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Diffusion of brownian particles in the isotropic phase of a nematic liquid crystal

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We report a light scattering study of the translational diffusion of a suspension of silica spheres in the liquid crystal, 4-*n*-pentyl-4'-cyanobiphenyl. We observe a small but significant increase of the effective hydrodynamic radius of the colloidal particles as the transition to the nematic phase is approached. This effect can be understood in terms of orientational pre-wetting of the silica spheres.

1. Introduction

The orientational ordering of a mesogen near a wall is an interesting phenomenon in both a fundamental sense and from the point of view of possible applications. There is ample experimental evidence [1] that some solid surfaces may induce local orientational order in an isotropic fluid at a temperature close to the transition to the nematic phase. This surface-induced ordering can be thought of as an orientational pre-wetting effect. Several theories have been put forward which relate the temperature dependence of the amplitude and range of the surface-induced order to properties of the bulk fluid and the nature of the solid–fluid interface [2, 3]. So far the emphasis in both experiment and theory has been on the study of static effects associated with orientational pre-wetting, such as birefringence or surface tension. However, the presence of an orientationally-ordered layer might also have an influence on transport phenomena in the vicinity of the interface. One reason why the dynamic effects associated with orientational wetting have been largely ignored is that they are very difficult to detect in the experimental geometry used to study static wetting. In this paper we report measurements that were designed specifically to detect the effect of orientational wetting on the viscosity of a fluid near a wall. To this end, we have studied the translational diffusion of small (diameter between 80 and 180 nm), fairly monodisperse silica particles in the isotropic phase of 4-*n*-pentyl-4'-cyanobiphenyl (5CB). In the absence of wetting effects, the self-diffusion constant D of spheres with radius R is related to the viscosity η of the solvent by the Stokes–Einstein relation

$$D = kT/6\pi\eta R;$$

here k is the Boltzmann constant, η is the dynamic viscosity of the solvent, R is the hydrodynamic particle radius and T is the temperature. However, if an orientationally-ordered layer forms around a sphere, then the viscosity will vary locally. This will alter the value of the effective hydrodynamic radius R which is deduced from D and η with the help of the Stokes–Einstein relation. Clearly, this change in R will be greatest if the thickness of the orientational wetting layer is comparable to the particle diameter

and the effective viscosity in the orientational ordered phase differs appreciably from that of the isotropic fluid.

2. Sample preparation

The 5CB used as the solvent was obtained from BDH Chemicals Ltd. Silica particles coated with a layer of 3-(trimethoxysilyl)-propyl methacrylate (TPM) were provided by the Colloidal Chemistry Group of the University of Utrecht. The coating served a dual purpose. First of all, it was needed to prepare a stable suspension of silica spheres in 5CB (uncoated silica particles would cluster and settle) and secondly, the coating was expected to induce local orientational order in the fluid, because similar coatings on flat glass surfaces cause nematic liquid crystals to align homeotropically, i.e. with the molecular axes on average perpendicular to the wall [4]. In order to prepare a suspension of silica spheres in the isotropic phase of 5CB, a dilute suspension of silica spheres in ethanol was added to a 5CB–ethanol mixture. Subsequently, the dissolved air and ethanol were removed by evaporation under vacuum. In samples with a silica volume fraction higher than 10^{-4} , aggregation and sedimentation were observed. This points to a strong attractive interaction between the colloid particles. Since aggregation makes it very difficult to determine the translational diffusion by dynamic light scattering, only very dilute samples were used. In the experiment reported below, two different suspensions were used. One (S1) contained a volume fraction of 2.13×10^{-5} silica spheres with a radius $R = 92.1$ nm. The other (S2), contained a volume fraction of 2.39×10^{-5} silica spheres with a radius $R = 39.8$ nm. These values for R were obtained from light scattering experiments performed on dilute suspensions of silica spheres in ethanol. At these low concentrations, we found that the silica spheres had no noticeable effect on the location of the isotropic–nematic transition ($T_{NI} = 34.9 \pm 0.1^\circ\text{C}$). The transition temperature was found to be the same (within experimental error) as that in [5].

