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Aqueous mixtures of spherical and rodlike (flexible) macroparticles: structure and dynamics of latex spheres in saltfree solutions

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Abstract. This paper resumes light scattering investigations of saltfree aqueous solutions of two component mixtures of charged spheres by extending those measurements to systems in which one component is replaced by essentially stiff rodlike particles. In a second step of investigations these were replaced by linear flexible particles. Fd-virus particles (length $l = 883$ nm) or macromolecules of NaPSS of four different contour lengths have been used as representatives. Mostly the concentration of latex spheres was fixed at 0.02 Vol%. The concentration of the other component was varied over a wide range. Concerning the scattering intensity, the contribution of the latex spheres dominates, in particular in the systems containing NaPSS particles. This simplifies the interpretation of data considerably. A rearrangement of the spheres is observed, depending on the shape of the other sort of particles. These conclusions can be drawn from the shift of measured static structure factor $S^{\mathrm{M}}(q)$ with concentration c. A power law is found for the q-value of the maximum. The exponent depends on the properties of the second component. For the lower molecular weight (MW) samples of NaPSS below a critical concentration, the exponent is smaller than 1/3, decreasing the more the smaller the MW of the samples is. A tentative explanation in terms of charge number of NaPSS particles is given. The short time dynamics has been explored too. From the data a "dynamically determined structure factor" can be derived, that can be compared with the measured static structure factor. Good (fd) and fair (NaPSS) agreement is obtained respectively. Only at small wavenumbers below the maximum of $S^{\mathrm{M}}(q)$ deviations occur which increase with concentration; they are consistent with hydrodynamic interaction.

PACS. 61.25.Hq Macromolecular and polymer solutions; polymer melts; swelling – 78.35.+c Brillouin and Rayleigh scattering; other light scattering – 83.70.Hq Heterogeneous liquids: suspensions, dispersions, emulsions, pastes, slurries, foams, block copolymers, etc.

1 Introduction

Much work has been done on two component mixtures of colloids and polymers immersed in a common solvent [1–8]. Different organic liquids and also water were used. Most of the measurements were performed with probe particles whose diffusive properties were investigated in the presence of a background of stiff chains or flexible polymers. In the majority the probe particles were of spherical shape. As light scattering of spheres dominates usually over that of the background particles, almost all of measurements were confined to the properties of the spheres. In some more recent investigations refractive index matching techniques were applied in the way that the matrix polymer is isorefractive with the solvent. In these cases also weakly scattering polymers could be used as probe particles [2,9,10]. Although electrostatic interactions between water soluble particles can become strong, no ordering phenomena of the probe particles were reported. In all papers their diffusion constant was extracted by means of dynamic light scattering (DLS) and related techniques as a function of ionic strength. The dependence of the sphere diffusion constant on the matrix particles concentration is well fitted by a stretched exponential [1]

$$\frac{D}{D^0} = \exp(-\alpha c^{\mu})$$

(D^0 = diffusion constant in the limit of neglectible matrix polymer concentration c). Problems occured in some of the works. Adsorption of the macromolecules onto the spheres and bridging of the spherical particles into clusters have been observed. Such features have also been treated theoretically [11].

There exist detailed experimental and theoretical studies of the simplest possible charged two component system. Aqueous solutions of charged spherical particles

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of two different diameters and charges, namely latex spheres. The static structure factor of the mixtures has been analyzed and the mean square displacement was investigated. Moreover, the polydispersity of the two components was taken into account [7,8].

In this paper we present results on a mixture of latex spheres in water, with the other component being either rodlike fd-virus particles (l = 883 nm) or flexible polymer particles of Na(H)PSS. Mostly, the concentration of the spheres is fixed and therefore their mean distance. The particle number of the other component is gradually increased. Because an electrostatic interaction exists between the different particles, a certain structure is built up. In most of the cases the scattering of the latex spheres dominates; thus we will gain information about the mixture's structure by essentially monitoring the structural properties of spheres after having added the second sort of macroparticles. In addition we are interested in the dynamic properties of the mixture. Especially we have concentrated on the short time behaviour of the time correlation function, since in the parent systems this is related to the structure of the particles. Fd-particles are a good representative of monodisperse rodlike macromolecules. They are only slightly flexible. There structural and dynamical properties are well known [12–14]. As a representative of a charged, rather flexible polymer NaPSS was selected. It can be purchased in various molecular weights and a wealth of information on the solution properties is available [15–17].

2 Experimental

2.1 Sample preparation

Monodisperse latex spheres of Ø = 67 nm and 91 nm were purchased by Dow Chemical. Samples of desired concentration were prepared with highly purified water ($R \geq 18$ MΩ). The solutions were deionized by pumping them with a tube pump [18] through mixed-bed-ion-exchange-resin (MB3, Serva Diagnostics, Heidelberg).

Fd-virus particles, which scattering power is about an order of magnitude weaker than that of spheres of diameter Ø = 67 nm at the same number concentration, can be produced with almost equal length l ($l = 883 \pm 24$ nm). As already described earlier, a stock solution was prepared with the help of Professor I. Rasched† (Universität Konstanz) following a method of Marvin and Wachtel [19]. Escheria coli bacteria were infected with the fd-virus. After 8 h at 37 °C the fd-virus bred by a factor 1000. The reproduction was stopped and the virus was separated from the bacteria by several steps of precipitation and centrifugation. Finally, the fd-virus suspension was ultracentrifuged in a CsCl gradient and dialyzed against deionized water to obtain a pure stock solution. After dilution the samples were processed further as above, using a filter of 1.2 nm pore size in the circuit.

NaPSS is a very weak scatterer compared to latex spheres ($I_{\mathrm{s,NaPSS}}$ (MW 744 kg/mol)/$I_{\mathrm{s,latex67}} < 10^{-2}$). The material was purchased by Polysciences Europe. Four molecular weights were used (Tab. 1).

According to the manufacturer, the polydispersity of the salt form is characterized by $M_{\mathrm{w}}/M_{\mathrm{n}} < 1.1$, and the degree of sulphonation higher than 90%. Again aqueous solutions of appropriate concentration were deionized by means of a tube pump before mixing with spheres. As already has been pointed out [15], almost all of the Na^+-counterions are exchanged by H^+-ions by this procedure, but we retain the molecular weights of NaPSS which has of course the same contour length as HPSS. It is very important that filtering of the Na(H)PSS solution in the circuit is done by filters of 0.1 μm pore size [20]. Otherwise aggregates will dominate the scattering at small angles. The concentration of the latex spheres was taken as given by Dow Chemicals. The concentrations of the fd- and Na(H)PSS samples were measured by a spectrophotometer (Beckman, DU 64, Darmstadt, Germany) at the absorption maximum of $\lambda = 269$ nm and 224 nm respectively.

2.2 Light scattering apparatus

A commercial light scattering apparatus (ALV 5000, Langen/Germany) consisting of a computer controlled goniometer table with focusing and detector optics, a power stabilized 3 W argon laser (Spectra Physics), a digital rate meter, and a temperature control for the sample cell was used.

