Chemical Physics 423 (2013) 167–172

Contents lists available at SciVerse ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

Discrimination of Sol and Gel states in an aging clay suspension

F. Shayeganfar [a,b,*], M. Sadegh Movahed [c,d], G.R. Jafari [c,d]

[a] Department of Physics, Sharif University of Technology, 11365-9161 Tehran, Iran
[b] Département de Génie Physique et Regroupement Québécois sur les Matériaux de Pointe (RQMP), École Polytechnique de Montréal, Montréal, Québec H3C 3A7, Canada
[c] Department of Physics, Shahid Beheshti University, G.C., Evin, 19839 Tehran, Iran
[d] The Abdus Salam International Centre for Theoretical Physics, Strada Costiera 11, I-34013 Trieste, Italy

ARTICLE INFO

Article history:
Received 20 December 2012
In final form 12 July 2013
Available online 24 July 2013

Keywords:
Stochastic analysis
Colloidal particles
Sol–gel
Light scattering
Coexistence state

ABSTRACT

The dynamical scattered light intensity and multiplicative cascade model was employed to characterize the anisotropic charged colloidal particles suspension during the so-called *Sol–Gel* transition. Generally we looked for finding a criterion to distinguish the properties of *Sol* and *Gel* states systematically. The probability density function (PDF) of the light scattering intensity shows an obvious change with proceeding of the sample aging process (during of gelation state). Our results confirmed that in the so-called *Sol* state, the value of non-Gaussian parameter, λ_w^2, as a function of time is larger than that of for weak-*Gel* or in coexistence *Sol–Gel* state. The number of cascades in the weak-*Gel* is smaller than the rest of states. In addition, we found out a deviation from Kolmogorov–Obukhov hypothesis concerning the linear dependance of λ_w^2 to the logarithm of scale.

1. Introduction

Colloidal suspensions have recently considered as a complex model with a very rich phase diagram, encompassing fluid, gel and glasses states therefore scientific researches have been dealt with the accumulation and gelation condensed colloidal suspensions from fundamental as well as technical points of view [1–6]. The terminology *Sol–Gel* transition as an important behavior in the aging phenomena, refers to a liquid mixture where solute particles are suspended in a solvent [7] and occurs in the various field ranging from advanced material preparation, biomaterial, agricultural, building products, household and personal care products to powder processing of ceramics [1,8,9]. The colloidal gels are ideal models for the study of the internal dynamics and elasticity of highly disordered networks, therefore there are many motivations to explore the physical properties and chemical characteristics of mentioned systems [10,11].

Initially the sol particles are separated (pre-gelation), but under appropriate conditions, with the proceeding of the laponite aging process and increasing the strength attraction, the coexistence region will be created (*Sol–Gel* transition) and eventually at the gelation point, they aggregate until a percolation network is formed and the system stops flowing [7]. For colloidal gels as physical gels bonds originate from physical interactions of order k_BT, therefore, they are transient and clusters break and reform continuously [7].

The first model and the mean-field theory of percolation to describe the *Sol–Gel* transition has been established by Flory and Stockmayer [12], where they have ignored the closed loops in the percolating picture and the gelation was modeled on a special type of lattice, the so-called Cayley tree. Another approaches to deal with the *Sol–Gel* transition are the chemical-kinetic theory [13] and percolation model [13,14]. Transition from *Sol* to *Gel* has been reported as a second order state transition [15]. Yilmaz et al. examined the percolation theory to measure the critical exponents and fractal dimension during *Sol–Gel* transition in the fluorescence intensity series sample. They also showed that during gelation the value of fractal dimension to be sensitive and could be a benchmark to demonstrate transition event [16].

The detection of gelation has been established through a variety of techniques and criteria [17,18]. Various groups have investigated the properties of colloidal gels at low particle density and their transition [19,20]. Many studies have been devoted to the *Sol–Gel* transition in systems based on polymers [21,22], natural gelatin [23], gels based on spherical colloids [2,3,24]. Generally, standard experimental method to investigate the gelation process with out disturbing system is known as dynamic of light scattering [2,3,25]. The following methods and benchmarks have been reported to examine the *Sol–Gel* transition based on dynamic light scattering (DLS) approach [26,27]: (1) At the gel point, an extreme change in the amplitude of scattering intensity is detected. (2) Power-law behavior or suppression in its initial amplitude of intensity time correlation represents state transition. (3) Gel point

* Corresponding author at: Département de génie physique et Regroupement québécois sur les matériaux de pointe (RQMP), École Polytechnique de Montréal, Montréal, Québec H3C 3A7, Canada.

