

Rheology of thermosensitive latex particles including the high-frequency limit

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Synopsis

The flow properties of aqueous suspensions of thermosensitive latex particles are investigated as a function of volume fraction and temperature. The particles consist of a solid poly(styrene) core and a shell composed of crosslinked poly(N-isopropylacrylamide) (PNIPA) chains. The PNIPA network shrinks with increasing temperature leading to a denser layer of polymeric chains on the surface of the core particles. The shear viscosity obtained from suspensions of these particles at low shear is compared to the viscosity measured in the high-frequency limit. In the limit of dilute suspensions the viscosity is modeled in terms of an effective hydrodynamic radius R_H . It is shown that R_H of highly swollen particles depends markedly on frequency. The data indicate that the swollen network on the surface of the particles is partially drained at high frequencies. For shrunken networks R_H measured in the low and high frequency limit coincides again. The high frequency shear modulus G'_∞ measured at high volume fractions demonstrates that the thermosensitive particles may be regarded as soft spheres. The repulsive interaction may be modeled in terms of a power law with an exponent of 9. © 2001 The Society of Rheology. [DOI: 10.1122/1.1357820]

I. INTRODUCTION

Suspensions composed of colloidal polymer particles play an important role in many technical applications, as e.g., in paints or paper production [Distler, (2000)]. The rheological behavior of these dispersions is relevant when processing these materials. Hence, a number of studies have been conducted that aim at a basic understanding of the flow properties of dispersions [Mellema (1997)]. In many cases the colloidal stability of the suspension is effected through linear or cross-linked polymers attached to the surface of the particles [Russel *et al.* (1989)]. The steric stabilization thus effected may be adjusted within a wide range by changing the grafting density and the thermodynamic interaction of the chains with the surrounding fluid in which the particles are embedded.

The influence of the polymeric layer on the viscosity of the dispersion can be modeled in terms of an appropriate increase Δ of the particle radius a . This is followed by a concomitant increase of the effective volume fraction ϕ_{eff} of the particle defined through

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$$\phi_{\text{eff}} = \phi_c \left(1 + \frac{\Delta}{a}\right)^3 = \phi_c k, \quad (1)$$

where ϕ_c denotes the volume fraction of the uncovered particles. The effective volume fraction of sterically stabilized particles may be determined from the relative zero-shear viscosity η_0/η_s by use of the expression of Batchelor (1977) [Brady and Vicic (1995)]

$$\frac{\eta_0}{\eta_s} = 1 + 2.5\phi_{\text{eff}} + 5.9\phi_{\text{eff}}^2, \quad (2)$$

where η_s denotes the viscosity of the solvent. If no draining of the surface layer takes place the magnitude of Δ thus determined coincides with the radial expansion of the shell. In this case the particles behave as hard spheres with an outer radius given by $a + \Delta$. If, on the other hand, the surface layer is partially drained, Δ will be decreased and the effective volume fraction will be lowered accordingly. The extension to which the surface layer will be drained is therefore highly important for a quantitative understanding of the flow behavior of sterically stabilized suspensions.

Sterically stabilized particles that may be used to investigate the above problem can be obtained through adsorption of nonionic surfactants on narrowly distributed latex particles [Raynaud *et al.* (1996)]. A recent study of η_0/η_s of particles obtained in this way has demonstrated that Δ and the maximum extension of a thin steric layer determined by small-angle x-ray scattering agree in good approximation [Weiss *et al.* (1998)]. In the limit of high frequencies, however, partial draining of the surface layer must be taken into account. Elliott and Russel (1998) have discussed the partial draining of polymer layers in terms of a hydrodynamic screening length ξ . These authors presented explicit calculations of the high-frequency viscosity η'_∞/η_s as a function of ϕ_{eff} for several ratios of Δ/ξ . Their prediction agrees qualitatively with recent experimental results of η'_∞/η_s measured by Weiss *et al.* (1999) by use of a torsional resonator [Bergenholtz *et al.* (1998a)]. No systematic study on the partial draining of steric layers attached to colloidal particles is available yet, however.