3 Theoretical

Although there are no theoretical treatments of the structural and dynamic properties of the two component systems to be discussed here, it is necessary to be familiar with the basic formulas for the "measured" static structure factor and the short time dynamics. They are a generalisation of the definitions for bidisperse sphere-systems [21,22]. Therefore, only a brief summary is given here.

3.1 Averaged scattered intensity

Monodisperse systems

The scattering of the particles in question may be treated in the Rayleigh-Gans-Debye approximation: The macromolecules are divided into small segments which are considered as point scatterer. The amplitude of the scattered electric field $E_{\mathrm{s}}(q,t)$ can be written as

$$E_{\mathrm{s}}(q,t) = \sum_i F_i(q) \mathrm{e}^{\mathrm{i}\mathbf{q}\mathbf{R}_i(t)}. \tag{1}$$

F_i is the amplitude of the electric field of the ith scattering center, and $\mathbf{R}_i(t)$ denotes the center of gravity vector of the particle i at time t

$$F_i(q) = f_i B_i(q) \tag{2}$$

Table 1. Characterisic properties of NaPSS-particles used in the experiments.

Molecular weight [g/mol]	Contour-length L_c [nm]	Number of monomers N	Conductivity-charge Q [e^-]	c_c^* [part./ml]
1 010 000	1226	4903	1149	5.43×10^{11}
744 000	903	3612	847	1.36×10^{12}
356 000	432	1728	405	1.24×10^{13}
183 000	222	888	213	9.14×10^{13}

where

$$B_i(q) = \frac{1}{f_i}\int \zeta_i(\mathbf{r})\mathrm{e}^{\mathbf{iqr}}\mathrm{d}\mathbf{r}$$
$$f_i = \int_{V_i} \zeta_i(\mathbf{r})\mathrm{d}\mathbf{r}. \tag{3}$$

Here $B_i(q)$ is named the normalized field-amplitude, $\zeta_i(r)$ is the distribution of scattering material inside the macroion i and V_i is the corresponding volume, f_i is the field amplitude at $q = 0$. The time averaged intensity then is

$$I_\mathrm{s}(q) = \langle |E_\mathrm{s}(q,t)|^2\rangle_t = \langle E_\mathrm{s}(q,t)E_\mathrm{s}^*(q,t)\rangle_t. \tag{4}$$

To calculate $E_\mathrm{s}(q,t)$ we may separate the scattering in an inter- and intramolecular part. Thus, we may write

$$E_\mathrm{s}(q,t) \propto \sum_{i=1}^{N} \mathrm{e}^{\mathbf{iqR}_i(t)} \sum_{\alpha=1}^{n} \mathrm{e}^{\mathbf{iqr}_{i\alpha}(t)}$$
$$\propto \sum_{i=1}^{N} \mathrm{e}^{\mathbf{iqR}_i(t)} F_i(q,t). \tag{5}$$

Here n is the number of scattering particles, $\mathbf{r}_{i\alpha}(t)$ is the position vector of scattering element α and n is the number of segments of the macroparticle i.

Introducing $E_\mathrm{s}(q,t)$ in equation (4) the intensity finally becomes

$$I_\mathrm{s}(q) \propto N\langle F_i^2(\mathbf{q},\mathbf{r}_{i\alpha})\rangle + \left\langle \sum_{i\neq j}^{N} \mathrm{e}^{\mathbf{iq}(\mathbf{R}_i-\mathbf{R}_j)} F_i(q)F_j(q)\right\rangle. \tag{6}$$

The factor $F_i(q)$ is known as form amplitude, the averaged squared quantity is the form factor $P(q)$. It has been calculated for spherical or rodlike particles. For spherical particles $F_i = F_j$ and, as is well known, the intensity is

$$I_\mathrm{s}(q) \propto N\langle F_i^2\rangle \left\{1 + \frac{1}{N}\sum_{i\neq j}^{N} \mathrm{e}^{\mathbf{iq}(\mathbf{R}_i-\mathbf{R}_j)}\right\} \tag{7}$$
$$= NP(q)S_\mathrm{sph}(q) \tag{8}$$

where $S_\mathrm{sph}(q)$ is the static structure factor of the spheres dissolved in water. For rodlike particles $F_i \neq F_j$, because they depend on the orientation of the particles. Nevertheless, to keep the above description of equation (8) the intensity is written

$$I_\mathrm{s}(q) \propto NP(q)\left\{1 + \frac{1}{NP(q)} \times \left\langle \sum_{i\neq j}^{N} \mathrm{e}^{\mathbf{iq}(\mathbf{R}_i-\mathbf{R}_j)} F_i(\mathbf{q}\cdot\mathbf{u})F_j(\mathbf{q}\cdot\mathbf{u})\right\rangle\right\} \tag{9}$$

where $\mathbf{u}$ is a unit vector, pointing along the rod axis. Equation (9) shows that the structure factor depends on the form factor. Considering $S(q,P(q))$ as function of concentration, it has been found experimentally and theoretically, that the wavenumber q_m of the first maximum of $S(q,P(q))$ scales as proportional to $c^{1/3}$ below the overlap concentration c^*, and as $c^{1/2}$ above it. The overlap concentration of a rodlike particle of length l is defined as $c^* = 1$ particle$/l^3$. A similar relation holds for flexible particles.

3.2 Two component fluids

Extension of equation (5) on p sorts of particles yields for the scattering intensity

$$I_\mathrm{s}(q) \propto N\left\langle \left|\sum_{\alpha=1}^{N}\sum_{i=1}^{N_\alpha} F_\alpha(q)\mathrm{e}^{\mathbf{iqR}_i^\alpha}\right|^2\right\rangle. \tag{10}$$

Defining the partial structure factors as

$$S_{\alpha\beta}(q) = \frac{1}{N}\sum_{i=1}^{N_\alpha}\sum_{j=1}^{N_\beta}\langle \mathrm{e}^{\mathbf{iq}(\mathbf{R}_i^\alpha-\mathbf{R}_j^\beta)}\rangle \tag{11}$$

leads to the intensity

$$I_\mathrm{s}(q) \propto N\sum_{\alpha=1}^{p}\sum_{\beta=1}^{p} F_\alpha(q)F_\beta(q)S_{\alpha\beta}(q) \tag{12}$$
$$= N\overline{f^2}\ \overline{P(q)}S^M(q) \tag{13}$$

where the quantities $\overline{f^2}$ and $\overline{P(q)}$ are given by the averages over the particle type distribution

$$\overline{f^2} = \sum_{\alpha=1}^{p} x_\alpha f_\alpha^2 \tag{14}$$

$$\overline{P(q)} = \frac{1}{\overline{f^2}}\sum_{\alpha=1}^{p} x_\alpha F_\alpha^2(q), \tag{15}$$

