

## Model for cage formation in colloidal suspension of laponite

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In this paper we investigate glass transition in aqueous suspension of synthetic hectorite clay, laponite. We believe that upon dispersing laponite clay in water, the system comprises of clusters (agglomerates) of laponite dispersed in the same. Subsequent osmotic swelling of these clusters leads to an increase in their volume fraction. We propose that this phenomenon is responsible for slowing down of the overall dynamics of the system. As clusters fill up the space, the system undergoes glass transition. Along with the mode coupling theory, the proposed mechanism rightly captures various characteristic features of the system in the ergodic regime as it approaches glass transition. © 2007 American Institute of Physics. [DOI: 10.1063/1.2779026]

### INTRODUCTION

Glasses are disordered materials, and in such state, system explores only a small part of the phase space. Molecular glasses are formed by quenching the liquid rapidly below the so-called glass transition temperature to obtain a disordered structure.<sup>1</sup> In colloidal suspensions, the glassy state is attained by increasing the concentration of the constituent particles such that the disordered state is obtained above a random loose packing threshold.<sup>2</sup> Generally, this is achieved by either centrifugation<sup>3</sup> or dialysis.<sup>4</sup> Thus, colloidal glasses are different from molecular glasses wherein the concentration, not the temperature, plays an important role in causing arrested or glassy state. In this paper, we investigate the kinetics of glass transition in colloidal glass of aqueous laponite suspension wherein osmotic swelling of laponite clusters brings about glass transition.

Lately, the colloidal glasses formed by aqueous suspensions of laponite have attracted considerable interest.<sup>5–10</sup> Laponite particle has a disklike shape, and due to negative charges on its surface, repulsive interactions prevail among particles in low ionic concentration aqueous medium that leads to a formation of the so-called Wigner glass.<sup>10</sup> Apart from having wide ranging industrial applications, these suspensions are considered as model systems to study slow dynamics of glass transition and gelation.<sup>11</sup>

The laponite disk has a diameter of 25 nm and a layer thickness of 1 nm. At very low ionic concentrations its suspension in ultrapure water leads to a glassy state for volume fractions less than 0.01 in contrast to colloidal glasses of uncharged spherical particles where the glassy state is attained at volume fractions only above 0.5. This is essentially due to anisotropic shape of a laponite disk and negatively charged surface. The latter gives rise to electrostatic screening length of 30 nm.<sup>12</sup> Hence, the effective volume of a single laponite disk increases by a factor of 60 and explains the requirement of approximately 60 times lower volume fraction for glass formation. (The volume of single laponite

particle is of the order of  $1 \times 25 \times 25 \text{ nm}^3$ . However, the effective volume of laponite particle including electrostatic screening length of 30 nm on both sides becomes  $60 \times 25 \times 25 \text{ nm}^3$ ).

In the past few years, several groups have studied liquid-glass transition of a laponite suspension at low ionic concentration using various optical techniques.<sup>5–10,12–14</sup> In general, laponite powder is mixed in ultrapure water with vigorous stirring and is passed through a microfilter to study the evolution of its structure with respect to age. The suspension shows two relaxation modes with the fast mode being independent of age.<sup>13,14</sup> Its inverse square dependence on wave vector ( $q$ ) highlights its diffusive character. The slow mode shows an initial rapid increase followed by a linear increase with respect to age.<sup>5,15</sup> The former regime is called the cage forming regime,<sup>15</sup> where the slow mode also shows inverse square dependence on  $q$ . In the full aging regime, it shows  $q$  dependence with power law index in the range of  $-1$  to  $-1.3$ . Furthermore, the age at which transition from rapid growth to linear growth occurs decreases with increase in clay concentration.<sup>5</sup> Very recently, Mossa *et al.*,<sup>16</sup> while studying aging of laponite suspension in the nonergodic regime using Brownian dynamics simulations, observed that anisotropy of the platelet along with repulsive Yukawa potential is responsible for the local disorder that takes the system into the metastable state. They further observed that aging dynamics strongly affects orientational degree of freedom which relaxes over the time scale of translational modes. There are various other morphologies proposed in the literature, and in general the state of the system in full aging regime, gel or glass, still remains a contentious issue.<sup>17</sup>