Here we present a study of this problem by comparing of η'_∞/η_s to η_0/η_s for a suitable model dispersion. The particles used in these measurements consist of narrowly distributed poly(styrene) (PS) particles onto which cross-linked poly(N-isopropylacrylamide) (PNIPA) chains are attached. The dispersion medium water is a good solvent for PNIPA chains at ambient temperature but becomes a poor solvent at temperatures above 35 °C. As a consequence of this, the network attached to the surface of the particles undergoes a volume transition around 32 °C similar to the volume transition of macroscopic networks [Shibayama and Tanaka (1993)]: At low temperature the network on the surface is highly swollen by the dispersion medium water and the extension of the surface layer attains its maximum. Raising the temperature leads to a gradual shrinking of the surface layer and a concomitant raise of the volume fraction of the polymer in the layer. In this way both the swollen and the shrunken state can be attained for a single given system. Hence, measuring η_0/η_s and η'_∞/η_s of a thermosensitive latex at different temperatures may give quantitative information on the degree of draining at different polymer densities on the surface of the particle.

The particles studied here have been prepared in a two-step process [Dingenouts *et al.* (1998)]: In the first stage PS particles with a thin PNIPA shell were made by a batch emulsion polymerization. The PS cores thus obtained are slightly negatively charged, which ensures colloidal stability even at elevated temperature when the collapsed net-

work does not provide sufficient steric stabilization anymore. In a second step these particles were covered by a shell of PNIPA chains cross-linked by N,N'-methylene bisacrylamide (BIS). The radial structure of the resulting thermosensitive particles has been studied in great detail by small-angle x-ray scattering (SAXS) [Dingenouts *et al.* (1998), Seelenmeyer *et al.* (2001)] and by small-angle neutron scattering [Seelenmeyer *et al.* (2001)]. These investigations demonstrated that the shell consisting of the PNIPA network is rather homogeneous. Furthermore, SAXS together with transmission electron microscopy demonstrated that the size distribution of the particles is narrow and effects of polydispersity can be neglected in good approximation.

Recently, a first study of suspensions of similar thermosensitive particles has been presented by Senff *et al.* (1999). Here the rheological properties of the suspensions have been measured over a wide range of concentrations and temperatures as function of shear rate. The results obtained from these measurements agree with data derived previously by dynamic light scattering [Dingenouts *et al.* (1998)]. At sufficiently high effective volume fractions ($\phi_{\text{eff}} \geq 0.6$) the suspensions became viscoelastic as expected. All results obtained in this study agree qualitatively with data obtained by Senff and Richtering (1999) for suspensions of spherical PNIPA microgels.

Previous measurements [Senff *et al.* (1999)] gave clear indication for the onset of attractive interaction between the core–shell particles. The viscosity data for temperatures above the volume transition did not fall on a master curve when plotted against the effective volume fraction ϕ_{eff} [see the discussion of Fig. 5 in Senff *et al.* (1999)]. In this regime η_0/η_s increased more rapidly as a function of ϕ_{eff} as compared to below the transition. No derivation from the master curve was seen in the limit of high shear, however [cf. Fig. 6 in Senff *et al.* (1999)]. As discussed above water becomes a poor solvent above the temperature of the transition, which impedes the steric stabilization of the particles. Hence, flocculation may occur under these conditions as observed for homogeneous PNIPA particles indeed [Senff and Richtering, (1999)]. Attractive interaction is therefore to be expected at higher temperatures and their influence must be discussed in detail [see Rueb and Zukoski (1998)].

Here these studies are extended to include the high-frequency viscosity and shear modulus of suspensions of thermosensitive core–shell particles. All measurements are done by the use of a torsional resonator. Recently, this device has been introduced to measure η'_∞ and the high-frequency modulus G'_∞ of electrostatically stabilized latexes [Bergenholtz *et al.* (1998a, 1998b)]. These workers demonstrated that the measuring frequency ω (8.9 kHz) is high enough so that the limiting values η'_∞ and G'_∞ are obtained. This is the case if the time scale of diffusive motion of the latex particles is long as compared to the frequency of the measurements. Therefore $\omega/2\pi \gg D_S^S/a^2$, where D_S^S denotes the short-time self-diffusion coefficient. For the system under consideration here the minimum frequency can be estimated to be ~ 0.5 kHz at most, which is far below the measuring frequency of 8.9 kHz. The torsional resonance device hence probes the high-frequency limits of the storage and the loss modulus G'_∞ and G''_∞ , respectively.

