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 $G'_{\infty}$ 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 $\Delta$ of the particle radius $a$. This is followed by a concomitant increase of the effective volume fraction $\phi_{\text{eff}}$ of the particle defined through

$\phi_{\text{eff}} = \phi + \frac{2\Delta a^2}{2a^2 - \Delta a^2}$

where $\phi$ is the volume fraction of the bulk suspension.

$\Delta a$ is the increase in radius due to the polymer layer.

$\phi_{\text{eff}}$ is the effective volume fraction, which includes the polymer layer.

$\phi$ is the volume fraction of the bulk suspension.

$2a^2 - \Delta a^2$ is the effective particle volume.

$\phi_{\text{eff}}$ is the effective volume fraction of the particle including the polymer layer.
where $\phi_c$ 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 $\eta_0 / \eta_s$ by use of the expression of Batchelor (1977) [Brady and Vicic (1995)]

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

where $\eta_s$ denotes the viscosity of the solvent. If no draining of the surface layer takes place the magnitude of $\Delta$ 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, $\Delta$ 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 $\eta_0 / \eta_s$ of particles obtained in this way has demonstrated that $\Delta$ 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 $\xi$. These authors presented explicit calculations of the high-frequency viscosity $\eta'_0 / \eta_s$ as a function of $\phi_{\text{eff}}$ for several ratios of $\Delta/\xi$. Their prediction agrees qualitatively with recent experimental results of $\eta'_0 / \eta_s$ measured by Weiss et al. (1999) by use of a torsional resonator [Bergenholtz et al. (1998)]. 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 $\eta'_0 / \eta_s$ to $\eta_0 / \eta_s$ 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 $\eta_0 / \eta_s$ and $\eta'_0 / \eta_s$ 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 (\( \phi_{\text{eff}} \gg 0.6 \)) 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 \( \phi_{\text{eff}} \) [see the discussion of Fig. 5 in Senff et al. (1999)]. In this regime \( \eta_0 / \eta_s \) increased more rapidly as a function of \( \phi_{\text{eff}} \) 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, floculation 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 \( \eta'' \) and the high-frequency modulus \( G'' \) of electrostatically stabilized latexes [Bergenholtz et al. (1998a, 1998b)]. These workers demonstrated that the measuring frequency \( \omega \) (8.9 kHz) is high enough so that the limiting values \( \eta''_0 \) and \( G''_0 \) 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 \( \omega / 2 \pi \gg D_S^{\frac{1}{2}}/a^2 \), where \( D_S \) denotes the short-time self-diffusion coefficient. For the system under consideration here the minimum frequency can be estimated to be \( \sim 0.5 \) 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 \( G'_\infty \) and \( G''_\infty \), 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 \(\sim 0.53\) 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 (±0.2 °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 \(\omega_0\) 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,

\[
R = K_1(\Delta \omega - \Delta \omega_{\text{air}}),
\]

\[
X = K_2(\omega_0 - \omega_0),
\]

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:

\[
G' = (R^2 - X^2)/\rho,
\]

\[
G'' = \eta_0 \omega = 2RX/\rho.
\]

The torsional resonance device requires 25 mL latex. Thermal equilibrium was therefore reached only after 60 min and the temperature range is restricted to 20–35 °C (±0.5 °C).

III. RESULTS AND DISCUSSION

The present study aims at a quantitative comparison of the layer thickness \(\Delta\) obtained at different frequencies. This quantity can be done in two ways: In the highly dilute
regime DLS allows us to determine the hydrodynamic radius \( R_H \) and hence the thickness \( D \) 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 \( D_B \) deduced from these measurements via Eq. (2) need not necessarily coincide with \( D_{DLS} \).

The crosses in Fig. 1 display the variation of \( D_{DLS} \) 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 \( \sim 33 \) °C. The volume transition is fully reversible and the same values of \( D_{DLS} \) 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 500–1000 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 \( \eta_0 / \eta_s \) 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 \( \Delta_B \) can be derived from these data without problems. Table I gathers \( \Delta_B \) obtained for different temperatures. A comparison of the layer thickness \( \Delta_B \) with \( D_{DLS} \) 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 concentrations regimes. The good agreement of \( \Delta_B \) and \( D_{DLS} \) therefore indicates that no disturbance of the radial structure of the particles is induced in the concentration regime in which \( \Delta_B \) 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. 1. Thickness \( \Delta \) of the surface layer of the particles as measured as function of temperature by different techniques: (crosses) data of \( D_{DLS} \) determined by dynamic light scattering; (hollow squares) thickness \( D_B \) derived from the effective volume fraction \( \phi_{eff} \) deduced by fits of Eq. (2) to experimental data (see discussion of Fig. 2); (filled circles) high-frequency limit \( D_{HF} \) deduced from fits of Eq. (6) to the data displayed in Fig. 3(a).](image-url)
The layer thickness $\Delta_{\text{DLS}}$ may now serve for the calculation of the effective volume fraction $\phi_{\text{eff}}$ as defined by Eq. (1). Figure 2(b) shows that plotting the relative viscosity against $\phi_{\text{eff}}$ thus determined leads to a master curve for data obtained below the transition. The dashed line displays $\eta_0/\eta_s$ for a suspension of hard spheres as established by Meeker et al. (1997). The relative viscosity of the composite particles $\eta_0/\eta_s$ is significantly smaller than expected for hard spheres at the same $\phi_{\text{eff}}$. 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 $\eta_0/\eta_s$ versus $\phi_{\text{eff}}$ obtained below the transition. The respective $\Delta_B$ deduced by application of Eq. (2) to the relative viscosity would in consequence lead to a value much higher than $\Delta_{\text{DLS}}$. As reasoned above this
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 displays a fit with the expression of Baxter (1968) derived for a system of sticky spheres [Cichocki and Felderhof (1990), Rueb and Zukoski (1998)]:

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

Here the parameter $\tau$ 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 $\phi_{\text{eff}}$ is calculated from $\Delta_{\text{DLS}}$, 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 $\sim 10$ wt %.

Table I gathers the respective data.

<table>
<thead>
<tr>
<th>$T/°C$</th>
<th>$\Delta_B/\text{nm}^4$</th>
<th>$\Delta_{\text{DLS}}/\text{nm}^4$</th>
<th>$\Delta_{\text{HF}}/\text{nm}^4$</th>
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<td>10</td>
<td>83</td>
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$^a\Delta_B$: thickness of layer determined from fits of Eq. (2) to $\eta_0 / \eta_s$ measured in dilute suspensions (see Fig. 2).

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

$^c\Delta_{\text{HF}}$: thickness of layer determined from fits of Eq. (6) to $\eta_0 / \eta_s$ measured in dilute suspensions [see Fig. 3(a)].

Figure 3(a) gives the relative high-frequency viscosities $\eta_0 / \eta_s$ 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:

$$\frac{\eta'_c}{\eta_s} = \frac{1 + 1.5 \phi_{\text{eff}} (1 + \phi_{\text{eff}} - 0.189 \phi_{\text{eff}}^2)}{1 - \phi_{\text{eff}} (1 + \phi_{\text{eff}} - 0.189 \phi_{\text{eff}}^2)}.$$  (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 $\Delta_{\text{HF}}$ 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 $\Delta_{\text{HF}}$ at 20 °C: The lower solid curve displays $\eta'_c / \eta_s$ calculated for a suspension of hard spheres having the
radius $a$ of the cores, whereas the upper solid line gives $\eta'_s/\eta_s$ for hard spheres with radius $a + \Delta_{\text{DLS}}$. The latter curve therefore refers to the low-frequency limit discussed in conjunction with Figs. 1 and 2. It is obvious that $\Delta_{\text{HF}}$ is smaller than the low-frequency limits $\Delta_B$ and $\Delta_{\text{DLS}}$. This points directly to a finite draining of the surface layer.

The filled circles in Fig. 1 give the entire set of $\Delta_{\text{HF}}$ as a function of temperature. The data deduced for 20 and 30 °C lie significantly lower than the $\Delta$ values deduced for the zero-frequency limit. Only at 35 °C do $\Delta_{\text{HF}}$ and $\Delta_{\text{DLS}}$ 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.
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 $h' / h_s$ with $h_0 / h_s$ taken below and above the volume transition of the particles. Here the question arises as to what extent the measurements of $h' / h_s$ are disturbed by the weak attraction between the particles that have been deduced from a discussion of $\eta_0 / \eta_s$ (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 $\Delta$ obtained by various methods is valid.

The analysis of the latex by the torsional resonance oscillation also gives $G_0' \alpha^3 / kT$ as a function of $\phi_{eff}$ at different temperatures. Figure 4 gives the respective data scaled by

**FIG. 4.** (a) Relative high-frequency shear modulus $G_0' \alpha^3 / kT$ as function of the effective volume fraction $\phi_{eff}$. (b) Same data but as a function of the average distance $r$ between the particles as defined through Eq. (9).
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 $G'_s$ because the concentrations necessary to see significant viscoelasticity were too high and slow flocculation occurred under these conditions. We reiterate that $\eta'_s/\eta_s$ could well be measured under these conditions since these measurements could be done at much lower concentrations.

The modulus $G'_s$ decreased with temperature as expected and a master curve was obtained when $G'_s a^3/kT$ is plotted versus the effective volume fraction $\phi_{eff}$ [see Fig. 4(a)]. Obviously, a power law $G'_s \propto \phi_{eff}^m$ with $m \approx 4$ is found. The quantitative evaluation of these data can be done as follows: First of all, $G'_s$ 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]

$$G'_s = NkT + \frac{2\pi}{15} N^2 \int_0^\infty g(r) \frac{d}{dr} \left( r^4 \frac{dU(r)}{dr} \right) dr.$$  \hspace{1cm} (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 $G'_s$ can directly be related to the second derivative of $U(r)$ [Buscall et al. (1982)]

$$G'_s \propto \frac{1}{r} \left( \frac{\partial^2 U}{\partial r^2} \right).$$  \hspace{1cm} (8)

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

$$r^3 = (2a)^3 \frac{\phi_{eff,max}}{\phi_{eff}},$$  \hspace{1cm} (9)

where $\phi_{eff,max}$ 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 $\phi_{eff}$ 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 $G'_s$ on $\phi_{eff}$. 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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References


