

Influence of the stabilizing coating on the rate of crystallization of colloidal systems

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Abstract: We report visual observations and preliminary light scattering experiments on the crystallization process in several colloidal systems. The main difference between the colloidal systems studied here is the range of their pair-interaction potential which is varied by changing the stabilizing coating of the particles. This range is found to have a pronounced influence on the rate of crystallization.

Key words: Colloidal crystals, phase behavior, light scattering.

1. Introduction

One of the most remarkable phenomena exhibited by concentrated suspensions of monodisperse spherical colloidal particles is the spontaneous transition from a fluid-like structure to a crystalline arrangement of the particles. This ordering was first observed by Williams and Smith [1] in centrifuged pellets of a purified virus suspension. Because the spacing of the particles is of the order of optical wavelengths, light is separated into colours when scattered giving rise to beautiful iridescence; hence the name, Tipula Iridescent Virus (TIV), given to the virus by Smith and Williams [2]. Subsequent to the discovery of this phenomenon in the TIV system it was also observed in dispersions of synthetic colloids notably in deionized dispersions of polymer latex particles [3, 4]. In fact most experiments in this area have been performed on quite dilute suspensions of these charge stabilized colloids exhibiting long range repulsive interactions [5].

More recently the phenomenon of crystalline ordering has also been observed in dispersions of sterically stabilized particles which have a steep repulsive interaction [6, 7]. From computer simulations on crystallization in atomic systems it is clear that the harshness of the repulsive part of the pair potential has a pronounced effect on the process of homogeneous nucleation and thereby on the rate of crystal growth [8]. Both the time lapse for the onset of nucleation and the time required for the completion of the nucleation

process are longer for steeper repulsive potentials. In view of the fact that the structure in colloidal dispersions may be treated in the same way as in simple liquids it appears reasonable to expect that the trend found for atomic liquids also applies to colloidal systems. In fact colloidal systems offer unique possibilities to investigate the influence of the range of the repulsive potential since by suitable modification of the surface properties of the particles the repulsive interaction can be varied more or less continuously.

In this study we describe first observations of the crystallization process of colloidal silica particles with different (steric) stabilization layers resulting in different ranges of the repulsive interaction.

Section 2 of this paper consists of a brief description of the systems used in this study. Then in Section 3 we describe our observations on each system and in Section 4 we describe preliminary light scattering experiments. Finally we make some concluding remarks in Section 5.

2. Materials

The colloidal particles used here consist of an amorphous silica core, synthesized according to Stöber's method [9] which were coated with different types of stabilization layers. The following four types of dispersions with increasing range of the repulsive interactions were studied.

The first dispersion is stearyl silica. The surface silanol groups of the amorphous silica particles are esterified with octadecyl alcohol

[10]. The hydrodynamic radius of the particles is $a = 160$ nm while the thickness of the coating is $d \approx 2$ nm. Extensive experimental work has led to the conclusion that these particles (nearly perfectly) behave as hard spheres [11].

The second dispersion is called PIB/1-silica. These particles are coated with terminally attached polyisobutene chains [12] with number averaged molecular weight $M_n = 1300$. In this case $a = 170$ nm and $d = 4-5$ nm.

The third silica is called PIB/2-silica. The difference with the previous system is that now the terminally attached polyisobutene chains have a number averaged molecular weight $M_n = 13000$. This results in $d = 30-50$ nm and $a = 210$ nm.

The fourth silica is referred to as TPM-silica. It consists of silica particles coated with γ -methacryloxy-propyltrimethoxysilane [13]. For this suspension $a = 160$ nm and $d = 2-4$ nm. The range of the repulsive interaction potential is large due to residual surface charges. In ethanol-toluene mixtures the additional range of the interaction due to these surface charges is of the order of 100 nm [14].

The range of the repulsive interaction clearly increases in going from stearyl silica to TPM-silica.

3. Observations of crystallization phenomena with the naked eye

In this section we present some characteristic observations on the crystallization process in the four systems described in the previous section. The rate of crystallization depends markedly on the type of system. On this basis the four systems studied here can be divided into two groups. On the one hand we have stearyl silica and PIB/1-silica. Here crystallization only occurs after (slow) sedimentation under gravity. On the other hand PIB/2-silica and TPM-silica crystallize rapidly whenever the appropriate concentration is achieved. We start with a description of our observations on the first group of systems.