II. EXPERIMENT

A. Materials

The core–shell latex used in this study was prepared as described recently [Dingenouts *et al.* (1998), Seelenmeyer *et al.* (2001)]. The core particles had a diameter of 114 nm as determined by dynamic light scattering. The crosslinking was achieved by 2.5 mol % N, N'-methylene BIS with regard to NIPA. The latex was purified by repeated

centrifugation and redispersion in 0.0025 M KCl solution. Possible traces of free PNIPA in the serum are removed by this procedure. The maximum weight concentration of the purified latex was 30 wt %.

B. Methods

The analysis of the size distribution was done by use of a Brookhaven DCP disk centrifuge. The ratio of the weight-average diameter d_w to the number-average diameter d_n was found to be 1.03, which was corroborated by transmission electron microscopy. The latex crystallizes at an effective volume fraction of ~ 0.53 which provides further proof of the narrow size distribution.

Dynamic light scattering (DLS) was done using a Peters ALV 4000 light scattering goniometer. Zero-shear viscosities of dilute suspensions were determined using an Ubbelohde viscometer. All measurements have been done with strict control of the temperature ($\pm 0.2^\circ\text{C}$).

C. Torsional resonator

All measurements have been done using a torsional resonator (Rheoswing, Physica) described recently [Bergenholtz *et al.* (1998a)]. The device consists of a rod oscillating (resonance frequency in air: 8.9 kHz) in the dispersion. The shear wave penetrates into the dispersion up to $\sim 50 \mu\text{m}$. This ensures that the method probes the viscoelastic properties of the bulk phase. The measuring cell, however, is much larger than this penetration depth and no disturbance may result from the walls of the container. The small amplitudes of the torsion of the cylinder ($\sim 50 \text{ nm}$) ensure that the maximum strain is small. The measurements are hence taken in the linear viscoelastic regime.

The damping of the motion of the rod is due to the impedance Z of the liquid in which the rod is immersed. Therefore the resonance curve is broadened about $\Delta\omega$ and the resonance frequency ω_0 is lowered compared to a measurement in air. The real and the imaginary parts of the liquid impedance $Z = R + iX$ are related to the damping and the frequency shift, respectively,

$$\begin{aligned} R &= K_1(\Delta\omega - \Delta\omega_{\text{air}}), \\ X &= K_2(\omega_{0,\text{air}} - \omega_0), \end{aligned} \quad (3)$$

with K_1 and K_2 being calibration constants. A series of Newtonian liquids, covering the viscosity range $1 < \eta < 80 \text{ mPa s}$, were used to calibrate the resonator. The constants of Eq. (3) result in $K_1 = 71.65 \text{ kg/m}^2$ and $K_2 = 127.06 \text{ kg/m}^2$ at all temperatures. The radius of the rod (6 mm) is much greater than the penetration depth of the shear wave. Hence, the plane wave approximation applies and R and X may directly be converted into the shear and the loss modulus of the liquid:

$$\begin{aligned} G' &= (R^2 - X^2)/\rho, \\ G'' &= \eta_\infty \omega = 2RX/\rho. \end{aligned} \quad (4)$$

The torsional resonance device requires 25 mL latex. Thermal equilibrium was therefore reached only after 60 min and the temperature range is restricted to $20\text{--}35^\circ\text{C}$ ($\pm 0.5^\circ\text{C}$).