In the literature, the rapid growth of relaxation time with respect to age in the ergodic regime is fitted by an empirical function ( $\ln \tau \sim t_w$ ) and hence is generally referred to as an exponential growth.<sup>5,13–15</sup> Tanaka *et al.*<sup>15</sup> proposed two-stage aging kinetics by expressing the relaxation time by using the average barrier height  $U$  for the particle motion as  $\tau \sim \exp(U/kT)$ . They suggested that the barrier height should grow linearly with aging time in the ergodic regime while logarithmically in the full aging regime to yield exponential

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and linear age dependence of relaxation time, respectively. However, they mentioned that the basis for logarithmic dependence that leads to exponential growth is not clear. They concluded by asserting that the rapid increase in slow mode with age in the ergodic regime remains an unanswered question. Schosseler *et al.*,<sup>5</sup> after experimentally investigating this phenomenon, linked it to liquid-glass transition, but did not conclude about the mechanism. In this paper, we investigate this very phenomenon. For the first time, we show that the osmotic swelling of laponite clusters bring about a rapid increase in the relaxation time as the system approaches arrested state. We limit our discussion only to cage forming regime.

## THEORY

We consider a system of aqueous suspension of laponite having basic pH that leads to net negative charge on the laponite particle.<sup>18</sup> The chemical formula for laponite is  $\text{Na}_{0.7}^+[(\text{Si}_8\text{Mg}_{5.5}\text{Li}_{0.3})\text{O}_{20}(\text{OH})_4]_{0.7}^-$ . Isomorphous substitution of magnesium by lithium atoms generates negative charges on its surface that are counterbalanced by the positive charge of the sodium ions present in the interlayer. We assume that immediately after stirring/filtration the system comprises of clusters (agglomerates) of laponite dispersed in water. In the present model, the word cluster should be referred to as agglomerate that is composed of domains of parallel stacks of laponite particles. As time progresses, the clusters of laponite undergo swelling due to diffusion (flux) of water into the cluster driven by an osmotic pressure gradient that is caused by repulsive interactions between neighboring particles.

We believe that the clusters of laponite get hydrated while the suspension is prepared by stirring. A filtration process breaks the clusters. For simplicity, we consider all the clusters to be spherical in shape, of the same size, and at the same level of hydration. Let  $\psi$  be the volume fraction of laponite inside a cluster of radius  $R_0$  at time  $t_w=0$ . Just outside the cluster, the volume fraction of water is unity and imposes an osmotic pressure gradient. As time progresses, water diffuses into the cluster until the concentration of water (or, alternatively, laponite or the osmotic pressure) becomes uniform over the space. If the overall volume fraction of laponite is  $\phi$ , the number of clusters per unit volume is given by

$$n = \phi/(\psi R_0^3). \quad (1)$$

The clusters swell due to osmotic diffusion. If the  $R(t_w)$  is the radius of cluster at any time  $t_w$ , then the fraction of total volume occupied by clusters is  $\xi(t_w)^3 \phi/\psi$  while the mode coupling distance parameter  $\varepsilon$  is given by

$$\varepsilon = [\phi_c - \xi(t_w)^3 \phi/\psi]/\phi_c, \quad (2)$$

where  $\xi(t_w)=R(t_w)/R_0$  is the dimensionless radius and  $\phi_c$  ( $\sim 0.56-0.64$ ) is the volume fraction at which growing spherical clusters touch each other. We believe that as  $\varepsilon \rightarrow 0$ , the system undergoes a transition from a cage forming regime to a glassy or full aging regime. The dimensionless radius at the onset of this transition can be obtained from Eq. (2) and is given by