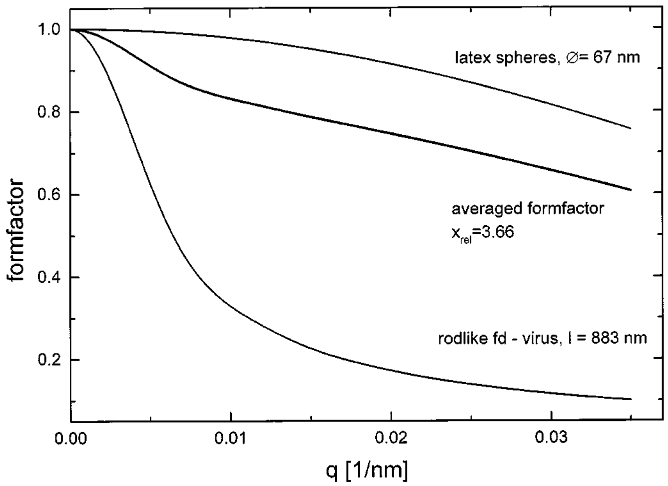

Fig. 1. Formfactor of spheres and rodlike particles together with an example of averaged formfactor ($x_{\mathrm{rel}} = x_{\mathrm{fd}}/x_{\mathrm{sph}}$).

x_α denotes the molar fraction of particles of sort α, and f_α is the field amplitude at $q = 0$. $S^M(q)$ is called measured structure factor. It is defined by

$$S^{\mathrm{M}}(q) = \frac{1}{\overline{f^2}} \frac{1}{\overline{P(q)}} \sum_{\alpha=1}^{p} \sum_{\beta=1}^{p} f_\alpha f_\beta B_\alpha(q) B_\beta(q) S_{\alpha\beta}(q). \quad (16)$$

Specializing the measured structure factor to the sphere-rod system it is useful to write

$$\begin{aligned} S^{\mathrm{M}}(q) = {} & N \frac{1}{\overline{f^2}} \frac{1}{\overline{P(q)}} f_{\mathrm{sph}}^2 \\ & \times P_{\mathrm{sph}}(q) \left\{ S_{\mathrm{sph}}(q) + \delta^2(q) S_{\mathrm{fd}}(q) + 2\delta(q) S_{\mathrm{sph,fd}}(q) \right\} \end{aligned} \quad (17)$$

where $\delta(q)$ is defined as

$$\delta(q) = \frac{f_{\mathrm{fd}} B_{\mathrm{fd}}(q)}{f_{\mathrm{sph}} B_{\mathrm{sph}}(q)} \cdot \quad (18)$$

The averaged form factor becomes

$$\begin{aligned} \overline{P(q)} & \propto x_{\mathrm{sph}} f_{\mathrm{sph}}^2 P_{\mathrm{sph}}(q) \left\{ 1 + \delta^2(q) x_{\mathrm{rel}} \right\}; \\ x_{\mathrm{rel}} & = \frac{x_{\mathrm{fd}}}{x_{\mathrm{sph}}} \cdot \end{aligned} \quad (19)$$

It should be noted that the field amplitudes of non spherical particles are angular dependent which has not explicitly been taken into account above.

Equivalent expressions can be written down for the sphere-flexible polyion system. The form factors of spheres (∅ = 67 nm) and fd-particles are compared with each other in Figure 1.

For the calculation of the averaged form factor the polarizability or the index of refraction of the two components of the mixture have to be known. We could not find the value for fd-particle solutions in the literature. Therefore we have estimated it as follows. The scattering intensity of a one component system m is given by

$$I_{\mathrm{s}}(q) = \frac{16\pi^4}{\lambda^4 R^2} \left\{ \frac{n_m^2 - n_s^2}{n_m^2 + 2n_s^2} \right\}^2 V_m^2 N_m P(q) S(q) I_0. \quad (20)$$

I_0 is the intensity of the incident beam. In a salt containing solution or at sufficiently large scattering angles $S(q)$ is equal to one. Thus for a solution of spheres we may write

$$I_{\mathrm{s,sph}}(q) = c'_{\mathrm{sph}}(q) I_0. \quad (21)$$

By calculating $c_{\mathrm{sph}}(q)$ a value of I_0 is obtained from the measurement of the scattering intensity. For fd-particle solutions we may write

$$I_{\mathrm{s,fd}}(q) = c''_{\mathrm{fd}}(q) \left\{ \frac{n_{\mathrm{fd}}^2 - n_{\mathrm{H_2O}}}{n_{\mathrm{fd}}^2 + 2n_{\mathrm{H_2O}}^2} \right\}^2 I_0. \quad (22)$$

By again measuring the scattering intensity the index of refraction can be determined to yield approximately $n_{\mathrm{fd}} = 1.56$.

4 Results and discussion

4.1 Sphere-rod system

For the first series of solutions latex spheres of ∅ = 67 nm were used at a concentration of 0.02 Vol% corresponding to 1.27×10^{12} particles/ml. Samples of mixtures of various concentrations up to about $10c^*_{\mathrm{fd}}$ were prepared. The overlap concentration $c^*_{\mathrm{fd}} = 1$ particle/length^3 corresponds to 1.5×10^{12} particles/ml. Similar samples were prepared with spheres of $c = 0.05$ Vol%.

In Figure 2 the static structure factors of some of the samples with 0.02 Vol% spheres are depicted. The light scattering at the scattering vector $q_{\max}$ of the maximum of the structure factor originates mainly from the spheres. This is estimated from the values of δ; especially for the mixtures with the larger spheres not only the contribution from the fd-term vanishes but also the prefactor of the mixed term (which is not known) is smaller than 0.1. At large enough values the measured structure factor is equal to one. In cases where the oscillations of $S^{\mathrm{M}}(q)$ had not yet decayed, it had to be adjusted by eye.

To investigate a possible dependence of the diameter ∅ of the spherical particles, measurements with latex spheres of ∅ = 91 nm (0.02 Vol%) were also performed (not shown).

A common feature of all three cases is a considerable broadening of the structure factor with increasing fd-concentration together with a decreasing of height of the maximum. Comparing the entities for spheres of ∅ = 67 nm and ∅ = 91 nm at equal molar fraction of the fd-particles it turns out that for the larger spheres the measured structure factor is more strongly affected (Fig. 3). The first maximum of the structure factor is shifted to larger wavenumbers as shown in Figures 4a-4c. The first two plots (top) refer to a sphere concentration of 0.02 Vol%.There diameter is 67 nm; the lowest