III. RESULTS AND DISCUSSION

The present study aims at a quantitative comparison of the layer thickness Δ obtained at different frequencies. This quantity can be done in two ways: In the highly dilute

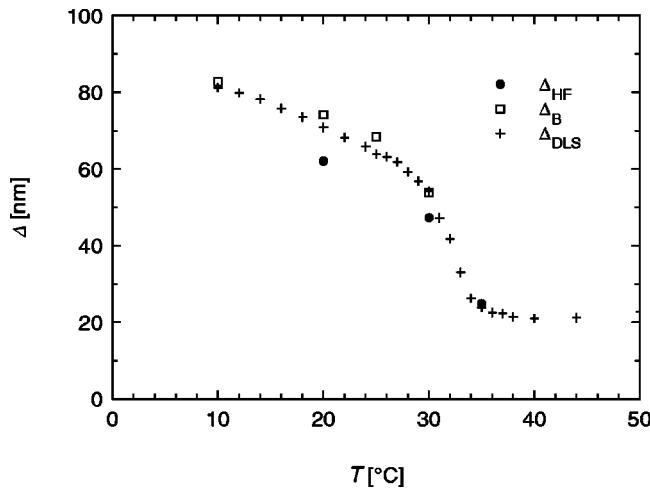


FIG. 1. Thickness Δ of the surface layer of the particles as measured as function of temperature by different techniques: (crosses) data of Δ_{DLS} determined by dynamic light scattering; (hollow squares) thickness Δ_B derived from the effective volume fraction ϕ_{eff} deduced by fits of Eq. (2) to experimental data (see discussion of Fig. 2); (filled circles) high-frequency limit Δ_{HF} deduced from fits of Eq. (6) to the data displayed in Fig. 3(a).

regime DLS allows us to determine the hydrodynamic radius R_H and hence the thickness termed Δ_{DLS} with high accuracy. Possible attractive interaction between the spheres will play no role because of the exceedingly low concentrations. Measurements of the relative zero-shear viscosity, on the other hand, will take place at concentrations of a few percent and the thickness Δ_B deduced from these measurements via Eq. (2) need not necessarily coincide with Δ_{DLS} .

The crosses in Fig. 1 display the variation of Δ_{DLS} with temperature that is typical for the core-shell particles under consideration here [see Kim and Ballauff (1999)]: The network affixed to the surface of the core particles shrinks in a continuous fashion and the temperature of the volume transition is located at ~ 33 °C. The volume transition is fully reversible and the same values of Δ_{DLS} are obtained upon cooling. DLS measurements are hence ideally suited to localize the transition temperature with high accuracy.

Figure 2(a) displays the relative zero-shear viscosity of the thermosensitive latex measured at different temperatures in the dilute regime. Here it can safely be assumed that the dilute suspensions exhibit a Newtonian flow despite the fact that the average shear rates in the Ubbelohde viscosimeters are $500\text{--}1000$ s $^{-1}$. This is borne out directly on the rheological data obtained by Senff *et al.* (1999) on a very similar system.

At first we discuss η_0/η_s measured for swollen particles, which are obtained below the temperature of the volume transition. The solid lines in Fig. 2(a) display the fits according to Eq. (2) for $T \leq 30$ °C. It is apparent that Δ_B can be derived from these data without problems. Table I gathers Δ_B obtained for different temperatures. A comparison of the layer thickness Δ_B with Δ_{DLS} is shown in Fig. 1. For temperatures below the transition there is quantitative agreement within the limits of error despite the fact that both sets of data derive from widely different concentration regimes. The good agreement of Δ_B and Δ_{DLS} therefore indicates that no disturbance of the radial structure of the particles is induced in the concentration regime in which Δ_B has been determined. Moreover, the good fits according to Eq. (2) demonstrate that repulsive interaction prevails and there is no indication of a strong attraction between the spheres.