Allowing a dilute (say 10 per cent volume fraction) dispersion of stearyl silica in cyclohexane to settle under gravity a sediment is formed in a few days. At this

stage no crystallization is apparent. However after a period ranging somewhere from one to three months crystallites appear at the interface between the dense sediment and the turbid layer of colloidal liquid just above the sediment. This course of events is schematically depicted in Fig. 1. Figure 2 shows a photograph of

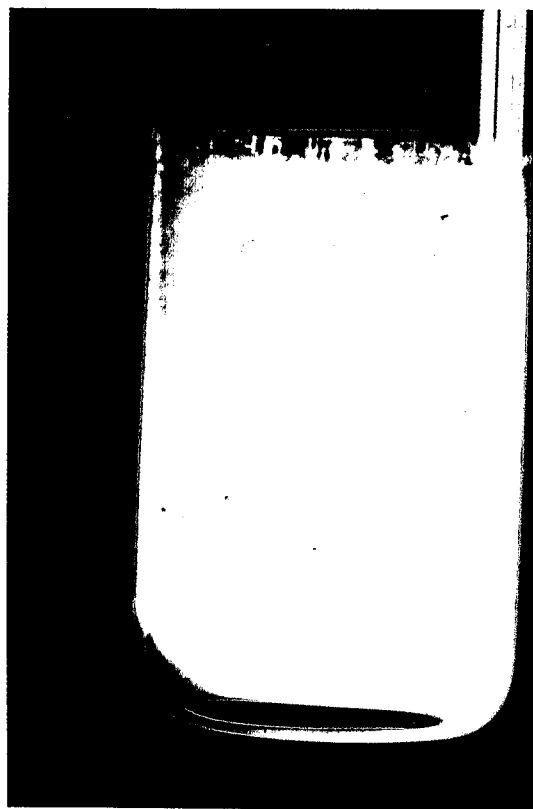


Fig. 2. Photograph of stearyl silica in cyclohexane after crystallization. This sample is approximately four years old and some crystallization can be observed in the lower part of the sediment

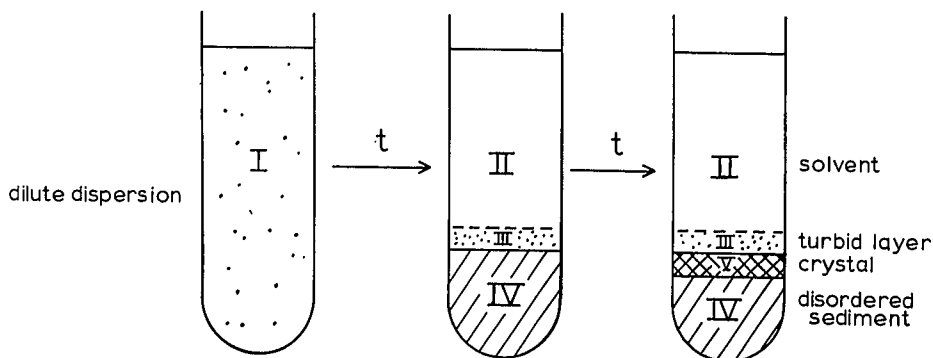


Fig. 1. The appearance of stearyl silica in cyclohexane as a function of time. I represents the dilute dispersion, II the solvent, III the turbid layer above the sediment, IV the disordered sediment and V the iridescent (crystalline) sediment

the system after crystallization has taken place. The crystallites have a columnar shape and are vertically oriented. Typically the crystalline region reaches a height up to 1–2 mm after which crystallization stops. If the liquid upper layer after completion of sedimentation was removed no evidence for crystallization was found even after extended periods of time (1 year or more).

In a mixture of cyclohexane and carbon tetrachloride which has a density closer to the density of the silica particles than pure cyclohexane the sedimentation process now requires 2 to 3 weeks. In this case the formation of crystallites occurs concurrently with the sedimentation process and starts at the bottom of the tube. However crystallization stops somewhere in the lower part of the sediment leaving the upper part of the sediment in a disordered state. By gently shaking the tube the disordered part of the sediment can be redispersed again without destroying the crystal at the bottom. Allowing the particles to settle again the crystallization process proceeds and may now lead to a crystalline phase extending over the whole sediment (see Figs. 3 and 4).