$$\xi^* = (\phi_c \psi/\phi)^{1/3}. \quad (3)$$

In the powder form, laponite disks are present in the domains of parallel stacks with sodium atoms present in the interlayer. Upon dispersion in water, swelling of clay occurs in two steps. In the first step, water is absorbed in successive monolayers on the surface that pushes the disks apart. As the hydration of clay takes place, the  $\text{Na}^+$  ions, though electrostatically attracted toward the oppositely charged surface, diffuse away from the surface into the bulk where their concentration is low. As some  $\text{Na}^+$  ions diffuse out of the gallery, the negatively charged surfaces of the opposite faces get exposed to each other and hence repel. In the second stage of swelling, double layer repulsion pushes the laponite disks further apart.<sup>18</sup> The larger the distance between the laponite disks, the lower is the osmotic pressure required to hold them in the same position. Recently, Martin *et al.*<sup>19</sup> proposed a scaling model to estimate the flux of water through concentrated sediment of laponite under an osmotic pressure gradient. Using analytical solution of Poisson-Boltzmann equation for the case where only counterions are present in the interlayer space,<sup>20</sup> they argued that the osmotic pressure varies as the inverse square of the plate separation distance in the concentration regime of usual interest (namely, plate separation distance of 0.5–30 nm for the present system that corresponds to concentration of about 33–1.6 vol %). Their expression for dependence of osmotic pressure on clay concentration gives excellent prediction of the experimental data. Since the osmotic pressure gradient drives the flow of water through porous sediment, they used Darcy's law to predict flow rate. If  $\Delta P$  is the pressure difference over the radius of the cluster, the flux of water having viscosity  $\mu$  is given by  $Q=k_p A \Delta P/(\mu R)$ , where  $k_p$  is a dimensionless constant that depends on the porosity and characteristic features of the cluster (porous object) and  $A$  is the surface area of the sphere. Considering an incremental swelling step, where flux  $Q$  over time  $dt_w$  causes an increase in volume by  $dV$ , we get  $Q dt_w = dV$ .<sup>19</sup> This leads to  $\mu R dR = \Delta P k_p dt_w$ . Based on the analytical solution for Poisson-Boltzmann equation, Martin *et al.*<sup>19</sup> argued that the dependence of product  $k_p \Delta P$  on volume fraction of laponite in the cluster (and hence time) can be neglected in the concentration regime of interest. The above equation can be easily integrated to predict the size of the swelling cluster under osmotic pressure gradient with respect to time to yield

$$\xi(t_w) = [1 + (D t_w/R_0^2)]^{1/2}, \quad (4)$$

where  $t_w$  is waiting time and  $D$  is characteristic diffusivity of the swelling process in the limit of small volume fraction of laponite. It is given as  $D=2\Delta P k_p/\mu \approx 4(\pi kT)^2 \varepsilon_0 \varepsilon_r a^2/45e^2 t_l^2 \mu$ , where  $k$  is Boltzmann constant,  $T$  is absolute temperature,  $\varepsilon_0$  is permittivity of vacuum,  $\varepsilon_r$  is relative permittivity of water medium,  $e$  is unit charge,  $t_l$  is thickness of laponite plate, and  $a$  is equivalent radius that gives the same mass per particle as a laponite particle (0.82 nm).<sup>19</sup> Thus, the characteristic diffusivity can be readily evaluated by knowing the temperature of the system.

Immediately after filtration, the system is filled with many clusters undergoing Brownian motion. As the volume

fraction of clusters  $\xi(t_w)^3 \phi / \psi$  goes on increasing, the available space that is not occupied by clusters decreases and the dynamics of the system slows down. This increases the corresponding characteristic time scale of the system. This process is akin to glass transition, where, as the temperature of a glass forming liquid is decreased, the movement of the constituent molecules gets constrained. If we apply this analogy to the present system, the growth of the cluster can be considered equivalent to decreasing the temperature of the molecular glass formers. Under such conditions we can estimate the characteristic relaxation time of the system using mode coupling theory, which describes the behavior of colloidal glasses very well. The relaxation time predicted by the mode-coupling theory is given by<sup>21</sup>

$$\tau = \tau_0 e^{-\gamma}, \quad (5)$$

where  $\tau_0$  and  $\gamma$  are the fitting parameters.

The characteristic relaxation time can be obtained by incorporating Eqs. (2) and (4) into Eq. (5). The model has three fitting parameters, volume of laponite in the cluster ( $R_0^3 \psi$ ),  $\tau_0$ , and  $\gamma$ . The first parameter arises naturally in the formulation and cannot be prescribed *a priori*. This is because the radius of cluster and the volume fraction of laponite inside a cluster at time  $t_w=0$  are strongly dependent on the time of stirring. The latter parameter  $\tau_0$  is observed to be of order unity for the present system. Equation (4) can be incorporated in Eq. (3) to predict the transition time at which the system enters a nonergodic or full aging regime and is given by

$$t_w^* = \phi_c^{2/3} (R_0 \psi^{1/3})^2 / (D \phi^{2/3}). \quad (6)$$

However, due to uncertainty in getting reproducible data,<sup>5</sup> it is difficult to validate this expression experimentally as it demands ( $R_0^3 \psi$ ) to be identical in every experiment. Combining Eqs. (2)–(6), we get

$$\tau / \tau_0 = [1 - (t_w / t_w^*)^{3/2}]^{-\gamma}, \quad t_w < t_w^*. \quad (7)$$

Thus, knowledge of  $\tau_0$  and  $t_w^*$  determine the nature of evolution of relaxation time for a given value of  $\gamma$ .