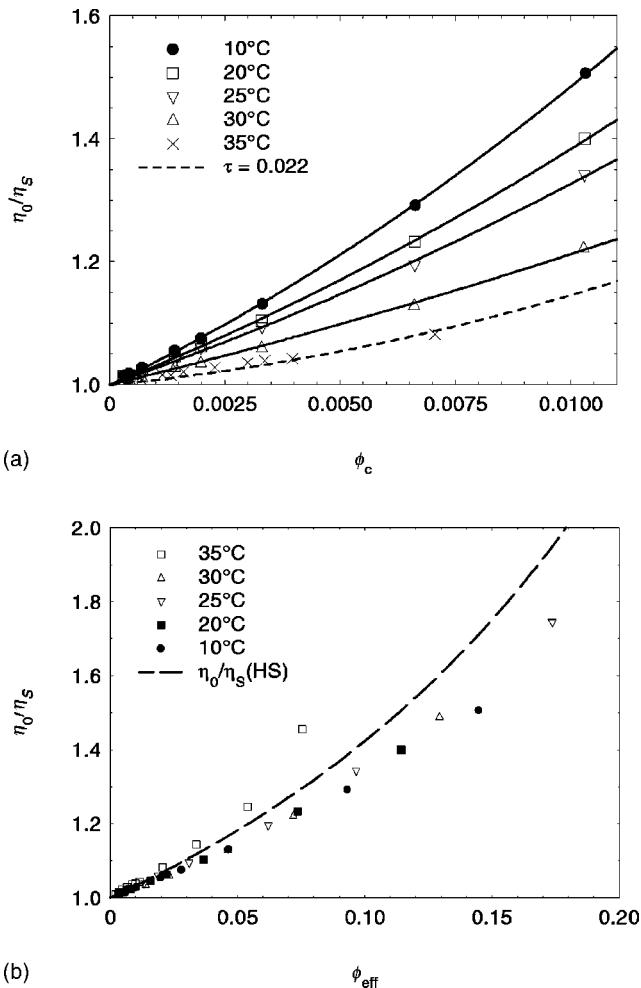


FIG. 2. Analysis of the relative viscosity obtained in the zero-shear limit. (a) Relative zero-shear viscosity η_0/η_s vs the volume fraction ϕ_c of the cores. The measurements have been done at five different temperatures indicated in the graph. The solid lines display the fit of Eq. (2) to the experimental data in order to obtain the effective volume fraction ϕ_{eff} valid at zero frequency. The dashed line gives the fit of the data taken above the volume transition by Eq. (5). (b) Reduced zero-shear viscosity η_0/η_s vs the effective volume fraction ϕ_{eff} . The dashed lines denotes the mastercurve obtained by Meeker *et al.* (1997) for suspensions of hard spheres.

The layer thickness Δ_{DLS} may now serve for the calculation of the effective volume fraction ϕ_{eff} as defined by Eq. (1). Figure 2(b) shows that plotting the relative viscosity against ϕ_{eff} thus determined leads to a master curve for data obtained below the transition. The dashed line displays η_0/η_s for a suspension of hard spheres as established by Meeker *et al.* (1997). The relative viscosity of the composite particles η_0/η_s is significantly smaller than expected for hard spheres at the same ϕ_{eff} . This points to a certain softness of the repulsive interaction that will be discussed further below. For temperatures above the volume transition, i.e., at 35 °C, Fig. 2(b) demonstrates that these data do not lie anymore on the master curve defined by η_0/η_s versus ϕ_{eff} obtained below the transition. The respective Δ_B deduced by application of Eq. (2) to the relative viscosity would in consequence lead to a value much higher than Δ_{DLS} . As reasoned above this

TABLE I. Thickness of polymer layer as determined by different methods.

T/°C	Δ_B/nm^a	$\Delta_{\text{DLS}}/\text{nm}^b$	$\Delta_{\text{HF}}/\text{nm}^c$
10	83	81	-
20	74	71	62
25	68	64	-
30	54	53	47
35	-	24	25

^a Δ_B : thickness of layer determined from fits of Eq. (2) to η_0/η_s measured in dilute suspensions (see Fig. 2).

^b Δ_{DLS} : thickness of layer as determined from the hydrodynamic radius measured by dynamic light scattering (see Fig. 1).

^c Δ_{HF} : thickness of layer determined from fits of Eq. (6) to η'_∞/η_s measured in dilute suspensions [see Fig. 3(a)].

finding may be traced back to the onset of weak attraction between the particles operative above the volume transition. This conjecture is corroborated by a comparison with rheological data obtained for weakly attractive particles [Rueb and Zukoski (1998)]. Moreover, the dashed line in Fig. 2(a) displays a fit with the expression of Baxter (1968) derived for a system of sticky spheres [Cichocki and Felderhof (1990), Rueb and Zukoski (1998)]:

$$\frac{\eta_0}{\eta_s} = 1 + 2.5\phi_{\text{eff}} + \left(5.9 + \frac{1.9}{\tau}\right)\phi_{\text{eff}}^2. \quad (5)$$