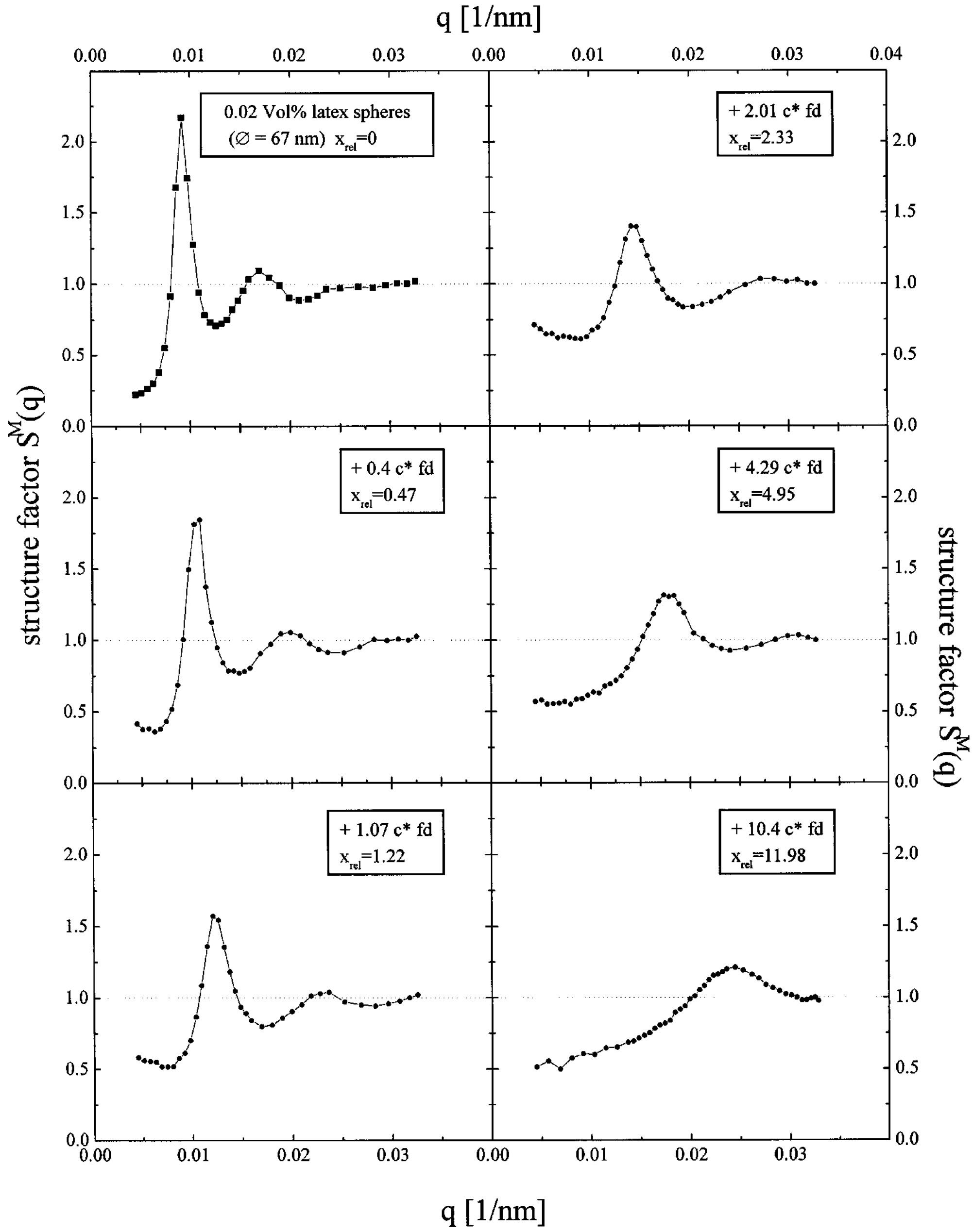

Fig. 2. Measured static structure factor of mixtures of 0.02 Vol% latex spheres (Ø = 67 nm, 1.27×10^{12} part./ml) and rodlike fd-particles ($l = 883$ nm).

plot shows results for spheres of Ø = 91 nm. It should be noted that the values of the abscissa are the total concentrations ($c_{\text{total}} = c_{\text{sph}} + c_{\text{fd}}$). The structure factor for $q \to 0$ increases with fd-concentration.

It is seen that for mixtures containing concentrations of fd-particles which do not yet overlap, $c_{\text{fd}} < c^*_{\text{fd}}$, the wavenumber of the first maximum is shifted proportional to $c^{1/3}_{\text{total}}$. Around and above c^*_{fd} the exponent takes values between 1/3 and 1/2. The best fit is obtained with an exponent of 0.38 and 0.39 respectively. No dependence of size and concentration of the latex spheres is observed.

Which is the mutual arrangement of the two components? One could think of a macroscopic phase separation of the two species (compare [23,24]), however there is no indication for this. Data were taken at different heights of the sample cell without observing any changes. Also, the change of the exponents of $q_{\max} \propto c^{\alpha}$ close to $c_{\text{fd}} = c^*_{\text{fd}}$ would not be understandable. For the same reason macroscopic clustering of spheres and rods can be excluded. Moreover, the solutions are very transparent.

If there is no macrocopic phase separation the mean distance between the spheres remains constant on a macroscopic scale. One therefore might conclude that $q_{\max}$

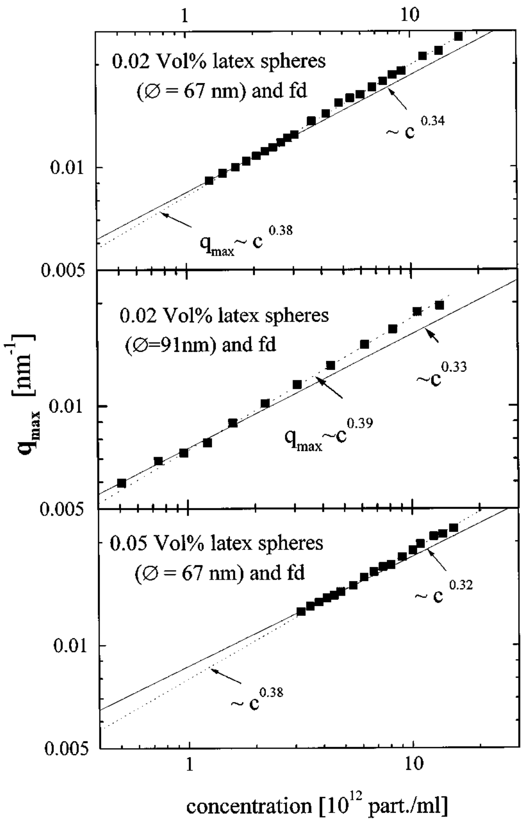

Fig. 3. Maximum value of the measured static structure factor relative to the one of the sample consisting of spheres only *versus* relative concentration of fd-particles.

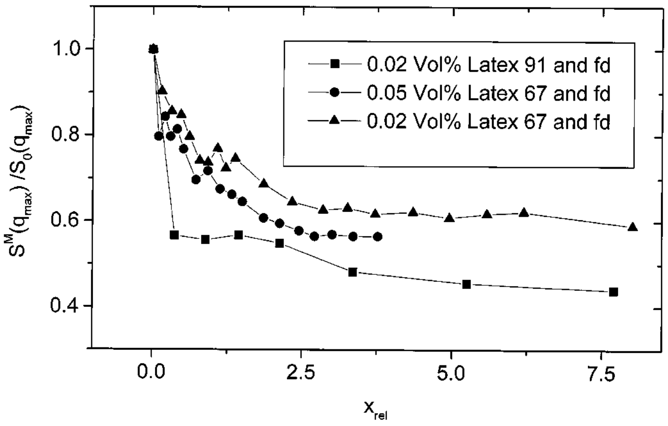

Fig. 4. Wavenumber of the maximum of measured structure factor of mixtures of latex spheres and rodlike fd-particles *versus* concentration.

should be constant. But this is only true if the particles are distributed uniformly. In reality the two sorts of particles are about equally charged, and we deal with a short range ordering in which all particles take part. For illustration let us think on a simplified two dimensional example of a (distorted) hexagonal arrangement of charged latex spheres. When fd-particles are added they will replace some of the latex spheres. The latter together with other fd-particles will form additional hexagons, and since the volume of the sample is constant the distance between all particles will diminish uniformly. Different combinations of the two sorts of particles will result on a hexagon which implies that microscopically there is no longer a uniform arrangement of latex- (and fd-) particles. As just explained the distance between any nearest neighbours and therefore that between nearest neighbour latex spheres, which give rise to the structure factor, will decrease as if the solution consists of spheres only of concentration $c_{\text{total}} = c_{\text{latex}} + c_{\text{fd}}$. Interactions between those spheres that are not nearest neighbours of each other are screened by the fd-particles between them. Therefore correlations between their positions are expected to be weak or even negligible.

