

### Dielectric relaxation in the glass phase of a liquid crystal

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The dielectric relaxation observed by Johari, Goodby, and Johanson in the glass phase of cholesteryl hydrogen phthalate has been analyzed in terms of the Dissado-Hill many-body cluster model. The correlation parameters evaluated from the slopes of the dielectric loss point to the large cooperativity of the reorienting molecules in the local and long-range scales. To describe the fractal-like features of the glass phase of cholesteric liquid crystal the fracton dimensionality  $D_s = 1.44$  and the waiting-time fractal dimensionality  $D_t = 0.18$  have been calculated from the correlation parameters.

The non-Debye relaxation of the electric permittivity  $\epsilon = \epsilon' - i\epsilon''$  is observed in various disordered dielectrics.<sup>1-3</sup> The frequency dependence of dielectric loss  $\epsilon''$  can be described by the following power-law expressions:

$$\epsilon''(\nu) \sim (\nu/\nu_{\max})^{n-1}, \quad \nu > \nu_{\max}, \quad (1)$$

$$\epsilon''(\nu) \sim (\nu/\nu_{\max})^m, \quad \nu < \nu_{\max}. \quad (2)$$

The value  $\nu_{\max}$  is the frequency at maximum loss. The Debye relaxation corresponds to the nonanomalous exponents  $n=0$  and  $m=1$ . For most materials the exponents are fractional and independent of the temperature in the thermodynamically stable phase. For glasses the  $m$  parameter is usually sensitive to temperature changes. The Dissado-Hill many-body cluster model<sup>3</sup> leading to relations (1) and (2) explains the non-Debye behavior by the presence of interactions between entities of the medium. The  $n$  and  $1-m$  parameters could be regarded as a measure of the size of the local correlations of reorienting molecules and as a measure of the size of the long-range correlations in the medium, respectively. In low-loss materials the loss tangent  $\tan\delta(\nu) = \epsilon''/\epsilon'$  reflects the dielectric loss  $\epsilon''(\nu)$  frequency dependence, since the dispersion of  $\epsilon'$  is negligible.<sup>1</sup>

In what follows the dielectric relaxation observed by Johari, Goodby, and Johnson<sup>4</sup> for the glass phase obtained by rapid cooling of liquid crystalline cholesteric phase of cholesteryl hydrogen phthalate will be analyzed. The structure of the molecule and the phase sequence are presented in Fig. 1. In the cholesteric phase the elongated molecules arrange themselves locally parallel to each other. Moreover, the director, indicating the local alignment of molecules, varies regularly, creating a helical axis normal to the subsequent planes where the molecules lay horizontally. In Fig. 2, the data  $\tan\delta(\nu)$  reported by Johari, Goodby, and Johnson for several temperatures are presented in the double logarithmic coordinates. The transformation of the subsequent  $\log_{10}(\tan\delta)$  vs  $\log_{10}(\nu)$  curves into a single master curve has failed. The slopes of the curves at the range of frequency lower than  $\nu_{\max}$  varied with temperature. At cooling, the  $m$  values decrease. The lower the temperature the smaller the frequency range  $\nu < \nu_{\max}$  where the loss data were experimentally accessible. The value of  $m = 0.18 \pm 0.05$ , evalu-

ated based on the frequency dependence of the data for 218 K ensures the highest accuracy. The slopes of the curves at the frequency range higher than  $\nu_{\max}$  seem independent of the temperature factor giving  $n = 0.87 \pm 0.05$ . However, it must be stressed that the  $n$  parameters have been evaluated with poor statistics.

Dielectric relaxation in the glass phase of cholesteryl hydrogen phthalate reveals a large deviation from the behavior typical for the Debye model. The anomalous exponents  $n \gg 0$  and  $1-m \gg 0$  in Eqs. (1) and (2) correspond to nonexponential decay of the polarization  $P(t)$  after switching off the constant electric field. In the first stage of relaxation, for  $t < \tau$ , the following power law can be expected:  $P(t) = P_0 - At^{1-n}$ . In the second stage of relaxation, for  $t > \tau$ , evolution of polarization follows the second power law  $P(t) \sim t^{-m}$ . For temperature 218 K, at which the relaxation time  $\tau$  is shorter than  $10^{-5}$  s,  $1-n = 0.13$  and  $m = 0.18$ , the relaxation of the sample to equilibrium goes very slowly. The values of the correlation parameters  $n$  and  $1-m$  indicate very high degrees of cooperativity of reorientational motions of molecules on both the local and the long-range scales.

It seems that the fractional power-law frequency dependence of the dielectric loss is the macroscopic manifestation of the statistical self-similar features present on the microscopic level of the sample's structure.<sup>5,3</sup> Due to the intermolecular hydrogen bonds in bulk samples of the cholesteryl hydrogen phthalate the network structure<sup>6</sup> can be expected. On the other hand, the typical planar

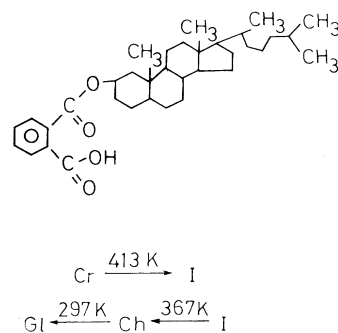


FIG. 1. Schematic structure of cholesteryl hydrogen phthalate molecule and the phase sequence.