Here the parameter τ provides a measure of the attractive forces between the particles. The data taken at 35 °C [crosses in Fig. 2(a)] may be satisfactorily described by Eq. (5) if the effective volume fraction ϕ_{eff} is calculated from Δ_{DLS} , i.e., using the hydrodynamic radius that has been determined at very small concentrations [dashed line in Fig. 2(a)]. The resulting $\tau = 0.022$ indicates at 35 °C a maximum attraction on the order of a few kT . The weak attraction is also evident from a slow coagulation of the latex at temperatures above 32 °C and concentrations above ~ 10 wt %. Given the weakness of the attractive interaction, possible disturbances of the rheological measurements come only into play at highest temperatures (35 °C) and the highest concentrations. They are directly evident from a drift of the readout of the torsional resonator with time.

Figure 3(a) gives the relative high-frequency viscosities η'_∞/η_s as a function of the core volume fraction. Here the strong variation with temperature becomes directly obvious. In order to evaluate the appropriate effective volume fractions for the high-frequency limit we use the expression given by Lionberger and Russel (1994) for suspensions of hard spheres:

$$\frac{\eta'_\infty}{\eta_s} = \frac{1 + 1.5\phi_{\text{eff}}(1 + \phi_{\text{eff}} - 0.189\phi_{\text{eff}}^2)}{1 - \phi_{\text{eff}}(1 + \phi_{\text{eff}} - 0.189\phi_{\text{eff}}^2)}. \quad (6)$$

The dashed lines in Fig. 3(a) display the corresponding fits of Eq. (6) to the measured data, which are described by theory in a satisfactory manner. From the effective volume fractions thus obtained and the core radius a the layer thickness Δ_{HF} as a function of temperature can be deduced by fitting the data up to $\phi_{\text{eff}} = 0.5$. Table I gathers the respective data.

Figure 3(b) demonstrates the influence of partial draining onto Δ_{HF} at 20 °C: The lower solid curve displays η'_∞/η_s calculated for a suspension of hard spheres having the