Allowing a dilute dispersion of PIB/1-silica in toluene to settle under gravity, sedimentation is complete in several days and concurrently crystallization occurs throughout the entire sediment reaching completion in about 2 weeks (see Figs. 5 and 6). This crystal is more easily deformed and consists of smaller crystallites than in the case of stearyl silica. Although the crystallization of PIB/1-silica definitely proceeds faster than for stearyl silica, if sedimentation takes place by gentle centrifugation (about 100 g) the resulting sediment locks into a disordered state where no crystallization is observed.

We now proceed to the second group of systems which are rapidly crystallizing. First we consider PIB/2-silica. Like the PIB/1-silica this system crystallizes after sedimentation under gravity. However contrary

to PIB/1-silica it also crystallizes from concentrated dispersions which are prepared by centrifugation of dilute suspension and decanting excess solvent (see Figs. 7 and 8). Under these conditions crystallization can be observed after one day. The crystalline phase has the same appearance as in the case of PIB/1-silica but it is much less rigid.

TPM-silica crystallizes from concentrated dispersions in less than a day. The crystal is very soft as is evi-

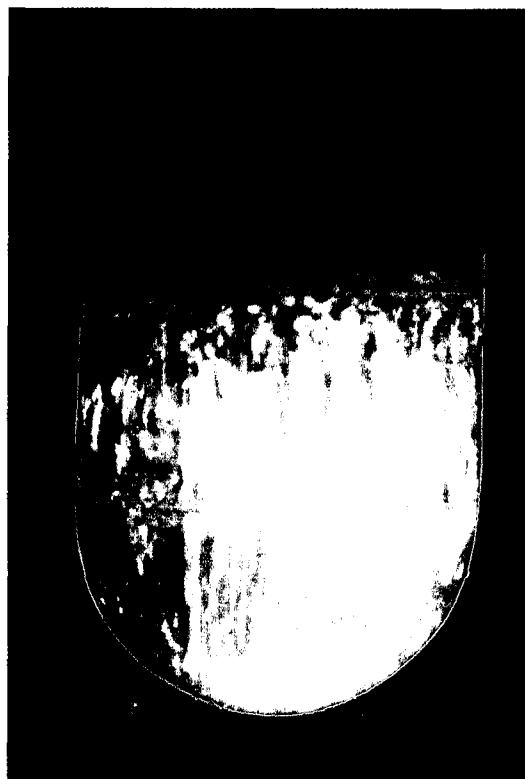


Fig. 4. Photograph of stearyl silica in a mixture of carbon tetrachloride and cyclohexane after crystallization. Note the boundary between the upper and lower part of the sediment, which is caused by growing the crystal in two stages

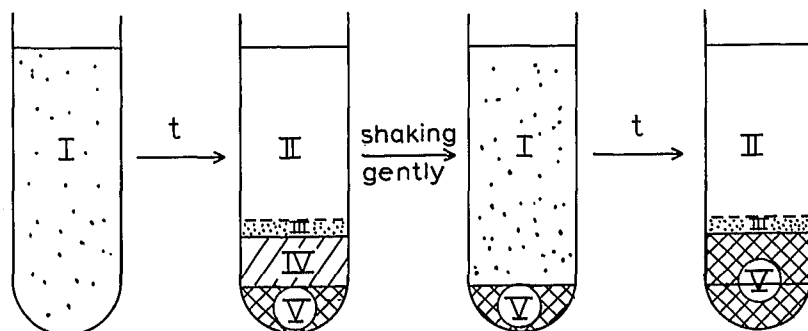


Fig. 3. The appearance of stearyl silica in a mixture of carbon tetrachloride and cyclohexane as a function of time, The numbers I to V have the same meaning as in Fig. 1

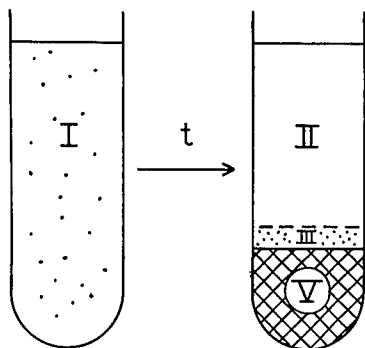
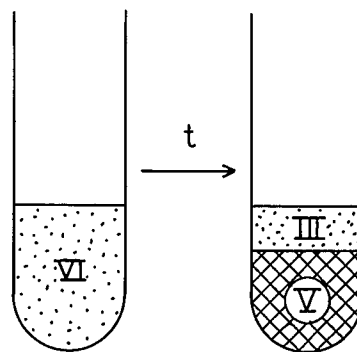