## DISCUSSION

In Fig. 1, the characteristic dimensionless time scale ( $\tau / \tau_0$ ) of the suspension is plotted as a function of dimensionless age of the sample ( $t_w / t_w^*$ ) for 2 and 2.75 wt % suspension of laponite in water,<sup>5</sup> while an inset shows a log-log plot of  $\tau / \tau_0$  vs  $1 - (t_w / t_w^*)^{3/2}$ . As shown in the figure, Eq. (7) with  $\gamma=2.58$  provides an excellent fit to the experimental data. Since the experimental data is made dimensionless by the model parameters that are obtained from the experiments (namely,  $\tau_0$  and  $t_w^*$ ), only a unique value of  $\gamma$  can fit the given data set. Interestingly,  $\gamma=2.58$  is the same value for which classic mode coupling theory predicts glass transition in the monodispersed spherical particles.<sup>21</sup> However, the real sample of laponite suspension is expected to have size distribution of clusters and hence a fit of  $\gamma=2.58$  to the experimental data might be coincidental. As the volume fraction of the clusters approaches  $\phi_c$ , the characteristic time scale approaches the age of the system and undergoes a transition

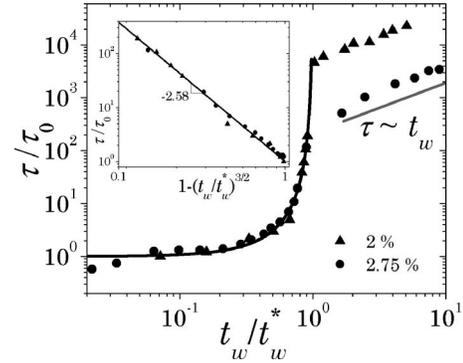


FIG. 1. The characteristic dimensionless time scale ( $\tau / \tau_0$ ) of the suspension is plotted against dimensionless age of the sample ( $t_w / t_w^*$ ) for 2 and 2.75 wt % suspensions, of laponite in water. Line is Eq. (7) while the experimental data is taken from Fig. 2 of Schosseler *et al.* (Ref. 5). For 2% sample,  $\tau_0=2.9$  s and  $t_w^*=13\,600$  s while for 2.75% sample  $\tau_0=0.94$  s and  $t_w^*=5500$  s. Inset shows the same data and the fit, plotted against  $1 - (t_w / t_w^*)^{3/2}$ , in the ergodic regime. A power law with exponent of  $-2.58$  uniquely fits the data.

from a cage forming regime (ergodic) to a full aging regime (nonergodic). This might not be a sharp transition as the glassy state is attained only after laponite particles occupy the available space completely, thus highlighting the role of the length scale probed in the experiment. Consequences of this result are discussed later in the paper. In the full aging regime, the system shows a linear relationship between characteristic time scale and age. In the present model, in order to keep the analysis simple, we have considered osmotic swelling of clusters having the same initial radius. According to Eq. (4), consideration of polydispersity in the initial radius of cluster will lead to a change in polydispersity with age. We believe that the simplistic model and assumptions proposed in the present manuscript is the first step to theoretically investigate the ergodicity breaking mechanism in this system. A quantitative prediction provided by the present model is indeed encouraging in that respect.

The relaxation time obtained by Eq. (7) is a slow mode representing the characteristic time associated with the cage diffusion process. In many experiments that observe the rapid increase in slow relaxation mode with respect to time employ submicron size tracer particles to strengthen the signal.<sup>5</sup> As clusters grow, the movement of these tracer particles gets confined to smaller and smaller regions in space. Although this does not significantly affect characteristic time associated with rattling motion within the confined space (fast mode), the time required to escape the cage formed by neighboring clusters increases rapidly. However, the dynamics of the tracers is still diffusive in nature leading to  $q^{-2}$  dependence. As growing laponite clusters fill the available space completely, cage diffusion becomes extremely sluggish and the corresponding hyperdiffusive time scale scales with age.