For small concentrations (averaged sphere-rod distance bigger than about the rod length) we may neglect the anisometry of the fd-particles, and $q_{\max}$ will change proportional to $(c_{\text{total}})^{1/3}$. By increasing the fd-concentration the interaction between the anisometric particles and also that between spheres and fd-particles become anisotropic. This obviously influences the positions of the spheres showing up as a deviation of the exponent from 1/3 to a bigger value; in parallel the decreasing and broadening of the measured structure factor expresses the loss of correlation between the spheres; in their neighbourhood more and more anisometric particles accumulate. This intuitive picture is in accord with measurements which were performed by varying the concentration of the two species in a way that the total concentration is kept constant. In this case, if the concentration of spheres is lowered, the position of the structure factor remains constant. (Only when the particles consist predominately of fd-particles a small shift of $q_{\max}$ is observed which is known from pure fd samples.)

Of course the above suggested model is based on qualitative arguments. To get a more detailed understanding of the structural properties of a sphere-rod-system all parameters of the solutions including the charges of the two components have to be taken into account quantitatively. Other arrangements of the particles might be possible. Very recently *e.g.* different microscopic phases have been observed in highly concentrated mixed systems of globular and rodlike particles [12].

Turning towards the dynamics of the system it should be repeated that for both parental spherical and rodlike macromolecules the dynamical properties have been explored experimentally and theoretically [12–14,25] except the long time behavior of the correlation function for salt-free solutions of rodlike particles which is only known experimentally [14]. The cumulant expansion method was applied to obtain an (effective) short time diffusion coefficient. This will be compared by the inverse of the static structure factor by means of a relation originally derived for spherical particles. The first cumulant $K_1(q)$ for a one component system is defined as

$$K_1(q) = \frac{\mathrm{d}}{\mathrm{d}t} \ln S(q,t)|_{t=0} \tag{23}$$

which for noninteracting spheres leads to [26]

$$K_1(q) = D^0 q^2. \tag{24}$$

For anisometric particles, D^0 has to be replaced by $D^{0,\mathrm{eff}}$. In the case of electrostatic interaction the effective diffusion coefficients are denoted both by D^{eff}. The coupling to the static structure factor of spheres is now given by

$$K_1(q) = q^2 \frac{H(q)}{S(q)} \tag{25}$$

where $H(q)$ takes into account hydrodynamic interaction. Combining the two expressions the static structure factor becomes

$$S(q) = \frac{H(q)}{D^{\mathrm{eff}}(q)} \cdot \tag{26}$$

The right side can be regarded as a dynamically determined static structure factor. Good agreement has been obtained between the two quantities not only for solutions of spheres but also of rodlike particles. For two component mixtures of spheres the first cumulant is written as [22,27]

$$\begin{aligned} K_1(q) = {}& \frac{q^2}{\overline{P(q)} S^{\mathrm{M}}(q)} \\ & \times \sum_{\alpha,\beta=1}^{2} (x_\alpha x_\beta)^{1/2} f_\alpha f_\beta B_\alpha(q) B_\beta(q) H_{\alpha\beta}(q,t). \end{aligned} \tag{27}$$

Neglecting the hydrodynamic interaction ($H_{\alpha\beta}(q,t) = D^0_\alpha \delta_{\alpha\beta}$) one obtains

$$K_1(q) = \frac{q^2}{\overline{P(q)} S^{\mathrm{M}}(q)} \sum_{\alpha,\beta=1}^{2} x_\alpha f_\alpha^2 B_\alpha^2(q) D^0_\alpha. \tag{28}$$

In the case of mixtures of spherical and rodlike particles we formally write for the measured static structure factor

$$\begin{aligned} S^{\mathrm{M}}(q) = {}& \frac{q^2}{\overline{P(q)} K_1(q)} x_{\mathrm{sph}} f^2_{\mathrm{sph}} \\ & \times P_{\mathrm{sph}}(q) \left\{ D^0_{\mathrm{sph}} + x_{\mathrm{rel}} \delta^2(q) D^{0,\mathrm{eff}}_{\mathrm{fd}} \right\} \cdot \end{aligned} \tag{29}$$

Strictly speaking, it has been shown for sphere-sphere mixtures that at small wavenumbers hydrodynamic interaction has to be taken into account. Again a corresponding expression holds for sphere flexible polyion mixtures. The diffusion coefficients for non interacting spheres and anisometric particles are of the same order of magnitude. For the same reason as above the contribution from the fd particles to the measured structure factor at not too high concentrations is small. This especially proves correct for mixtures containing Na(H)PSS polyions.

To determine the "dynamically obtained structure factor" we have to divide (see Eq. (26)) the first cumulant without interaction by the one with interaction, equation (28). The former has been measured for x_{rel} up to 7. A constant value was obtained independent of q.

Figure 5 shows an example of the experimental results for the dynamically obtained ("measured") structure factor of mixtures with 0.05 Vol% latex spheres (Ø = 67 nm). It may be compared with the measured static structure factor. By and large there is good agreement between the two quantities. Only at small wavenumbers deviations occur with increasing fd concentration. The structure factor increases to higher values up to about 20%. Qualitatively this effect is in agreement with contributions from hydrodynamic interaction [26]. Detailed theoretical treatments are available only for monodisperse and polydisperse spherical particles.

4.2 Sphere flexible-linear-polyion system

We now want to present our results on two-component mixtures of aqueous solutions of monodisperse latex spheres and Na(H)PSS, a flexible linear polyion. As already stated, samples with chains of four different molecular weights were investigated. In Figure 6 an example of the measured static structure factor (MW 744 kg/mol) is shown for various Na(H)PSS concentrations. Since the scattering power of the latter particles is more than an order of magnitude weaker than that of fd particles, the data refer entirely to the spheres. At the first glance, the overall behaviour of the measured static structure factor $S^{\mathrm{M}}(q)$ seems similar as before: with increasing concentration of the flexible polyions the maximum of $S^{\mathrm{M}}(q)$ moves to larger wavenumbers the latter thereby broadening and decreasing in height. The shift of $q_{\max}$ is shown again in a double logarithmic presentation in Figures 7a-7d. Straight lines are obtained. This is only the case if the total concentration is used. Replacing it by the Na(H)PSS-concentration results in a bending of the formerly straight lines to higher values. For the flexible polyions of biggest contour length $q_{\max}$ changes with total concentration proportional to $c^{0.40}$. Almost all data points refer to the semidiluted regime. Therefore the result corresponds to mixtures with rodlike particles. However, a kink is developing when the molecular weight gets smaller. Below a certain critical concentration c_{crit} the exponent decreases from 0.36 to 0.14 for MW185 (Tab. 2). The critical concentration c_{crit} depends on the particle concentration of Na(H)PSS. For MW 744 a value of 2×10^{12} part./ml is observed, for MW183 $c_{\mathrm{crit}} = 5 \times 10^{12}$ part./ml. Asking for the corresponding monomer concentration values between 7224 and 4400 are found. When the concentration of the spheres is doubled, the critical Na(H)PSS concentration seems doubled too).

