Effects of the Molecular Rotational Dynamics on Dielectric and Far-Infra-red Spectra of Anisotropic Liquids (*) (**) 

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Summary. — Dielectric and far-infra-red spectra of uniaxial liquid-crystal phase are analysed in terms of correlation functions calculated by a memory function formalism. SAIL (strong anisotropic interaction limit) conditions are always found to apply, resulting in diffusional regime at low working frequencies. Dipole friction has been also included in the calculations to consider many-particle interactions, its effect being analogous to the introduction of slowly relaxing local structures.

1. — Introduction.

The rotational dynamics of molecules in liquids is often the most important mechanism of relaxation in various spectroscopical techniques, e.g. NMR, ESR, IR and Raman spectroscopy, dielectric dispersion and absorption, neutron and light scattering. In the theoretical analysis, a « diffusive » process is generally assumed for the molecular motion, i.e. one in which reorientations occur through a sequence of very small angular steps, and inertial effects are completely neglected. Although these assumptions preclude the analysis of interesting phenomena such as far-infra-red absorptions and spin-rotational inter-

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actions, however, they are well justified for most molecular liquids when the frequency dependence of physical properties is investigated at frequencies not higher than the typical reorientational frequencies \(10^{16} \text{ s}^{-1}\). Under these conditions the angular variables provide the complete set of stochastic variables and the motional processes are well described in terms of a "diffusion equation" for the orientations \(^{(1)}\). Deviations from the diffusional behaviour may, however, occur if the intermolecular interactions in the liquid determine "local structures" relaxing in the time scale of the molecular reorientations; this may be the case of the interactions in polar liquids which give rise to a frequency-dependent "dipole friction" in addition to the normal, frequency-independent, "viscous" friction \(^{(2,3)}\).

In anisotropic liquids such as liquid crystals, the situation is more complicated and even the straightforward generalization of the diffusion equation, suitably modified with the introduction of the orientational pseudopotential \(^{(4)}\), must be adopted with some care. In fact, the diffusional constants which enter as parameters in the equation become meaningless in the limit of complete ordering. An account on this argument has been discussed in a previous paper on the basis of the memory function formalism \(^{(5)}\).

In the present paper, the validity of the diffusional assumption in liquid crystals will be discussed in detail. The correlation functions pertinent to the description of dielectric relaxation and far-infra-red absorption in oriented fluids will be calculated by generalizing theoretical procedures developed for isotropic liquids \(^{(6,7)}\). The effect of the dielectric friction will be also considered in the attempt of including many-body interactions into single-particle correlation functions.

The theoretical results will be discussed in connection with the data reported for dielectric \(^{(8)}\) and far-infra-red \(^{(9)}\) experimental measurements in nematic and smectic phases.