E-mail address: shayegan-far.farzaneh@polymtl.ca (F. Shayeganfar).

0301-0104/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.chemphys.2013.07.007

could be recognized by a characteristic broadening in the distribution function obtained by inverse Laplace transform of intensity-time correlation function. Beside DLS method, oscillatory Shear Rheology reported by Chambon and Winte is also another method to find out gel point [28].

Despite the capability of utilized methods from various points of view [16,25,29], but limitations and ambiguities to use this framework emerge some problems. As an example, the interference of light scattering due to different clusters in the DLS experiment imposes the ambiguity in the nature of correlation function. In addition during state transition the ergodicity of the sample is under debate so to find reliable results one must use ensemble average instead of time average.

This work investigates a robust method which is known as the notion of cascade model [30–33] to examine the *Sol–Gel* transition during the aging process in a typical system, namely Laponite XLG, a synthetic layered silicate (see more details in Section 3) [34–36]. Castaing et al. proposed a multiplier method to model the PDF of the data set at different time scales [37]. This method is known as log-normal cascade model and was introduced to study of fully developed turbulence [31,32,37–41]. However it has been applied in diverse fields of research such as solar and wind energies [42], foreign exchange rate [43], stock index [44,45], human heartbeat fluctuations [46] and seismic time series [47]. Here we will put particular emphasis on the non-Gaussian nature of the detrended light scattering intensity fluctuations, using a multiplicative model. As the gelation approached, the PDF of scattered light intensity changes, exhibiting a state transition from a scale-invariant to a scale-dependent behavior. Meanwhile, It must point out that colloidal dispersions offer a powerful testing ground for fundamental issues in statistical with attention turning to non-equilibrium phenomena [48–50].

The rest of this paper is organized as follows: In Section 2 we will give a brief explanation about probability density function in the multiplicative log-normal cascade model. The sample preparation and experimental setup to record the intensity of light scattering are introduced in Section 3. Application of cascade model to explore state transition in colloidal suspension will be presented in Section 4. The last section is devoted to discussion and conclusions.

2. Multiplicative log-normal cascade models

It has been suggested that the probability density function (PDF) associated with a stochastic variable in a typical multiplicative process can be modeled by a non-Gaussian function with fat tails [39,40,51–53]. In this approach, for a fixed t, the relation between stochastic fluctuation, $u_w(t)$ at scale w and $u_\tau(t)$ at scale $\tau \equiv \eta \times w$ is given through the cascading rule,

$$u_{\eta\times w}(t) = \psi_\eta u_w(t), \quad \forall w,\ \eta > 0, \tag{1}$$

where $\ln(\psi_\eta)$ is a random variable. A typical hierarchy phenomenon constructed by using iterative procedure can be modeled as follows:

$$u_w(t) = \xi_w(t)e^{\omega_w(t)} \tag{2}$$

where $\xi(t)$ and $\omega(t)$ possess both independent Gaussian probability density function with zero mean and variance σ_w^2 and λ_w^2, respectively. Eq. (2) was demonstrated to model turbulent fluctuations describing how the stochastic fluctuations evolve from coarse to fine scales. The probability density function associated with stochastic variable, u_w, has been introduced by Castaing et al. [37], and it has the following expression,

$$P_w(u_w) = \int_0^\infty G(\ln\sigma)\, F\left(\frac{u_w}{\sigma}\right) d(\ln\sigma), \tag{3}$$

where

$$\begin{aligned} G(\ln\sigma) &= \tfrac{1}{\sqrt{2\pi\lambda_w^2}} \exp\left(-\tfrac{\ln^2(\sigma/\sigma_w)}{2\lambda_w^2}\right) \\ F\left(\tfrac{u_w}{\sigma}\right) &= \tfrac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\tfrac{u_w^2}{2\sigma^2}\right) \end{aligned} \tag{4}$$

For $\lambda_w^2 \to 0$ the $P_w(u_w)$ converges to a Gaussian function. Therefore, λ_w can be a criterion to determine the non-Gaussianity of underlying process.