Above c_{crit} only a small reduction from 0.40 to 0.32 takes place. This result can be qualitatively explained by the decrease of the contour length of the flexible particles. Concerning the highest MW-particles the measurements range in a concentration regime in which spheres and elongated chains are close to each other or overlap. Therefore similarly as in pure Na(H)PSS the pair potential becomes angular dependent, and the exponent deviates from 1/3.

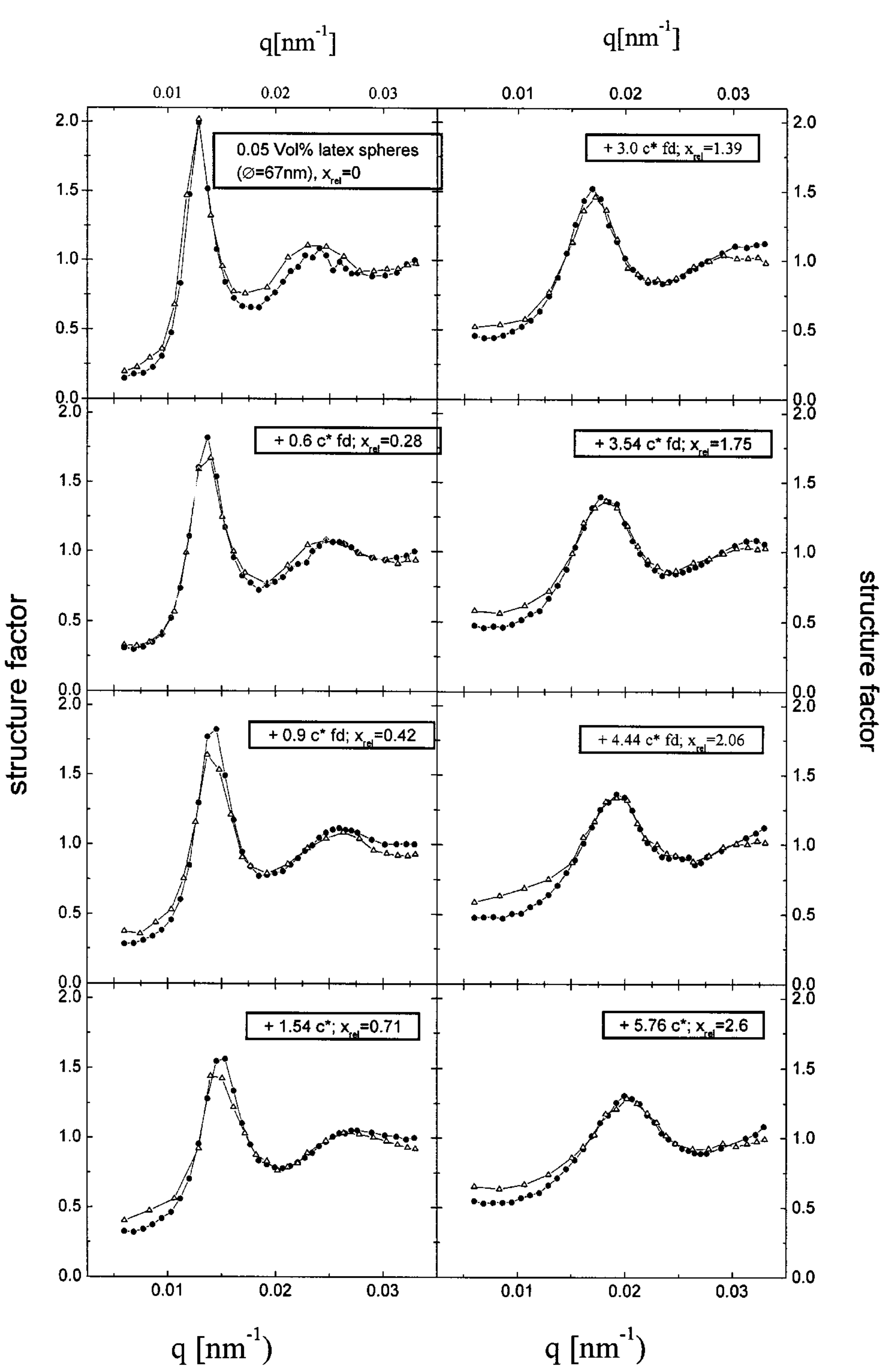

Fig. 5. Dynamically determined static structure factor of 0.05 Vol% latex spheres (∅ = 67 nm) and rodlike fd-particles (△). The measured static structure factor is plotted too for comparison (●).

When at constant chain concentration the contour length decreases the measurements refer more and more to the diluted regime where anisometry of particles gets less important. Consequently the exponent will approach 1/3. This is particularly true since the ionic strength is higher than in pure Na(H)PSS systems due to the presence of highly charged spheres. Consequently the Na(H)PSS particles are more bent, and the overlap concentration increases.

The small exponent below c_{crit} is more difficult to explain. We again have looked for different phases in the sample, but the result was negative. For further clarification, Figure 8 shows the relative height of the first peak as function of Na(H)PSS monomer concentration. It is seen that the values are rather similar with regard to the MW (when plotted *versus* particle concentration, the curves are somewhat more separated from each other).

Table 2. Critical concentrations and the exponents of $q_{\max} \propto (c_{\text{total}})^{\alpha}$.

Molec. Weight	c_{sphere}	c_{crit}		Exponent	
[g/mol]	[part./ml]	[monom./ml]	[part./ml]	$c < c_{\text{crit}}$	$c > c_{\text{crit}}$
1 010 000	1.27×10^{12}			0.40	
744 000	1.27×10^{12}	7.224×10^{15}	2.0×10^{12}	0.28	0.36
356 000	1.27×10^{12}	6.048×10^{15}	3.5×10^{12}	0.17	0.32
183 000	1.27×10^{12}	4.400×10^{15}	5.0×10^{12}	0.14	0.32
183 000	3.54×10^{12}	9.946×10^{15}	11.2×10^{12}	0.14	0.31

