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Influence of Molecular Stiffness on the Dynamic Structure Factor

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SUMMARY: Characteristic features of the influence of molecular stiffness on the dynamic structure factor of macromolecules are briefly outlined. The relaxation times characterizing the internal dynamics of the macromolecules exhibit a crossover from Rouse-Zimm to bending modes with increasing mode number. As a consequence the dynamic structure factor is strongly influenced by the molecular stiffness. In particular, a stretched exponential relaxation of the dynamic structure factor at scattering vectors larger than the inverse persistence length is predicted and confirmed by a comparison with experimental data. Moreover, the influence of polydispersity is discussed.

Introduction

The understanding of dynamical properties of semiflexible macromolecules is of fundamental as well as practical interest, and studies of such systems have been the subject of various light scattering experiments. The challenging problems associated with semiflexibility have received recent attention. In this article characteristic features of dynamic aspects of semiflexibility are discussed. A theoretical approach to the dynamic structure factor is presented and the findings are compared with experimental data. In particular, analytical expressions are derived for the dynamic structure factor. The persistence length of macromolecules is shown to define a characteristic length scale for both equilibrium and dynamical properties.

Theory of Dynamic Structure Factor

In general, for a solution containing macromolecules of different molecular weight the dynamic structure factor is given by the z-average

$$\langle S(\mathbf{q},t)\rangle_z = \frac{\int_0^\infty dL\, w(L) L S(\mathbf{q},L,t)}{\int_0^\infty dL\, w(L) L}\,, \tag{1}$$

where $w(L)\,dL$ is the fraction of macromolecules with contour length between L

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and $L + dL$. $S(\mathbf{q}, L, t)$ is the dynamic structure factor for a solution of identical macromolecules of contour length L. Thus, the dynamic structure factor for polydisperse macromolecular solutions has to be calculated as a function of contour length and the result then averaged over the distribution $w(L)L$. The Schulz-Zimm distribution applies for the polymerisation kinetics and is characterized by the ratio L_w/L_n, where L_w and L_n are the weight-average and number-average contour lengths, respectively$^{1)}$. From the calculation of $w(L)L$ it follows that for polydisperse solutions with a broad Schulz-Zimm length distribution ($L_w/L_n > 4$) even macromolecules with contour lengths larger than three times the weight-average contour length contribute significantly to the dynamic structure factor.

In the calculations a macromolecule is represented as a continuous, differentiable space curve $\mathbf{r}(s)$, where s indicates distances along the molecule. The partition function of this chain of contour length L is calculated using the maximum entropy principle together with constraints on the contour length and on the curvature of the chain$^{2)}$:

$$Z = \int \mathcal{D}^3\mathbf{u} \exp\left[-\frac{3p}{2}\int_0^L \mathbf{u}^2(s)ds - \frac{3}{4}(\mathbf{u}^2(L) + \mathbf{u}^2(0)) - \frac{3}{8p}\int_0^L \left(\frac{\partial \mathbf{u}(s)}{\partial s}\right)^2 ds\right], \quad (2)$$

where $1/(2p)$ is the persistence length and $\mathbf{u}(s) = \partial\mathbf{r}(s)/\partial s$. The first three terms in the exponent characterize a flexible chain. The last term represents the bending energy, which accounts for the molecular stiffness. Calculated second moments of the position vector distribution function, such as the mean square radius of gyration r_g^2, are identical with those of the Kratky-Porod wormlike chain model$^{2,3)}$. Due to the Gaussian nature of the model the static structure factor $S(\mathbf{q}, L, 0)$ can be calculated and the following scattering vector dependence is obtained ($q = |\mathbf{q}|$):

$$S(\mathbf{q}, L, 0) \sim q^{-1}, \qquad \forall\, q > 2p. \quad (3)$$

This q-dependence is characteristic of rigid rods$^{4)}$. For $r_g^{-1} < q < 2p$ the relation $S(\mathbf{q}, L, 0) \sim q^{-2}$ is valid, as is known for a random coil.

Identifying the exponent in the partition function (2) as the intramolecular mean field potential energy of a chain molecule (multiplied by $1/(k_BT)$) and applying Hamiltons principle, the equation of motion is obtained. Since there is always strong damping in a macromolecular solution, the equation of motion is supplemented by frictional forces and the hydrodynamic interaction mediated by the motion of the solvent. Omission of the inertial term leads to the Langevin equation

$$\frac{\partial}{\partial t}\mathbf{r}(s,t) = \int_0^L ds_1\, M(s,s_1)\left(3p\frac{\partial^2}{\partial s_1^2}\mathbf{r}(s_1,t) - \frac{3}{4p}\frac{\partial^4}{\partial s_1^4}\mathbf{r}(s_1,t) + \mathbf{f}(s_1,t)\right). \quad (4)$$

$\mathbf{f}(s_1, t)$ is a stochastic force and η the viscosity of the solvent. The hydrodynamic interaction tensor is given by the Rotne–Prager tensor $M(s, s_1)$. To solve Eq. (4) an expansion of the position vector and of the stochastic force in terms of the eigenfunctions $\psi_l(s)$ of the eigenvalue problem is used:

$$\mathbf{r}(s,t) = \sum_{l=0}^{\infty} \psi_l(s) \int_{-\infty}^{t} dt' \exp\left(-\frac{t-t'}{\tau_l}\right) \mathbf{f}_l(t') \,. \tag{5}$$

τ_l are the relaxation times of the normal mode analysis discussed in detail in Refs.[5,6]. Without hydrodynamic interaction the relaxation times for small mode numbers l are proportional to L^2 and vary as l^{-2} representing the well known Rouse relaxation times. In the limit of large mode numbers the relaxation times are proportional to L^4 and exhibit the dependence l^{-4} on the mode number, as known for bending modes. The model yields a crossover from Rouse to bending modes with increasing mode number. This simply reflects the fact that any real polymer looks increasingly rigid on small length scales. Therefore, normal modes describing motions on small length scales are bending modes[6]. The influence of the hydrodynamic interaction on the relaxation times becomes more important with both increasing chain flexibility and decreasing mode number l. Bending relaxation times are only slightly modified due to hydrodynamic interaction. This means that the correlation between two parts of a macromolecule which are separated a small distance are almost unaffected by the moving solvent.

