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**V. A. Lomakin.** *Study of the internal dynamics of macromolecules by the method of laser correlation spectroscopy.* In those cases when the local optical density is determined not only by the position but also by the internal state of the scatterers, correlation spectroscopy of quasielastically scattered light enables the study of the dynamics of fluctuations of this state. The existence of internal degrees of freedom is similarly manifested in the spectrum of the scattered light irrespective of whether or not one is talking about orientational dynamics, chemical transformations, or the most interesting object of such studies—the correlation dynamics of macromolecules. In all cases, in addition to the diffusion relaxation, the spectrum acquires a set of internal relaxation modes, and it is a sum of Lorentzians with discrete values of the half-widths.

The polarizability of the chemical bonds of a macromolecule is usually independent of its conformation, and the fluctuations of the scattering power are determined solely by the changes in the form factor. For this reason, for small particles these fluctuations are small in terms of the parameter  $qR$ , where  $R$  is the size of the scatterer and  $\mathbf{q}$  is the momentum transfer vector:  $q = (4\pi n/\lambda) \sin[(\theta/2)]$ , where  $\theta$  is the scattering angle. For  $qR \ll 1$  the effect of fluctuations of the diffusion coefficient  $D$  is also small, since in many cases (polymers, orientational dynamics) the relaxation time of the state is of the order of  $R^2/D$ , and there is enough time for these fluctuations to be averaged over the phase correlation time of the scattered wave, equal to  $(Dq^2)^{-1}$ .

The foregoing considerations explain why polymer balls are a convenient model object for studying internal dy-

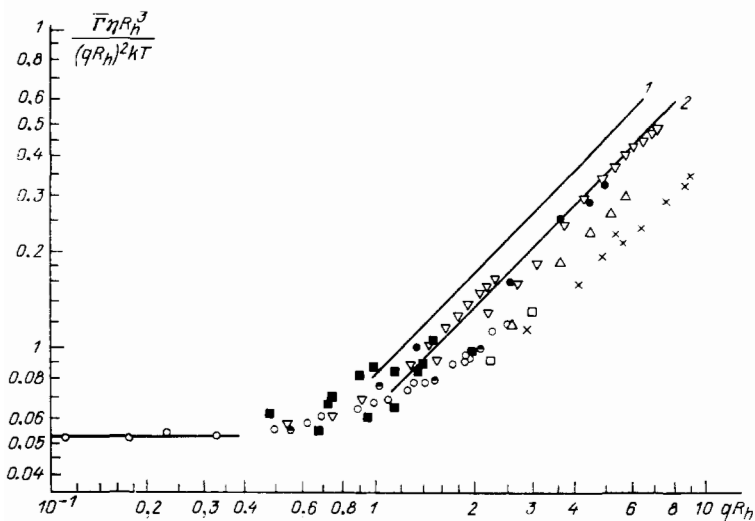


FIG. 1. Angular dependence of the average half-width of the spectrum of light scattered by a polymer ball.<sup>5</sup> a) Good solvent; 2)  $\theta$ -conditions.

namics. First of all, they are quite large. Second, the fluctuations of the conformation of a polymer in solution are also large. Third, the properties of polymer balls are well known and are universal. On the other hand, there are serious omissions in the theoretical description of the dynamics of polymers; they are associated with difficulties in taking into account the fact that self-intersection of a polymer chain is forbidden, which makes the experimental study of this dynamics of great importance in itself. We note that laser correlation spectroscopy is essentially the only direct method for studying the large-scale, "global" dynamics of macromolecules in solution.

The observation of fluctuations of the conformation of a polymer does not in itself present any great difficulty. Figure 1 shows the average half-widths  $\bar{\Gamma}$  of the Lorentzians, comprising the spectrum of light quasielastically scattered by a number of polymers. One can see that for  $qR > 1$  the purely diffusion dependence  $\bar{\Gamma} \sim q^{-2}$  breaks down. As shown by de Gennes,<sup>1</sup> in this region the characteristic half-width of the spectrum is determined by the motion of sections of the polymer ball of size  $q^{-1}$  and hence with diffusion coefficient of the order of  $(kT/\eta)q$ ; therefore  $\bar{\Gamma} \sim (kT/\eta)q^3$ . The coefficient

of proportionality in this dependence can be calculated<sup>2</sup> and is expressed only in terms of the index  $\nu$  (Ref. 3) in the relationship between ball size and the molecular mass.

The quantity  $\bar{\Gamma}$  is the starting slope of the correlation function of the scattered light field and can be easily determined with the help of the method of cumulants.<sup>4</sup> This quantity, however, characterizes the dynamics of a ball to such an averaged extent that it contains information only about its statistical properties. This method can be used to determine the value of  $\nu$  on different spatial scales depending on the properties of the solvent, and only if there exists an effective method for taking into account the systematic underestimation of  $\bar{\Gamma}$ ,<sup>5</sup> clearly seen in Fig. 1. Cumulants do not really give any information about internal relaxation times.

Completely new prospects in the study of internal dynamics with the help of laser correlation spectroscopy are opened up by the method of regularization.<sup>6</sup> For  $qR \ll 1$ , among all internal relaxation modes the mode with the largest scale and the longest relaxation time makes the main contribution to the spectrum, and although this contribution is small compared with the contribution of the purely diffusion mode in terms of the parameter  $(qR)^2$ , the ratio of their relaxation times is characterized by the same parameter. This makes it possible to distinguish with the help of the method of regularization the contributions of the diffusion and lowest relaxation mode and, by extrapolating the inverse half-width of the latter of  $q = 0$ , to determine the longest relaxation time of the scattering object.

Figure 2 shows the relaxation times of some polymers measured in this manner. The excellent agreement with the dependence  $\tau \sim \eta R^3/kT$  predicted by the theory,<sup>7</sup> on the one hand, and the numerical discrepancy by a factor of 2-3, on the other, are interesting. The latter circumstance is not surprising, since the fact that the theory ignores the fact that the polymer chain cannot self-intersect obviously leads to underestimation of the relaxation time.

In conclusion we must mention the promising applications of non-Gaussian correlation spectroscopy,<sup>8</sup> primarily the method of mutual correlation,<sup>9</sup> for studying the internal dynamics. These methods make it possible to distinguish in the spectrum of fluctuations of the intensity of the recorded radiation the contribution of fluctuations of the intensity of separate scatterers. Since these fluctuations are in no way

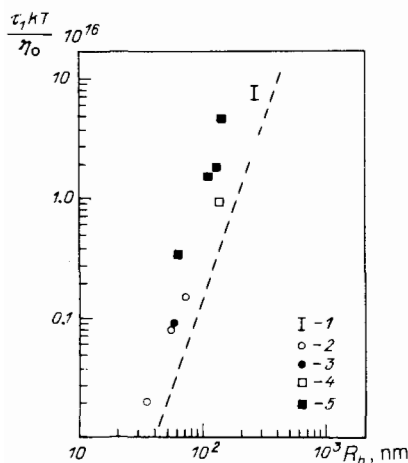


FIG. 2. Relaxation times of the lowest mode of polymer balls of different size.  $\theta$ -conditions: 1) DNA<sup>9</sup>; 2, 3) polystyrene<sup>10</sup>; 4) polyacrylamide<sup>5</sup>; the broken line corresponds to the theory.<sup>7</sup> Good solvent: 5) polycrylamide.<sup>5</sup>

associated with the translational motion of the scatterers as a whole, non-Gaussian correlation spectroscopy enables the study of the internal dynamics of macromolecules in "pure" form.

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