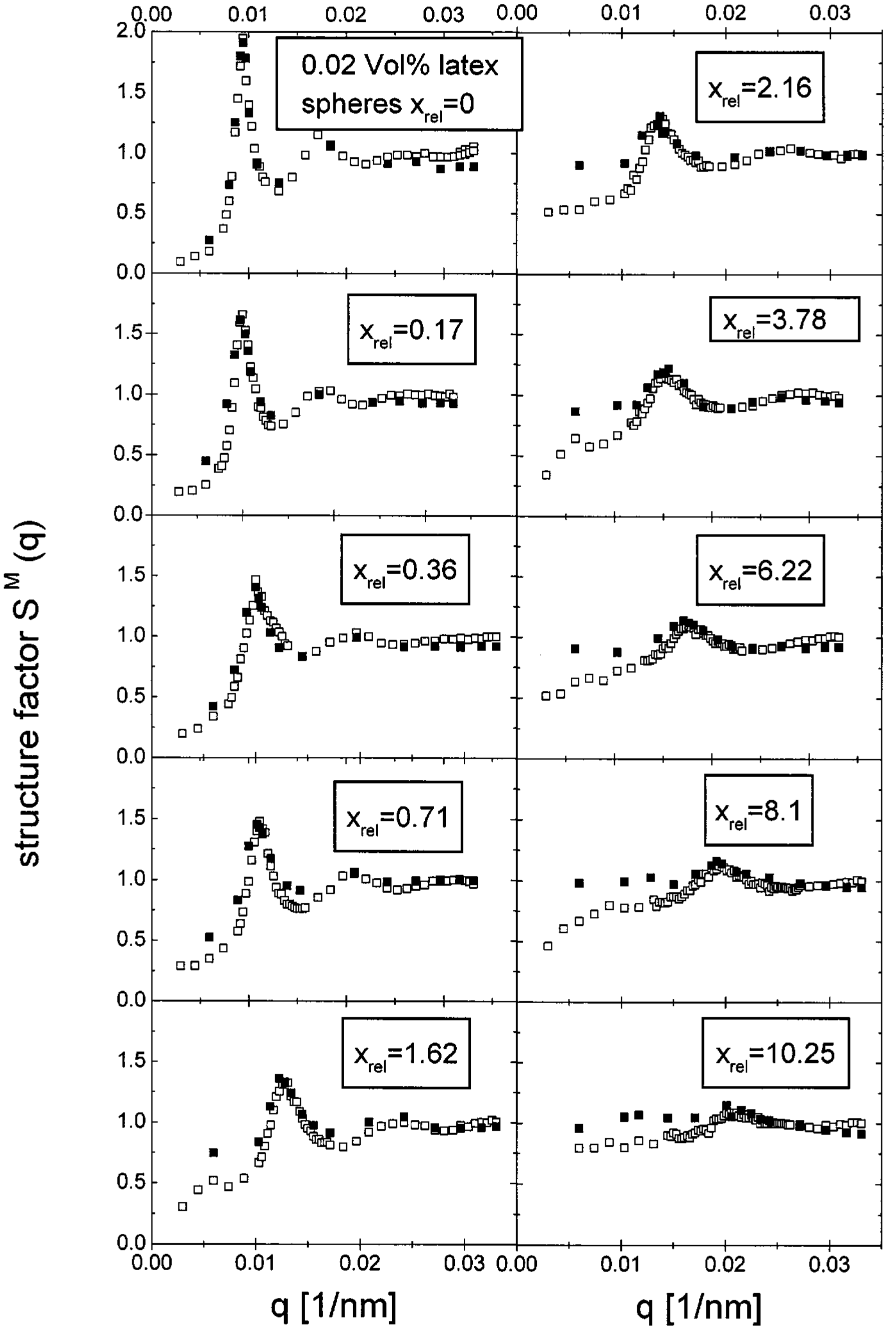

Fig. 6. Measured static structure factor (□) of mixtures of 0.02 Vol% latex spheres and NaPSS-particles (molecular weight MW = 744 kg/mol) together with dynamically obtained structure factor; ($x_{\text{rel}} = 0-10.25$).

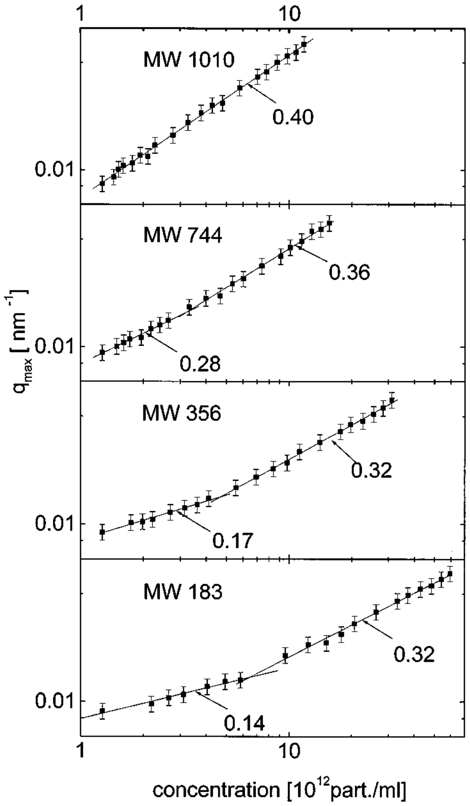

Fig. 7. Wavenumber of the first maximum of the measured static structure factor *versus* total particle concentration, $c_{\rm sph} = 1.27 \times 10^{12}$ part./ml, $\varnothing = 67$ nm.

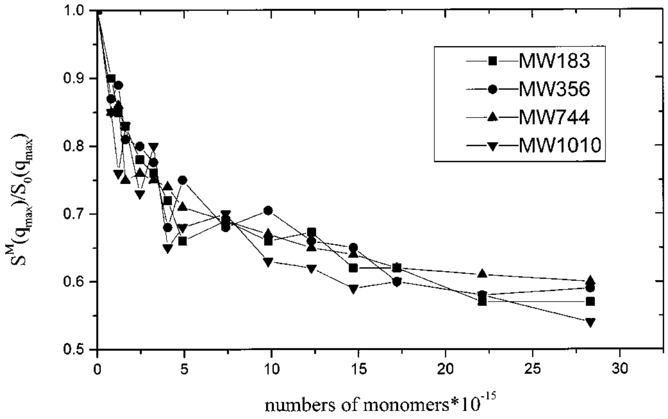

Fig. 8. Relative height of first peak of measured static structure factor of latex/NaPSS-mixtures *versus* numbers of monomers (The maximum of structure factor of pure latex-sample is denoted by $S_0(q_{\rm max})$.

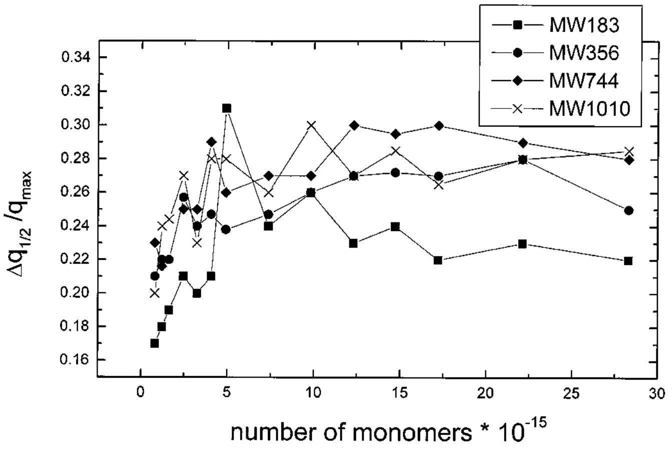

Fig. 9. Relative halfwidth of first peak of measured static structure factor of latex/NaPSS-mixtures *versus* numbers of monomers.