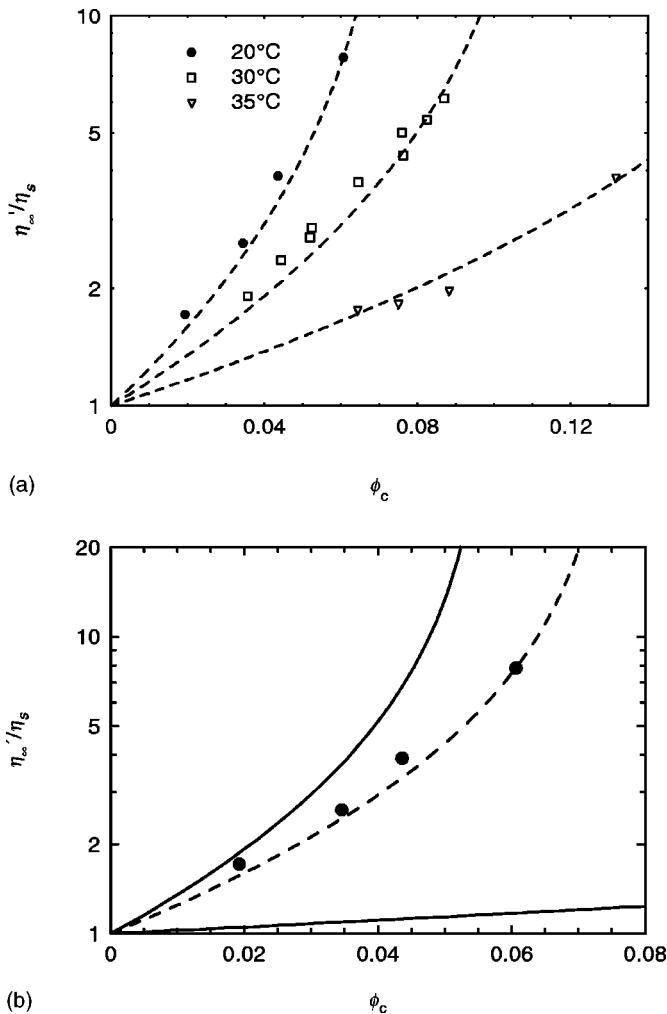


FIG. 3. Relative high-frequency viscosities η'_0/η_s as function of ϕ_c , the volume fraction of the core particles. (a) Measurements done at three different temperatures indicated in the graph. The dashed lines display the fits of Eq. (6) to the data in order to obtain the effective volume fraction of the particles in the high-frequency limit. (b) Data obtained at 20 °C together with the relative high-frequency viscosity calculated according to Eq. (6) for a system of hard spheres having the radius a of the core particles (lower curve) and the radius $a + \Delta_{DLS}$, i.e., the hydrodynamic radius effective at zero frequency.

radius a of the cores, whereas the upper solid line gives η'_0/η_s for hard spheres with radius $a + \Delta_{DLS}$. The latter curve therefore refers to the low-frequency limit discussed in conjunction with Figs. 1 and 2. It is obvious that Δ_{HF} is smaller than the low-frequency limits Δ_B and Δ_{DLS} . This points directly to a finite draining of the surface layer.

The filled circles in Fig. 1 give the entire set of Δ_{HF} as a function of temperature. The data deduced for 20 and 30 °C lie significantly lower than the Δ values deduced for the zero-frequency limit. Only at 35 °C do Δ_{HF} and Δ_{DLS} coincide within the limits of error. For the latter temperature the shell of the spheres has undergone the volume transition and the network has been shrunken considerably. Hence, in this rather dense state the residual solvent water within the network is immobilized and the nondraining limit is reached. If the particles are cooled down below the volume transition, the network swells

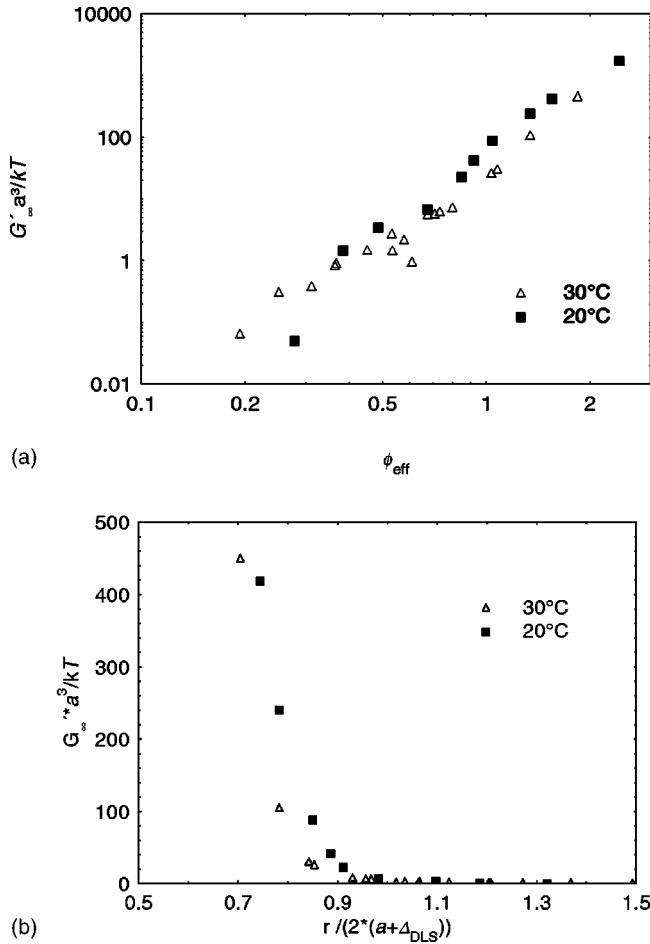


FIG. 4. (a) Relative high-frequency shear modulus $G'_\infty a^3/kT$ as function of the effective volume fraction ϕ_{eff} . (b) Same data but as a function of the average distance r between the particles as defined through Eq. (9).

again. Here the solvent within the network is immobilized only in the zero-frequency limit (cf. the discussion of Fig. 1) but considerable draining takes place at high frequencies. The present data therefore point to a direct connection between the volume fraction of the polymer in the surface layer of the particles and the degree of draining.