Comparison with Experimental Data

The dynamic structure factor $S(\mathbf{q}, L, t)$ can be evaluated using the solution of the equation of motion for the position vector. In the regime of small scattering vectors $qr_g < 1$ only the overall translational motion of the macromolecules is observable. Calculating the diffusion coefficient $D(L)$ for a dilute solution one obtains the length dependence $D(L) \sim 1/\sqrt{L}$ for flexible macromolecules and $D(L) \sim \ln L/L + const/L$ for rodlike macromolecules[2]. For scattering vectors $qr_g > 1$ internal modes become essential and must be taken into account explicitly. Using Rouse relaxation times the well known stretched exponential function $-\ln(S(\mathbf{q}, L, t)) \sim (q^4 t)^{1/2}$ is obtained[4]. Taking hydrodynamic interaction into account the dynamic structure factor is given by $-\ln(S(\mathbf{q}, L, t)) \sim (q^3 t)^{2/3}$. Assuming that all relaxation times are bending relaxation times an analogous calculation yields

$$-\ln(S(\mathbf{q}, L, t)) \sim (q^{8/3} t)^{3/4}, \qquad \forall\, q > 2p \,. \tag{6}$$

This stretched exponential function is only slightly changed if hydrodynamic interaction is taken into account.

Figure 1 displays the computed dynamic structure factor together with experimental data for alkane chains in a melt$^{7,8)}$. As is obvious the theoretical approach is in good agreement with the experimental data. In particular, the dynamic structure factor at large scattering vectors is given by the stretched exponential function (6) as is indicated by the dashed line in the figure. Similar results are obtained for the dynamic structure factor of polyisobutylene$^{9)}$. At large scattering vectors the single chain motion on small length scales is probed in the experiments.

Figure 1 shows a set of dynamic structure factors $\langle S(\mathbf{q},t)\rangle_z$ for a polydisperse macromolecular solution at two scattering vectors. The weight-average contour length L_w and persistence length were fixed to $L_w = 600$ nm and $1/(2p) = 100$ nm. From the figure it is apparent that the influence of polydispersity on the shape of the dynamic structure factor becomes less important with increasing scattering vector. The dynamic structure factor at scattering vector $q = 0.035$ nm^{-1} for a monodisperse solution is close to that for the polydisperse solutions considered in the figure. At this large scattering vector only short sections of the macromolecules are probed. Therefore the dynamic structure factor is rather independent of contour length and polydispersity. Bending modes become important at large scattering vectors as discussed above. The shape of the dynamic structure factor at the small scattering vector exhibits a strong upturn in comparison with the single-exponential function for a monodisperse solution. This has also been observed experimentally for polydisperse polysaccharides$^{10)}$.

Conclusion

In this article it has been demonstrated that molecular stiffness influences equilibrium and dynamical properties of macromolecules significantly. The persistence length defines the characteristic length scale. On length scales smaller than the persistence length the mean square internal distance and the scattering vector dependence of the static structure factor are similar to the ones obtained for a rodlike molecule. Dynamic properties on small length scales are dominated by bending modes and the dynamic structure factor differs from the well-known results for the Rouse-Zimm model. Polydispersity is found to influence the dynamic structure factor mainly at small scattering vectors.

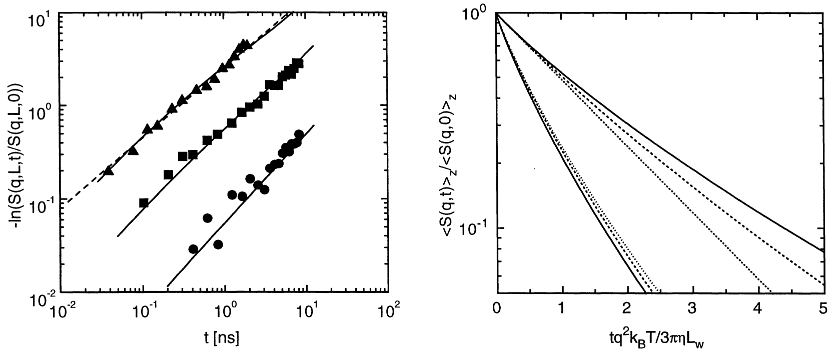

Fig.1: Left: Computed dynamic structure factor (solid lines) for three scattering vectors q together with experimental results for alkane chains in melt (circles, $q = 0.55$ nm^{-1}; squares, $q = 1.4$ nm^{-1}; triangle, $q = 2.6$ nm^{-1}) $^{7,8)}$. The dashed line displays the stretched exponential function (6) for the largest scattering vector.
Right: Dynamic structure factor for a polydisperse macromolecular solution at two scattering factors ($q = 0.005$ nm^{-1}: upper curves, $q = 0.035$ nm^{-1}: lower curves). The Schulz-Zimm distribution is used in the calculations (dotted lines, $L_w/L_n = 1$; dashed lines, $L_w/L_n = 1.5$; solid lines, $L_w/L_n = 5$).

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