In Figure 9 the relative halfwidths are plotted. The values for MW183 range typically 10% below the others. At small concentrations below $c_{\rm crit}$ a strong increase of $\Delta q_{1/2}/q_{\rm max}$ is observed which becomes essentially constant at larger $c_{\rm mono}$. It remains constant as a function of total concentration which means that the correlation length scales as $q_{\rm max}$. No peculiarity exists at $c_{\rm crit}$ besides a weak maximum for MW183. This was observed in two independently prepared series, but was not found in the concentration dependence of the series with doubled concentration of spheres.

There is one quantity that has not yet included in the discussion so far, namely the charge of the particles. Since the four MW's used in the experiments differ by a factor of 5.5, the corresponding charges will also vary considerably. For pure Na(H)PSS aqueous solutions a so-called conductivity charge can be derived from the measured conductivity. For each MW they are listed in Table 1. The corresponding charge of latex spheres ranges at about $350e^-$. Therefore, using these values for the mixtures too, the charge of the flexible ions at the highest MW are larger and at the lowest MW are smaller than that of the spheres. It might be possible that short flexible particles with low charge will indeed displace surrounding spheres slightly (see the broadening of the $S^{\rm M}(q)$), but they are not yet built in "regularly" to yield a new "ordered" first neighbour shell of a given sphere, because the electrostatic interaction is too small. When the concentration of the added macroions increases more and more, the distance between the spheres and the flexible polyions becomes smaller and at a certain concentration the interaction will be strong enough to rearrange the spheres and chains.

It has been mentioned in the introduction that adsorption of flexible macroparticles onto spheres or bridging takes place in some cases. Adsorption is unlikely here since the particles bear charges of the same sign. Also, above $c_{\rm crit}$ $q_{\rm max}$ is proportional to $c_{\rm total}^{1/3}$, which means that in this regime there is no adsorption. Bridging between spheres below $c_{\rm crit}$ can be excluded at least for the two smallest MW's, because the distance between neighbouring spheres on an average is longer than the contour length. To underline the argumentation we have plotted in Figure 10 the short time self diffusion coefficient of the spheres. This quantity can be obtained by dynamic measurements at wavenumbers above $q_{\rm max}$, where $S^{\rm M}(q) \approx S_{\rm sph}(q) = 1$. Our intention was to check whether the diffusion

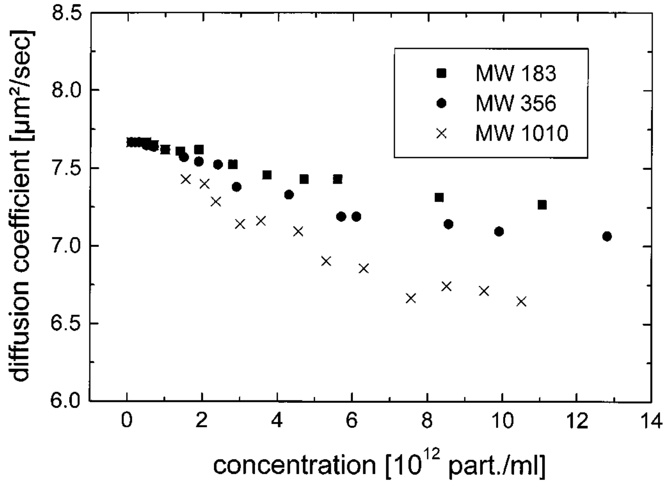

Fig. 10. Short time diffusion coefficient of latex/Na(H)PSS-mixtures of three MW's as function of particle concentration.

coefficient below and above c_{crit} respectively show marked differences which could be an indication of aggregation of the flexible polyions onto the spheres. No such effect has been observed.

Finally we turn to the short time dynamics. Measurements of the time autocorrelation function have again been performed in the same concentration regime that has been covered by the static measurements. The number of q-values at which data have been taken were somewhat reduced. The first cumulant was determined and put into equation (29), adjusted for the present system. In general, it is not possible to calculate the "measured structure factor" since the averaged form factor and the diffusion coefficient $D^{0,\mathrm{eff}}_{\mathrm{mixt}}$ are not known. However, because of the very small scattering amplitude of Na(H)PSS, contributions from the flexible polyions to it are negligible. In Figure 6 an example (MW 744 kg/mol) of the dynamically determined structure factor is compared with the measured static structure factor. To avoid any uncertainties in $D^{0,\mathrm{eff}}_{\mathrm{mixt}}$ the dynamically determined $S^{\mathrm{M}}_{\mathrm{d}}(q)$ adjusted to $S^{\mathrm{M}}(q)$ at q_{max}. In this way in most of the cases fair agreement is obtained around the first peak and at wavenumbers above. Small deviations occur in the way that the structure in $S^{\mathrm{M}}_{\mathrm{d}}(q)$ above the peak position for larger c is washed out faster with increasing Na(H)PSS concentration than in $S^{\mathrm{M}}(q)$. This phenomenon is known from bidisperse mixtures of spheres [7].

At small q's the situation is in principle similar as for mixtures with rodlike particles. With increasing concentration of Na(H)PSS the dynamically obtained structure factor $S_{\mathrm{d}}(q)$ increase stronger than the measured structure factor. Comparing the results of the latex-fd-mixtures with those of latex-Na(H)PSS mixtures with the latter having the same contour length as fd similar deviations are found. Comparing the deviations amongst the four MW series, they scale rather with monomer concentration than with particle number. Taking into account hydrodynamic interaction might again improve the agreement between static and dynamic results.

5 Summary

This work resumes on light scattering results on saltfree aqueous solutions of two component mixtures of spherical and anisometric particles. In a first step rodlike particles have been added to latex spheres. In the second part of the paper, the stiffness of the rods has been dropped. Fd-virus and NaPSS-particles meet these conditions. In aqueous solution all particles are highly charged. Therefore configurations with nearest neighbour ordering exist in which the two sorts of particles contribute; their positions are correlated with each other. On a microscopic scale the two sorts of particles are inhomogeneously mixed. The mean distance between any two particles is determined by the total number of particles. A sensitive measure of the new arrangements of the spheres is the measured static structure factor $S^{\mathrm{M}}(q)$. With inceasing concentration of anisometric particles the maximum of $S^{\mathrm{M}}(q)$ scales like $q_{\mathrm{max}} \propto c^{\alpha}_{\mathrm{total}}$. The magnitude of α depends on the shape of the anisometric particles. Only for globular macromolecules α is 1/3. The latter is observed for Na(H)PSS chains of MW $\leq$ 800 kg/mol above a critical concentration. Below c_{crit} a smaller exponent than 1/3 is found for these MW's. Tentatively this effect is associated with the small charge of these macromolecules, which is not sufficient for a rearrangement of spheres. The strong decrease of the measured static structure factor with added particle number reflects the loss of correlation of the spheres. The short time dynamics reflects essentially the structural properties of the systems. At small wavenumbers below the first peak discrepancy of the dynamically determined and the measured structure factor occur. The deviations are of similar magnitude for latex-fd and latex-Na(H)PSS. Hydrodynamic interaction, which was not taken into account, might be one reason for the differences.

More measurements are necessary to clarify the concentration dependence of q_{max} below the critical concentration. One way to do this are light scattering experiments with mixtures of latex spheres and Na(H)PSS particles whose sulfonation is reduced. Such experiments could no longer be performed because of retirement of one of us (R.W.).

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