text{eff}} = \frac{\mathbf{r}}{r} \frac{Ze}{r_0^2} \exp(-r/R_2), \tag{6}$$

which correctly transfers the coordinate dependence of the director both near an ion and some distance from it.

The field $\mathbf{D}_0$ in Eq. (5), which determines the orientation of the director at large distances from an ion, should be reduced to zero in the final results, as is customarily done in calculations of the quasi-average fields, or set equal to the external field (if such field is applied). In the last case, if the external field is sufficiently strong, then $R_2 \sim (Ze/D_0)^{1/2}$. For typical parameters R_1 and R_2 in Eq. (5) are of the same order of magnitude.

By satisfying the condition $\mathbf{n}^2 = 1$, we can examine $\delta \mathbf{n} \perp \mathbf{n}_0$ in the first approximation and hence the following equation is valid for δn

$$J\left(\frac{\partial}{\partial t} + v\nabla\right)\delta n - K\nabla^2 \delta n + \gamma\left(\frac{\partial}{\partial t} + v\nabla\right)\delta n - \frac{\rho_a}{4\pi}\delta D\,(n_0 D) = 0, \tag{7}$$

where δD is the variation of an ion field due to oscillations in the region of radius r_T. Disregarding the delay of the electro-magnetic wave, the average (around the sphere) variation of the field is

$$\delta \mathbf{D} \sim -\frac{Z e r_T}{2 r^3} \exp(i\Omega t) \tag{8}$$

where $\delta \mathbf{D} \perp \mathbf{D}$.

After substituting Eq. (8) in Eq. (7), the latter can be solved in analytic form. Knowing δn, we can easily determine the free Franck energy, which is related to δn by the following simple relation:

$$\mathcal{F} = 4\pi K \int_{r_0}^{R} \left\{ 4 + \left[\frac{\partial}{\partial r} (r\,\delta n) \right]^2 \right\} dr\,. \tag{9}$$

(For simplicity, we assume that $n_0^r = 1$ and $n_0^\theta = 0$ for $r_0 \leqslant r \leqslant R$.) After determining the free energy from Eq. (9), we can find the force $\bar{f}$ in Eq. (1). The coefficient of v^2 in Eq. (1) determines the additional term of the mass of an ion that moves in the liquid crystal. As a result, we obtain for the effective mass

$$m_{\text{eff}} \approx m_4 \left\{ 1 + 2\pi \left(\frac{\rho_a}{\rho_\perp} \right)^2 \left(K^2 s^2 / \gamma^2 r_0^2 v_T^4 \right) \right\}. \tag{10}$$

In deriving the final expression (10), we took advantage of the large dissipation ($J\Omega \ll \gamma$) and, for simplicity, we used the average moment of induced force (acting from the direction of the ion)

$$\bar{\alpha} = \frac{1}{R - r_0} \int_{r_0}^{R} \left(\frac{\rho_a}{4\pi} \delta D D \right) dr,$$

instead of its exact value. Moreover, the frequency Ω was expressed in terms of the

thermal velocity of an ion $v_T(\Omega \sim v_T/r_T)$, and R_1 was used for R. At $R = R_2$ the expression for m_{eff} is more complex.

For typical parameters of the medium $K \sim 10^{-6}$, $\rho_\alpha \sim 10^{-2}$ cm, $r_0 \sim 10^{-7}$ cm, $m_4 \sim 10^{-22}$ g, and $\gamma \sim 10^{-2}$ Ps*, the additional term is comparable to the ion mass, and in some cases it can be much larger than the ion mass.

Thus, the mechanism of ion "loading" examined above may indeed be one of the causes of anomalously low ion mobilities in the liquid crystals.

In conclusion, the authors thank V. L. Pokrovskiĭ whose critical comments were very useful.

[1)]Notice the peculiar distribution of the director near $D_{\text{eff}} \approx -D_0$, which is responsible for the logarithmic divergence of the elastic energy. We shall disregard the additional contribution to the effective mass due to this divergence. We note that such allowance can only increase the effective ion mass.

---

[1]P. de Gennes, The Physics of Liquid Crystals, Oxford, 1975.
[2]I. Z. Fisher, Ukr. Fiz. **12**, 1669 (1967).
[3]C. Croxston, Liquid State Physics, London, 1974. Russian Translation, Mir, Moscow, 1978, p. 333.
[4]L. D. Landau and E. M. Lifshitz, Mekhanika, Nauka, Moscow, 1973.
[5]S. I. Pikin, Zh. Eksp. Teor. Fiz. **60**, 1185 (1971) [Sov. Phys. JETP **33**, 641 (1971)].