The concept modeled in this paper is similar to one of the ideas proposed by Tanaka *et al.*,<sup>15</sup> where they speculate that the system becomes nonergodic after the growing clusters of aggregates fill up the space. However, the present model is very different from that proposed by the same group,<sup>15</sup> where they argue that the average barrier height for

particle motion grows linearly with age in the ergodic regime. They estimate the conductivity of the laponite suspension with respect to its age. They found that the conductivity increases almost linearly with the aging time in the ergodic regime, but tends to saturate in the nonergodic regime. The increase in conductivity reflects the reduction in the number of strongly bound counterions. Our model is in agreement with this observation. As the cluster size increases, more and more counterions diffuse away into the bulk increasing the conductivity. As the clusters fill up the space, along with laponite particles, the concentration of counterions also becomes uniform, leading to saturation in the conductivity.

The present model clearly distinguishes between the ergodic state and nonergodic state based on the physical structure that exists in these two states. In the former state, clusters or agglomerates of laponite platelets are present, while in the latter regime, single laponite particle is an independent entity. It is well-known that aqueous suspension of laponite, when it is in the nonergodic regime, undergoes rejuvenation due to excessive deformation.<sup>22</sup> However, according to the proposed physical picture, the model clearly states that, due to rejuvenation, the system cannot cross the ergodic-nonergodic transition point and enter the ergodic regime. This means that exponential-like rapid increase in slow relaxation mode cannot be observed again. This observation has significant implications in analyzing the rheological behavior of laponite suspensions. Furthermore, Eq. (6) predicts inverse relationship between transition time and characteristic diffusivity. We have seen that temperature dependence of characteristic diffusivity ( $D \propto (kT)^2 \epsilon_r / \mu$ ) comes from three terms, namely,  $(kT)^2$ , permittivity of water, and viscosity of water. Viscosity of water can be considered to depend on temperature as  $\mu = \mu_0 e^{\bar{U}/kT}$ , while permittivity of water, though explicit analytical expression for its dependence on temperature does not exist,<sup>23</sup> decreases weakly compared to that of viscosity of water. Overall, transition time is expected to show significant decrease with respect to temperature. Ramsay<sup>24</sup> studied the effect of temperature on rheological properties of aging laponite suspension and observed pronounced increase in elastic modulus with age at higher temperature. This observation matches very well with the prediction of the model.

Nicolai and Cocard<sup>25</sup> carried out static light scattering experiments on the aqueous laponite dispersions in the concentration range of 0.025 to 0.5 wt %. They observed that intensity of scattered light decays significantly in the initial 5 h followed by a very sluggish decay. Dynamic light scattering experiments on the same sample after one day showed the system to be still ergodic, as expected for such low concentration of laponite, and suggested the presence of individual laponite particles or an incomplete dispersion of the oligomers with a broad size distribution. An initial decay in the intensity of scattered light, which eventually leads to oligomers or individual laponite particles, can be very well explained by the present model. As various clusters grow in size, water content in the same increases, which decreases with relative difference in the refractive index between water and the cluster, decreasing the intensity of scattered light.

Schosseler *et al.*<sup>5</sup> have discussed various features of er-

godic to nonergodic transition in great detail. They observed that immediately after filtration, the viscosity of the suspension as recorded by the diffusivity of the tracer particles is of the order of a few millipascals. This observation further strengthens the assumption that laponite is present in the form of tiny clusters immediately after filtration. Schosseler *et al.*<sup>5</sup> further observed that the full aging behavior is first seen while investigating large length scales in the aging suspension of laponite. In the present paper, we argue that transition to nonergodic regime occurs when growing clusters of laponite touch each other. However, the space between the clusters when they touch each other still contains low viscosity aqueous medium which is ergodic in nature. Thus, the transition to full aging regime will not be observable until the probed length scale is larger than the space between the growing clusters. The model captures this behavior very well. Thus, the proposed model rightly captures various experimental observations in the ergodic regime of aqueous suspension of laponite.