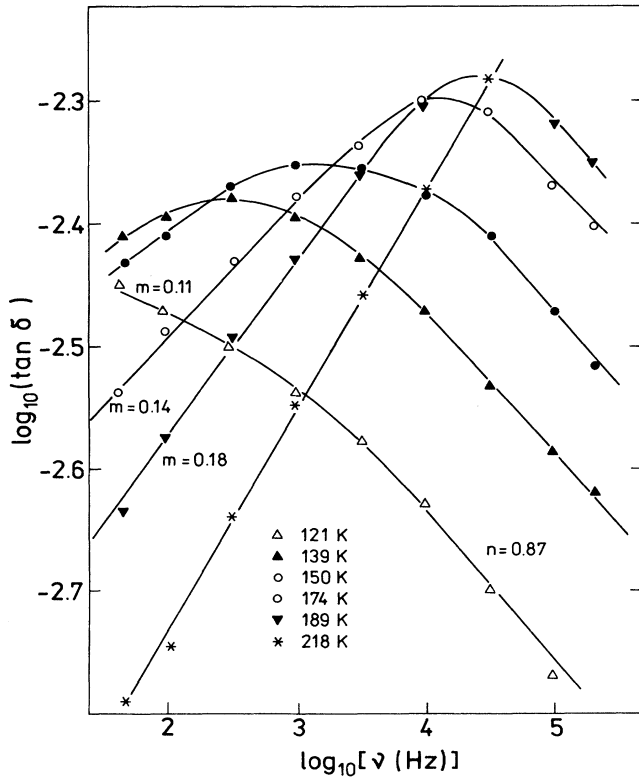


FIG. 2. The  $\log_{10}(\tan\delta)$  vs  $\log_{10}(\nu)$  dependences for several temperatures of the glass of the cholesteric phase of the cholesteryl hydrogen phthalate based on literature data of Johari, Goodby, and Johanson (Ref. 10).

texture of the cholesteric phase reveals the network of disclination lines between various sized clusters with different orientations of helical axes (see, e.g., plates 109 and 112 in Ref. 7). Those two premises seem to justify the fractal concepts into the description of the properties observed in glassy phase of cholesteryl hydrogen phthalate.<sup>8</sup> The network structure ensures some forms of self-similarity at least on certain range scale changes. The process of growth of rigid regions of the sample at the expense of the flexible ones during quenching also favors such an approach. The structure of glass can be regarded as a case of force constraints percolation.<sup>9,10</sup>

Relaxation phenomena could be related to diffusion processes. There are several theoretical models<sup>11-16</sup> describing the transport processes on the fractal structure. The time-dependent diffusion coefficient  $D(t)$  has the following form:

$$D(t) \sim t^{(-1+2/D_w)}, \quad (3)$$

where the diffusion fractal dimensionality  $D_w$  determines the distance covered by the randomly walking particle in a given time.<sup>11</sup> For the Euclidean space the  $D(t)$  is constant as  $D_w=2$ . Meanwhile, for the fractal lattice  $D_w$  exceeds 2, thus giving the decay of  $D(t)$ . In addition, diffusion can occur in steps of nonfixed rates with the self-similar distribution  $\psi(t)$  of intervals<sup>14,15</sup>

$$\psi(t) \sim t^{(-1-D_t)}. \quad (4)$$

The waiting-time fractal dimensionality  $D_t$  is determined by the temporal disorder present in the sample.<sup>16</sup> Then, the exponent  $2/D_w$  in Eq. (3) should be replaced by the exponent approximated by  $2D_t/D_w$ .

The temporal disorder in glass phases is related to the fact that there are many locally stable configurations.<sup>17</sup> Each region of the sample is often partially constrained by the motions of other regions which results in a hierarchy of degrees of freedom from fast to slow.<sup>18</sup> The long-time decay of polarization is characterized mostly by the distribution of waiting times determined by the long-range interactions in the system. For charged carrier systems it has been shown that the parameter  $m$  describing the long-range correlations can be identified with  $D_t$ .<sup>19</sup> For dipolar disordered materials with many degrees of freedom the introduced external energy is stored in excited low-energy correlated states of interacting dipoles. During relaxation, in times longer than  $1/2\pi\nu_{\max}$ , the energy is gradually dissipated to the heat bath. The lower the  $m$  parameter, the longer the process of reaching the equilibrium. For cholesteryl hydrogen phthalate the temporal disorder, measured by  $D_t=0.18$ , is rather small. This shows that reorientations of the molecules in the glass phase are strongly correlated. For the Cantor set of events self-similarly distributed in time,  $D_t=0.63$ .<sup>19</sup>

The short-time decay of polarization is sensitive not only to the long-range interactions but also to the close environment of each relaxing dipole. The local structural regularities are characterized by the fractal dimensionality  $D_f$ . For relaxation in charged carrier systems the correlation parameter  $n$  can be presented as follows:<sup>19,20</sup>

$$n = 1 - D_f D_t / D_w = 1 - D_s D_t / 2. \quad (5)$$

The fracton or the spectral dimensionality  $D_s$  has been introduced by Alexander and Orbach<sup>21</sup> to describe the propagation of low-energy local excitations on fractals. The fractal network of equalized masses connected by the strings of equal force constants can be regarded as analogous to the disordered materials.<sup>11</sup> For cholesteryl hydrogen phthalate in glass of the cholesteric phase at 218 K ( $n=0.87$ ), the fracton dimensionality  $D_s=1.44$ . It should be mentioned that the evaluation of the  $D_s$  parameter is very sensitive to the accuracy with which the  $n$  and especially  $m$  parameters have been obtained. This value of  $D_s$  can be compared with very few experimental results. For low-temperature systems of naphthalin in some glasses and polymeric samples, the  $D_s \cdot D_t$  product obtained by exciton annihilation technique ranges from 0.6 to 1.8—the  $D_t$  itself has not been measured.<sup>22</sup> For percolation network there is the Alexander-Orbach conjecture that  $D_s$  equals 1.33 while for the lattice of the Sierpiński gasket embedded in three-dimensional Euclidean space,  $D_s$  equals 1.55.

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