Fig. 5. The appearance of PIB/1-silica in toluene as a function of time. The numbers I to V have the same meaning as in Fig. 1



concentrated dispersion

Fig. 7. The appearance of PIB/2-silica in carbon tetrachloride and of TPM-silica in a mixture of ethanol and toluene as a function of time. The numbers III and V have the same meaning as in Fig. 1 and VI represents a concentrated dispersion

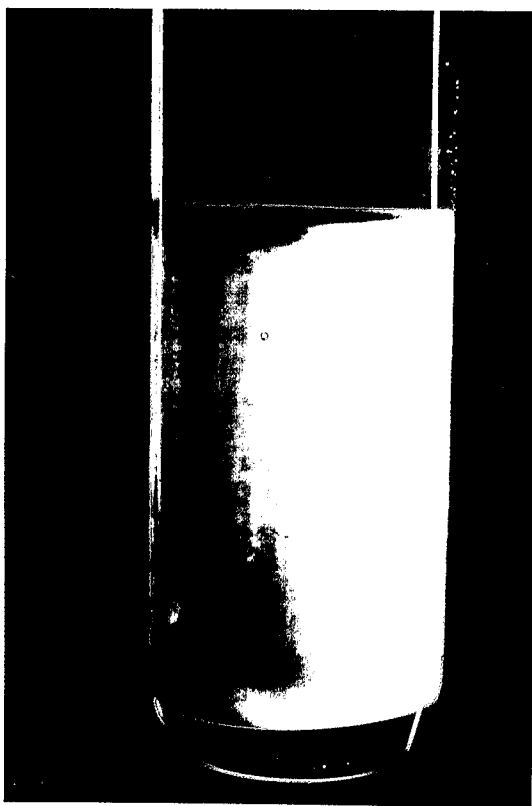


Fig. 6. Photograph of a PIB/1-silica crystal in toluene

denced by the fact that it flows under gravity which can be observed by tilting the tube (see Fig. 9).

4. Preliminary light scattering measurements

Because the spacing of the particles in the systems under investigation is of the order of optical wavelengths it is possible to probe the structural arrange-

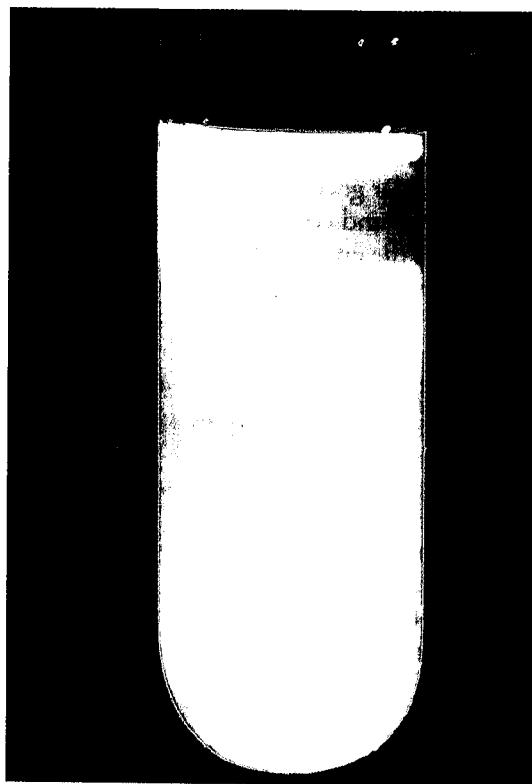


Fig. 8. Photograph of a PIB/2-silica crystal in carbon tetrachloride. After crystallization had been completed, some sedimentation under gravity occurred

ment of the particles with light scattering. Under favourable conditions also the development in time of ordered structures can be studied with light scattering.



Fig. 9. Photograph of a TPM-silica crystal in a mixture of ethanol and toluene. After completion of the crystallization process some sedimentation has occurred. Note that the crystal follows gravity after tilting the tube

Light scattering experiments were performed with a FICA-50 photometer using vertically polarized light. The measurements were done on the rapidly crystallizing systems PIB/2-silica and TPM-silica prepared at concentrations where crystallization takes place.

The “normalized” light scattering intensity (the “Rayleigh ratio”) of a system of monodisperse spheres is given by,

$$R(K) = cP(K)S(K), \quad (1)$$

where c is determined by the number concentration of the particles, the refractive indices of particles and liquid and the wavelength of the light. K is the scattering vector,

$$K = \frac{4\pi n}{\lambda_0} \sin(\theta/2). \quad (2)$$

Here λ_0 is the wavelength of the light in vacuo, n is the refractive index of the solvent and θ is the angle between the incident and scattered light, the “scattering angle”. The form factor $P(K)$ is determined by the optical properties of one single particle. The structure factor $S(K)$ measures the statistical arrangement of the particles in the system. For a crystalline structure $S(K)$ consists of a series of peaks located at K values where the Bragg scattering condition is fulfilled.