## CONCLUSION

We have modeled a new mode of glass transition in which clusters of laponite particles undergo osmotic swelling and enter the nonergodic state as they span the available space. As the clusters fill up the space, cage diffusion process becomes very sluggish. The mode coupling formalism along with the proposed mechanism provides an excellent prediction of the associated relaxation time dependence on age. The model also predicts that the ergodic to nonergodic transition is first observed at large length scales and it occurs at early age for higher temperature. These predictions are in agreement with experimental observations.

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<sup>1</sup>P. G. Debenedetti and F. H. Stillinger, *Nature (London)* **410**, 259 (2001).

<sup>2</sup>K. J. Dong, R. Y. Yang, R. P. Zou, and A. B. Yu, *Phys. Rev. Lett.* **96**, 145505 (2006).

<sup>3</sup>P. N. Pusey and W. Van Meegen, *Phys. Rev. Lett.* **59**, 2083 (1987).

<sup>4</sup>V. Viasnoff and F. Lequeux, *Phys. Rev. Lett.* **89**, 065701 (2002).

<sup>5</sup>F. Schosseler, S. Kaloun, M. Skouri, and J. P. Munch, *Phys. Rev. E* **73**, 021401 (2006).

<sup>6</sup>S. Bhatia, J. Barker, and A. Mourchid, *Langmuir* **19**, 532 (2003).

<sup>7</sup>B. Ruzicka, L. Zulian, and G. Ruocco, *Phys. Rev. Lett.* **93**, 258301 (2004).

<sup>8</sup>R. Bandyopadhyay, D. Liang, H. Yardimci, D. A. Sessoms, M. A. Borthwick, S. G. J. Mochrie, J. L. Harden, and R. L. Leheny, *Phys. Rev. Lett.* **93**, 228302 (2004).

<sup>9</sup>P. Levitz, E. Lecolier, A. Mourchid, A. Delville, and S. Lyonnard, *Europhys. Lett.* **49**, 672 (2000).

<sup>10</sup>D. Bonn, H. Tanaka, G. Wegdam, H. Kellay, and J. Meunier, *Europhys. Lett.* **45**, 52 (1998).

<sup>11</sup>F. Sciortino and P. Tartaglia, *Adv. Phys.* **54**, 471 (2005).

<sup>12</sup>D. Bonn, H. Kellay, H. Tanaka, G. Wegdam, and J. Meunier, *Langmuir* **15**, 7534 (1999).

<sup>13</sup>B. Abou, D. Bonn, and J. Meunier, *Phys. Rev. E* **64**, 215101 (2001).

<sup>14</sup>M. Bellour, A. Knaebel, J. L. Harden, F. Lequeux, and J.-P. Munch, *Phys. Rev. E* **67**, 031405 (2003).

- <sup>15</sup>H. Tanaka, S. Jabbari-Farouji, J. Meunier, and D. Bonn, *Phys. Rev. E* **71**, 021402 (2005).
- <sup>16</sup>S. Mossa, C. De Michele, and F. Sciortino, *J. Chem. Phys.* **126**, 014905 (2007).
- <sup>17</sup>P. Mongondry, J. F. Tassin, and T. Nicolai, *J. Colloid Interface Sci.* **283**, 397 (2005).
- <sup>18</sup>H. Van Olphen, *An Introduction to Clay Colloid Chemistry* (Wiley, New York, 1977).
- <sup>19</sup>C. Martin, F. Pignon, A. Magnin, M. Meireles, V. Lelievre, P. Lindner, and B. Cabane, *Langmuir* **22**, 4065 (2006).
- <sup>20</sup>D. F. Evans and H. Wennerstrom, *The Colloidal Domain* (Wiley, New York, 1994).
- <sup>21</sup>W. Gotze and L. Sjogren, *Rep. Prog. Phys.* **55**, 241 (1992).
- <sup>22</sup>D. Bonn, S. Tanasc, B. Abou, H. Tanaka, and J. Meunier, *Phys. Rev. Lett.* **89**, 157011 (2002).
- <sup>23</sup>A. Catenaccio, Y. Daruich, and C. Magallanes, *Chem. Phys. Lett.* **367**, 669 (2003).
- <sup>24</sup>J. D. F. Ramsay, *J. Colloid Interface Sci.* **109**, 441 (1986).
- <sup>25</sup>T. Nicolai and S. Cocard, *Langmuir* **16**, 8189 (2000).