3. Light scattering

The light scattering experiments were performed by illuminating a cylindrical scattering cell with a krypton-ion laser (Spectra Physics 165-01, $\lambda = 647.1$ nm). The scattering cell was placed in a temperature-controlled vessel with stability of $\pm 0.03^\circ\text{C}$. The vessel was filled with toluene which has a refractive index comparable to the refractive index of glass. This resulted in reduced specular reflection of light at the cell walls.

The scattered light was detected by a fast photomultiplier (EMI 9863 KB/100) at a constant angle $\theta = 90^\circ$ (cf. figure 1). A Malvern-K7026 digital correlator system controlled by a microprocessor was used to measure the intensity correlation function of the scattered light.

The polarization of incoming and detected light was normal to the scattering plane. In the rest of our paper this direction is denoted by the symbol \parallel . Since multiple scattering [6] can be a serious problem near a phase transition it was necessary to reduce the dimensions of the scattering volume. The scattering volume was defined by a pinhole of diameter 4×10^{-4} m at a distance of 0.35 m from the scattering cell. The diameter of the incoming laser beam was reduced to 5×10^{-4} m. Using the procedure of Dhont [7], we estimate the relative contribution of double scattering to be less than 2 per cent. The intensity autocorrelation function $g^{(2)}(t)$ was estimated from a series of ten independent measurements each of about 45 min.

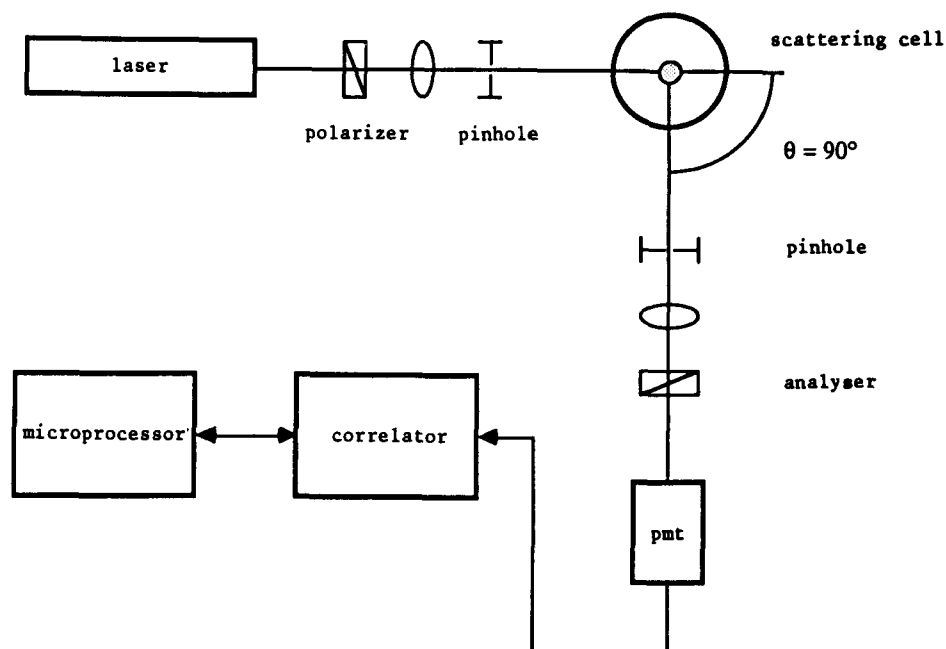


Figure 1. Experimental set-up.