As described in the previous section the TPM-silica system crystallizes rapidly. For this system it was not possible to follow the crystallization process by light

scattering since the time required to obtain a single scattering curve is of the same order as the time during which major structural changes occur. For these rapidly crystallizing systems the FICA-50 photometer cannot be used to study the dynamics of the crystallization process. A typical scattering curve at a late stage of the crystallization process is given in Fig. 10. The peak positions can be indexed by the Miller indices 111 and 200 of a FCC crystal.

In the PIB/2-system the crystallization process was sufficiently slow to be followed by doing light scattering experiments at various stages of the development of the crystalline structure. The results of these

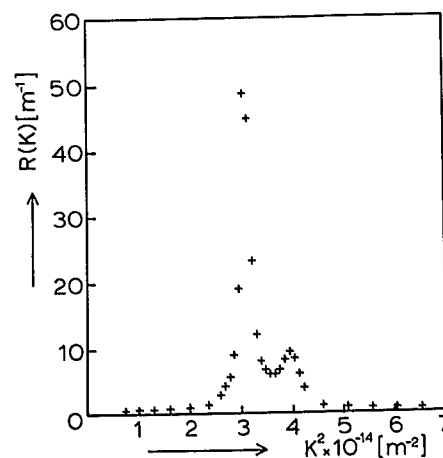


Fig. 10. Light scattering intensity as a function of the scattering vector from crystallized TPM-silica in a mixture of ethanol and toluene

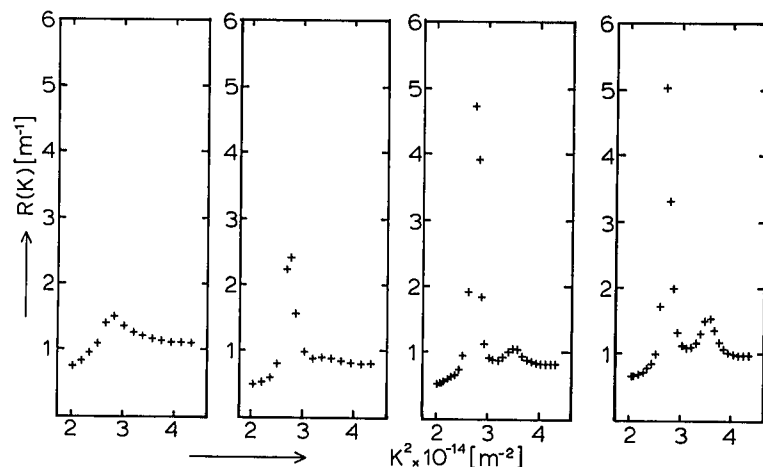


Fig. 11. Light scattering intensity as a function of the scattering vector from crystallizing PIB/2-silica in carbon tetrachloride. From left to right the scattering curves represent measurements directly after homogenizing, after 18 hours, after 24 hours and after 167 hours respectively

measurements are presented in Fig. 11. The scattering curves clearly display the transition from a "disordered" liquid-like structure to an ordered structure with peaks that can be indexed by the Miller indices 111 and 200 of a FCC crystal.

5. Concluding remarks

From the observations presented here it is clear that colloidal silica systems offer interesting possibilities to study the dependence of the rate of crystallization on the range of the repulsive interaction. The range of interaction was varied either by changing the thickness of the stabilizing coating or by the effect of surface charges. It turns out that with increasing range of interaction the rate of crystallization increases dramatically.

In systems where the repulsive interaction is very short ranged (as is the case for stearyl silica) the rate of sedimentation appears to be an important parameter as well. The formation of colloidal crystals is favored by slow sedimentation. To study this effect in more detail knowledge of the concentration pattern in the sample as a function of time would be valuable. It would also be interesting to monitor the velocity pattern during the sedimentation process.

Quantitative information on the crystallization process can be obtained by light scattering experiments. To exploit this possibility for rapidly crystallizing systems such as TPM-silica a light scattering apparatus is required that allows one to measure in shorter times than is possible with the FICA-50 apparatus used in the present study.

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