The above discussion rests on the comparison of η'_∞/η_s with η_0/η_s taken below and above the volume transition of the particles. Here the question arises as to what extent the measurements of η'_∞/η_s are disturbed by the weak attraction between the particles that have been deduced from a discussion of η_0/η_s (see the discussion of Fig. 2). Data taken from a similar system by Senff *et al.* (1999) had indicated that there is no influence of attraction when going to high shear rates. The same should hold true for the high-frequency limit under consideration here as already shown by Horn *et al.* (2000) for other systems. From these arguments it is evident that attractive interaction between the particles may be disregarded when going to the limit of high frequencies and the above comparison of Δ obtained by various methods is valid.

The analysis of the latex by the torsional resonance oscillation also gives G'_∞ as a function of ϕ_{eff} at different temperatures. Figure 4 gives the respective data scaled by

a^3/kT to ensure better comparison with the literature [Elliott and Russel (1998), Weiss *et al.* (1999)]. Only the data obtained for 20 and 30 °C are given. Data taken at 35 °C did not lead to meaningful values of G'_∞ because the concentrations necessary to see significant viscoelasticity were too high and slow flocculation occurred under these conditions. We reiterate that η'_∞/η_s could well be measured under these conditions since these measurements could be done at much lower concentrations.

The modulus G'_∞ decreased with temperature as expected and a master curve was obtained when $G'_\infty a^3/kT$ is plotted versus the effective volume fraction ϕ_{eff} [see Fig. 4(a)]. Obviously, a power law $G'_\infty \propto \phi_{\text{eff}}^m$ with $m \approx 4$ is found. The quantitative evaluation of these data can be done as follows: First of all, G'_∞ is obtained in a frequency range in which the mobility of the particles was so small that no significant diffusion was possible within an oscillatory cycle. On the other hand, the employed frequencies were too small in order to probe internal dynamics of the crosslinked polymer shell. Therefore the elastic modulus is related to the interaction potential and can be described as [Zwanzig and Mountain, 1965]

$$G'_\infty = NkT + \frac{2\pi}{15}N^2 \int_0^\infty g(r) \frac{d}{dr} \left(r^4 \frac{dU(r)}{dr} \right) dr. \quad (7)$$

Here N is the particle number density, k the Boltzmann constant, $g(r)$ the radial distribution function with r the center–center separation, and $U(r)$ the pair interaction potential. If a lattice-like microstructure is assumed G'_∞ can directly be related to the second derivative of $U(r)$ [Buscall *et al.* (1982)]

$$G'_\infty \propto \frac{1}{r} \left(\frac{\partial^2 U}{\partial r^2} \right). \quad (8)$$

The average distance r between the particles can be related to the volume fraction at closed packing as [Paulin *et al.* (1996)]

$$r^3 = (2a)^3 \frac{\phi_{\text{eff,max}}}{\phi_{\text{eff}}}, \quad (9)$$

where $\phi_{\text{eff,max}}$ denotes the maximum packing fraction set to 0.64. The effect of swelling on the modulus is canceled out when the effective volume fraction is used which is a temperature-dependent quantity. This is observed indeed as evident from Fig. 4(a). Figure 4(a) clearly demonstrates, however, that it is a small but finite elasticity of the suspension even at volume fractions ϕ_{eff} below 0.6. This is a clear indication of hydrodynamic interaction as discussed previously by Wagner (1993). Figure 4(b), however, shows that a strong raise of the modulus occurs only if the average distance r [Eq. (9)] is smaller than the hydrodynamic diameter of the spheres measured at the given temperature, that is, when the particles start to touch each other.

For high volume fractions, however, Eqs. (7)–(9) may be used to study the details of the repulsion between the particles. Paulin *et al.* (1996) have modeled the particle potential $U(r)$ as a power law $U(r) \propto r^{-n}$. This leads to the observed power law dependence of G'_∞ on ϕ_{eff} . The exponent m is related to n as $m = 1 + n/3$ and the data displayed in Fig. 4(a) lead to $n \approx 9$. This result indicates the finite softness of the particles under consideration here. Similar findings have been reported recently for related systems [Senff *et al.* (1999), Senff and Richtering (2000)].

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