For a stationary and gaussian process, the intensity correlation function is related to the electric field autocorrelation

$$g^{(1)}(t) = \langle E(0)E(t) \rangle / \langle E(t)^2 \rangle \text{ by } g^{(2)}(t) = 1 + C|g^{(1)}(t)|^2,$$

where C is a constant which depends on the scattering geometry. The data were fitted to

$$g^{(2)}(t) - 1 = A(1) \exp(-2t/\tau_D) + A(2),$$

where τ_D is the correlation time associated with particle diffusion $\tau_D = (Dq^2)^{-1}$. q is the scattering vector, $q = (4\pi n/\lambda_0) \sin \theta/2$, n is the refractive index and λ_0 is the wavelength of the laser light in vacuum. The fit to one exponential is only valid for a single scattering process of diffusing identical spheres.

The degree of deviation from monodispersity can be estimated from the magnitude of the second cumulant of the correlation function, given by

$$\sigma^2 = \int F(\Gamma)(\Gamma - \langle \Gamma \rangle)^2 d\Gamma, \quad \Gamma = Dq^2,$$

where $F(\Gamma)$ is the distribution function of Γ [8]. Typical values for $(\sigma/\Gamma)^2$, and hence for $(\Delta R/R)^2$, are 6 per cent for sample S1 and about 12 per cent for sample S2.

Let us now consider the possible effect of scattering processes other than particle diffusion. In the scattering process there will also be a contribution due to collective orientational fluctuations of the solvent. The intensity of this scattering will increase considerably near the nematic-isotropic phase transition. However this contribution from the solvent can easily be distinguished from the former since the characteristic times are very different (typically $\tau^{\text{orientation}}/\tau_D \approx 10^{-4}$) [9]. Hence, orientational scattering only reduces the signal-to-noise ratio. The contribution of the solvent to the background is estimated by measuring the perpendicularly-polarized intensity I_{\perp} .

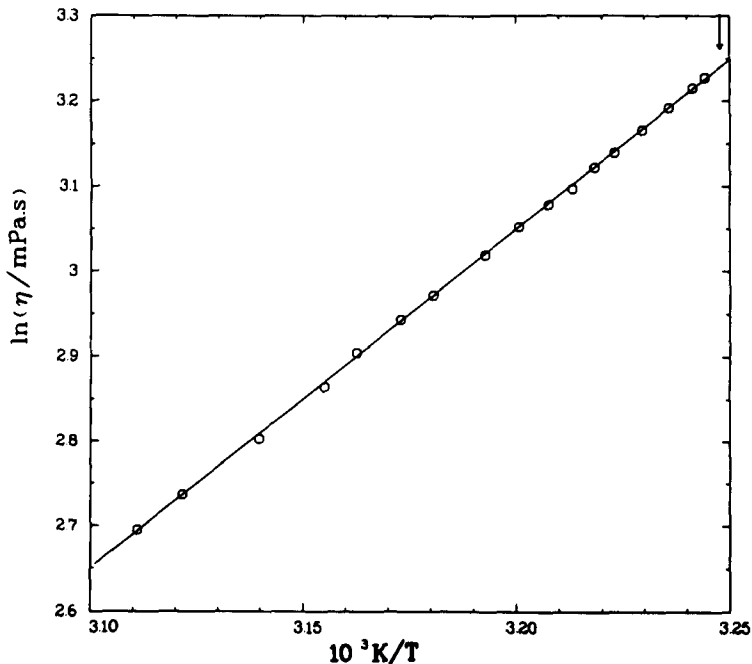
Assuming that I_{\perp} is mainly due to orientational fluctuations of the solvent and that $I_{\parallel}^{\text{orientation}}/I_{\perp}^{\text{orientation}} = 4/3$ [10], we find that the ratio $I_{\parallel}^{\text{orientation}}/I_{\parallel}^{\text{particle}}$ ranges from 13 to 25 per cent near T_{NI} . Any effect of fluctuations in the number of colloidal particle in the scattering volume can be safely ignored: $\tau^{\text{number}}/\tau_{\text{D}} \sim L^2 q^2 \gg 1$, where L is a typical dimension of the scattering volume. The scattering due to fluctuations in the solvent density can be neglected as well.