In order to estimate the non-Gaussian parameter λ_w^2, we use likelihood statistics [54,55]. To this end the model parameters is labeled by $\{\theta\} : \{\lambda_w, \sigma_w\}$. The so-called chi-square, χ^2 parameter marginalized over the nuisance parameter, σ_w is defined as:

$$\chi^2(\lambda_w) = \sum_{u_w} \int d\sigma_w \frac{\left[P_w(u_w) - P_{\text{Casting}}(u_w; \lambda_w, \sigma_w)\right]^2}{\left[\sigma^2_{\text{numeric}}(u_w) + \sigma^2_{\text{Castaing}}(u_w, \lambda_w, \sigma_w)\right]} \tag{5}$$

here $P_w(u_w)$ is computed directly from series and $P_{\text{castaing}}(u_w; \lambda_w, \sigma_w)$ is given by Eq. (3). Also, σ_{numeric} is the mean standard deviation of $P_w(u_w)$ and σ_{castaing} is associated with probability density function derived by the left hand side of Eq. (3). The global minimum value of χ^2 corresponds to the best value of λ_w^2. The numerical marginalizing over the so-called nuisance parameter, σ_w, is more time consuming, to resolve this inconvenience, one can rewrite cascade model as:

$$P_w(u_w) = \int_0^\infty \frac{1}{\sqrt{2\pi\lambda_w^2}} \exp\left(-\frac{\ln^2(\sigma/\sigma_w)}{2\lambda_w^2}\right) \times \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{u_w^2}{2\sigma^2}\right) d(\ln\sigma). \tag{6}$$

Since we use data with zero mean and unit variance through this study, then to make consistency in Eq. (6), we choose $\sigma_w = \exp(-\lambda_w^2)$ [53].

There is also another method to determine non-Gaussian parameter λ_w^2, which is proposed by Beck [56]. To this end, the λ_w^2 is related to the flatness of the increments as $\lambda_w^2 = \ln(F_w/3)$, where $F_w = \langle u_w^4 \rangle / \langle u_w^2 \rangle^2$. In addition to two mentioned methods, there is also another robust method proposed by Ken Kiyono et al. to determine non-Gaussian parameter, λ_w^2. In this approach, the qth order of absolute moments is computed [53]. According to Eq. (6), the qth order of absolute moment can be read as:

$$\begin{aligned} \langle |u|^q \rangle &= \int_{-\infty}^{+\infty} |u|^q\, P_w(u)\, du \\ &= \int_{-\infty}^{+\infty} du |u|^q \int_0^\infty \frac{1}{\sqrt{2\pi\lambda_w^2}} \exp\left(-\frac{\left(\ln(\sigma) + \lambda_w^2\right)^2}{2\lambda_w^2}\right) \\ &\quad \times \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{u^2}{2\sigma^2}\right) d(\ln\sigma) \\ &= \exp\left(\frac{q(q-2)\lambda_w^2}{2}\right) \frac{2^{\frac{q}{2}}\Gamma\left(\frac{1+q}{2}\right)}{\sqrt{\pi}} \end{aligned} \tag{7}$$

From above equation we can determine λ_w as follows

$$\lambda_w^2 = \frac{2}{q(q-2)} \left[\ln(\langle |u|^q \rangle \sqrt{\pi} 2^{-\frac{q}{2}}) - \ln\Gamma\left(\frac{1+q}{2}\right)\right] \tag{8}$$

where $q > -1$ and $q \neq 0, 2$. The value of $\langle |u|^q \rangle$ is evaluated from data set, $\{u(t)\}$, with zero mean and unit variance. It has been demonstrated that the uncertainty in determining λ_w based on Eq. (8) is small for small values of q [52].

In present work, we explore time evolution of experimental scattered light intensity. We use the light intensity fluctuations as an input data set and investigate taking place a peculiar transition from a low viscosity liquid like state expressed as the so-called