4. Results

The dynamic light scattering of coated spheres in the isotropic phase of 5CB was measured over a temperature range from T_{NI} to $T_{\text{NI}} + 10^{\circ}\text{C}$ (the highest temperature at which the scattering cell could operate). Since very dilute suspensions of silica spheres in 5CB were used we can safely neglect interaction between the spheres. Then the diffusion coefficient can be written as $D = kT/6\pi\eta R$. Any ordering of the solvent around the colloidal particles results in an apparent change in R , the effective hydrodynamic radius. In order to measure R , we need to know the viscosity η . To this end, we have measured the kinematic viscosity of 5CB with an Ubbelohde viscometer (diameter 1 mm). The dynamic viscosities are then obtained using the densities of 5CB given by Gannon and Faber [11]. The resulting viscosities, plotted in figure 2, show no pretransitional behaviour, which is in agreement with other measurements [13]. A least-squares fit to

$$\ln \eta = \ln \eta_0 + (E/kT)$$

leads to $E = (5.513 \pm 0.001) \times 10^{-20} \text{J}$ and $\eta_0 = (5.91 \pm 0.015) \times 10^{-5} \text{mPas}$. From the light scattering experiments we obtain the translational correlation time



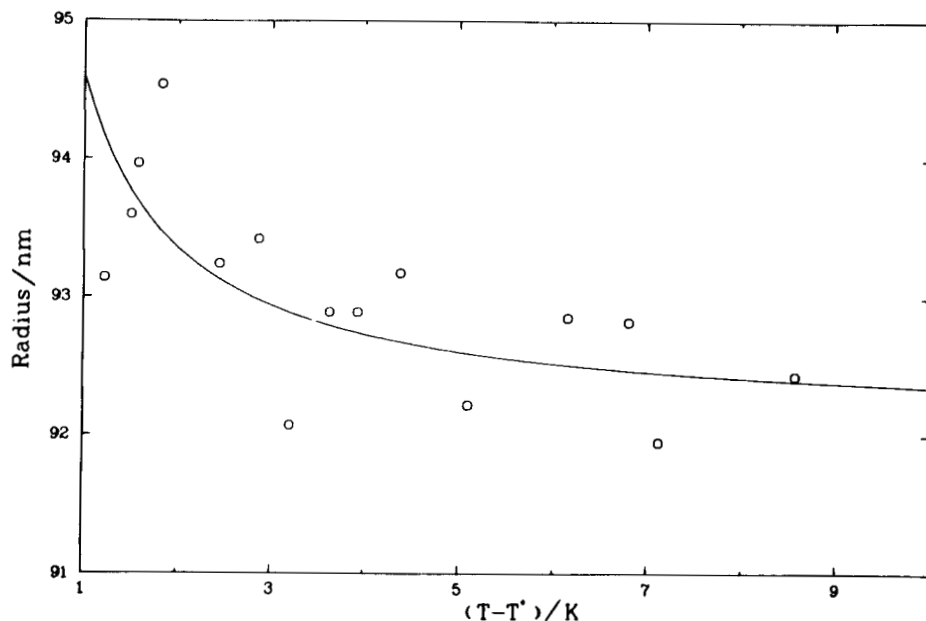


Figure 3. The hydrodynamic radius of silica spheres in the isotropic phase of 5CB. Full line is a fit to $R = R_0 + (c/T - T^*)$, with $R_0 = 92.2 \pm 0.3$ nm and $c = 2.5 \pm 0.7$ nm K.

$1/Dq^2$, where q is a function of the refractive index n . In order to compute D , we have measured the refractive index of 5CB with an Abbe refractometer. The temperature dependence $\Delta n/\Delta T = -5.6 \times 10^{-4} \text{K}^{-1}$ is in agreement with that reported in [12]. The estimated statistical error in the computer values of R from a single experiment is of the order of 0.5 per cent. Repeated measurements at the same temperature showed that the value of R was reproducible to within 1 per cent. It is this random error which causes the uncertainty in the computed hydrodynamic radii. The plots in figures 3 and 4 show R as a function of $T - T^*$, with $(T^* - T_{\text{NI}}) = 1$ K [5]; here T^* is the extrapolated temperature at which the isotropic phase becomes absolutely unstable. Both plots show an increased radius near T_{NI} . A least-squares fit to a temperature dependent function

$$R = R_0 + \frac{c}{T - T^*}$$

leads to a reduced χ^2 of 0.9 and 1.2 for S1 and S2, respectively. A fit of the data to a constant $R = R_0$, on the other hand, doubled the reduced χ^2 for S1, but did not change χ^2 for S2 significantly. The same trend was seen in all of our measurements. The hydrodynamic radius of the smaller particles appears to be less influenced by the proximity of the phase transition. Although at first sight this may seem surprising, we shall argue later that this behaviour is actually to be expected. The apparent growth of the particles can be explained by an increased orientational order of the solvent near the silica surface. This orientational order causes anisotropic behaviour of the viscosity. In general η_{eff} , the effective viscosity, can be written as

$$\eta_{\text{eff}} = \eta_{\text{iso}} + K(Q_{ij}),$$

with η_{iso} the viscosity of the isotropic phase approximately equal to $\frac{1}{4}\alpha_4$ where α_4 is a Leslie coefficient and K is a function of the tensor order parameter Q in the liquid [14].

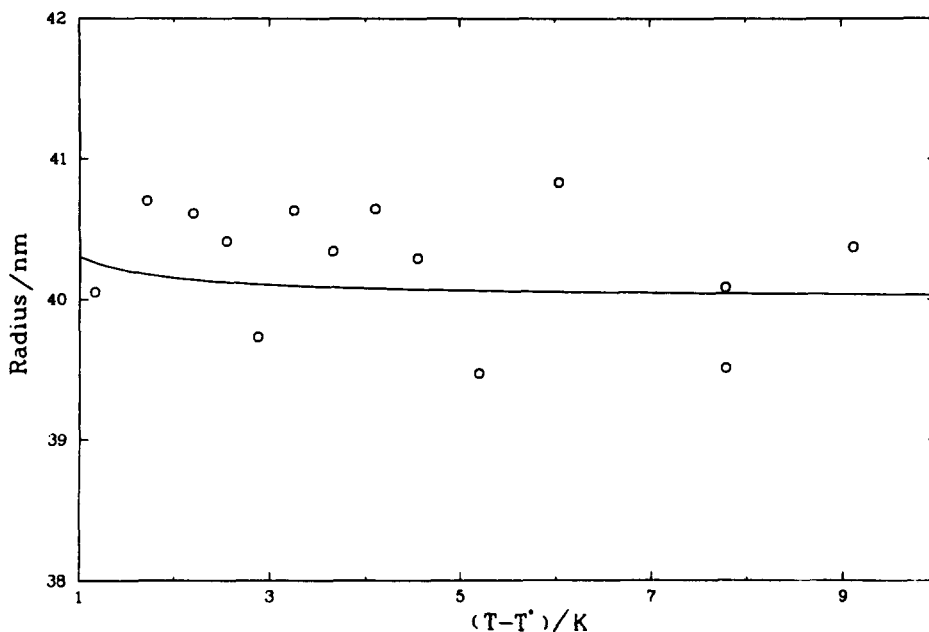


Figure 4. The hydrodynamical radius of silica spheres in 5CB. Solid line is a fit to $R = R_0 + (c/T - T^*)$, with $R_0 = 40.1 \pm 0.4$ nm and $c = 0.3 \pm 0.6$ nm K. Note that the data fit equally well to a straight line.

Clearly, several factors determine the magnitude of the observed effect. First of all, the effective viscosity must change noticeably with the order parameter S . For 5CB the Miesowicz viscosities η_b , η_c in the nematic phase are known [13] to differ from η_{iso} by 10 and 20 per cent respectively; note that $\eta_b < \eta_{iso}$ and $\eta_c > \eta_{iso}$. The effective viscosity therefore depends on the flow pattern around the particle. Secondly, there must be appreciable orientational ordering of the solvent at the surface of the colloidal particles. Finally, the thickness of the orientationally ordered layer must be non-negligible compared to the radius of the silica spheres. Later we shall discuss how the orientational ordering profile around a sphere can be computed within the framework of the Landau–de Gennes theory. However, for the moment a rough estimate will suffice. To a reasonable approximation the thickness of the orientationally ordered layer equals the correlation length $\xi(T)$ of the collective orientational fluctuations. When $T \rightarrow T_{NI}$, the correlation length $\xi(T)$ will increase from a value corresponding to a typical molecular dimension (1 nm, say) [15] to a value of order 10–40 nm [22]. Clearly, this thickness is not negligible compared to the radius of the silica spheres. So, provided the other factors are not too small, some effect of orientational pre-wetting on the diffusion of the particles should be observable.

From the plots in figures 3 and 4 it is clear that S must be smaller near the small particles than near the 90 nm particles. This can be understood by the simple model described in the following section.

5. Landau–de Gennes theory

Orientational ordering near a wall is due to the interaction between the fluid molecules and the substrate [16]. Its magnitude depends strongly on the microscopic

structure of the surface. The molecular orientation that minimizes the interfacial energy is referred to as a unit vector, \mathbf{d} . In order to discuss the orientation near a spherical surface it is useful to introduce a tensor order parameter Q_{ij} with its principal axis along \mathbf{d} [17]

$$Q_{ij} = \frac{1}{2}S(d_i d_j - 1/3\delta_{ij}).$$

In order to compute the local order parameter $S(\mathbf{r})$ as a function of \mathbf{r} , the distance from the centre of the sphere, we make the following assumptions. (1) The easy axis is perpendicular to the surface: $\mathbf{d} = \mathbf{r}/r$ and $\nabla \cdot \mathbf{d} = 2/r$. This assumption is reasonable because it has been observed with a polarization microscope that on flat surfaces TPM causes homeotropic alignment. (2) S is spherically symmetric, i.e. $S(\mathbf{r}) = S(r)$. The Landau–de Gennes free energy F_{LG} [19] can be written as a function of S , ∇S and \mathbf{d} . Contributions to F_{LG} which do not depend on S are ignored in the calculation. We also neglect cubic and higher-order terms in S . By using the spherical symmetry of the problem, we can write F_{LG} as

$$\begin{aligned} F_{LG} = & \int_V dV \left[\frac{3}{4} a(T - T^*)S^2 + \frac{3}{4}(L_1 + \frac{1}{6}L_2)(\nabla S)^2 + \frac{3}{8}L_2(\nabla S \cdot \mathbf{d})^2 \right. \\ & + \frac{9}{4}(L_1 + \frac{1}{2}L_2)S^2(\nabla \cdot \mathbf{d})^2 + \frac{3}{2}(L_2 + \frac{3}{2}L_1)S(\nabla \cdot \mathbf{d})(\mathbf{d} \cdot \nabla S) \\ & \left. + \int \frac{9}{4}L_1 S^2 \mathbf{l}_z \cdot [\mathbf{d}(\nabla \cdot \mathbf{d})] d\Sigma - \int GS d\Sigma, \right. \end{aligned} \quad (2)$$

where a , L_1 and L_2 are material parameters, G denotes the strength of the surface interaction and \mathbf{l}_z is a unit vector perpendicular to the surface. The last two terms in equation (2) are integrals over the surface of the sphere and contain elastic effects and the strength G of the interaction respectively [18]. The profile $S(r)$ is obtained by minimizing the total free energy with respect to $S(r)$. This is done in two steps. First we fix the value of $S = S_R$ at the surface and carry out the functional differentiation of F_{LG} with respect to $S(r)$. The condition that F_{LG} must be at a minimum leads to the differential

$$S'' + 2\frac{S'}{r} - \left[\xi(T)^{-2} + \frac{6}{r^2} \right] S = 0, \quad \xi(T)^2 = \frac{L_1 + \frac{2}{3}L_2}{a(T - T^*)}, \quad (3)$$

with boundary conditions $S(r \rightarrow \infty) = 0$ and $S(R) = S_R$. The solution of this equation is

$$S(r) = S_0 \exp(-r/\xi) \frac{\xi}{r} \left[1 + 3\frac{\xi}{r} + 3\left(\frac{\xi}{r}\right)^2 \right].$$

Note that S_0 and S_R are linearly related: $S_R = S(r = R)$. Next, the total free-energy is minimized with respect to S_R . S_R will be dependent on R , as shown in figure 5. It is clear that a small radius of curvature of the surface tends to reduce the order at $r = R$. In particular, we can estimate the difference in S at the surface for spheres with a radius of 40 and 90 nm. Assuming $\xi \simeq 20$ nm we find a ratio $S_R(90 \text{ nm})/S_R(40 \text{ nm}) \sim 2$. This qualitative argument explains why the effect of orientational pre-wetting is less for smaller spheres, as we have observed experimentally.

Note that the higher-order terms in ∇S become important near strongly curved surfaces. These higher order terms may change the quantitative predictions of the Landau–de Gennes theory. However, the qualitative arguments presented in this section should still be valid.

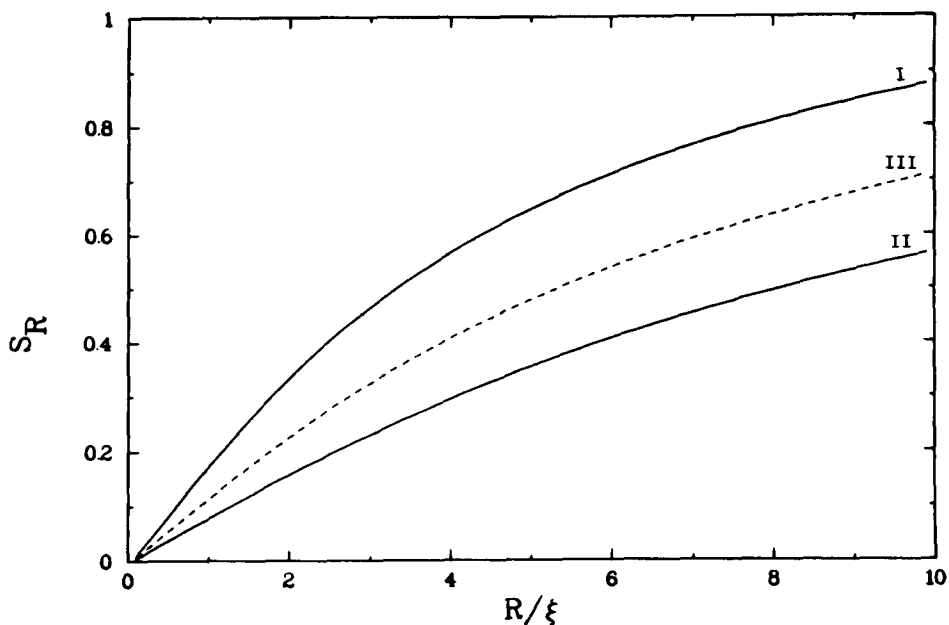


Figure 5. The effect of the radius of curvature of the surface on the order parameter at the surface of a sphere with radius R for different values of L_1 and L_2 ; $L_1 = 0$ (I), $L_2 = 0$ (II) and $L_2 = 2L_1$ (III), which was found for 5CB from data in [21].

6. Conclusions

We have presented the first experimental evidence that surface-induced orientational order in an isotropic fluid has a measurable effect on the dynamics of colloidal particles. Similar experiments have however been done near the liquid–liquid critical point in binary liquid mixtures [20]. From a consideration of the Landau–de Gennes free energy in the presence of a spherical symmetric surface it is seen that strong curvature causes elastic effects which reduce the order parameter. This agrees with our experimental observations.

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