Colloids and Surfaces A 531 (2017) 93–98

Contents lists available at ScienceDirect

Colloids and Surfaces A

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

Dynamic particle packing in freezing colloidal suspensions

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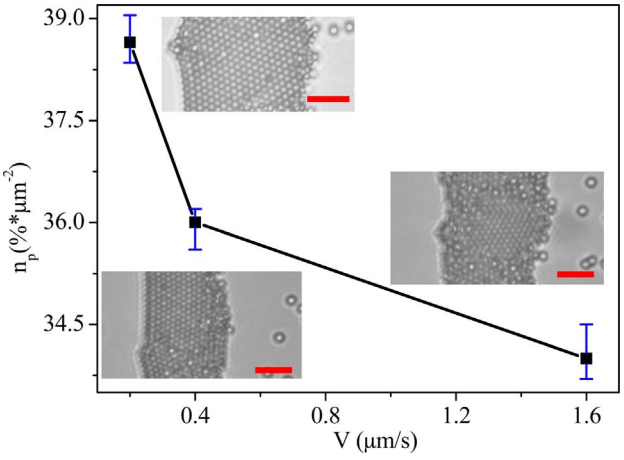
GRAPHICAL ABSTRACT

(n_p is number density in close-packed state. V is pulling speed).

In the field of freezing colloidal suspensions, it is important to understand the particle-scale behavior of particle packing. Here, we reveal the dynamics of particle packing by identifying the behavior of each single particle in situ. The typical pattern consists of locally ordered clusters and amorphous defects. The microscopic mechanism of pattern formation is ascribed to the non-equilibrium particle-packing process on the particle scale, described with the dimensionless Péclet number. The macroscopic migration of a particle layer is also revealed by an analytical model involving parameters of freezing speed and initial volume fraction of particles.



ARTICLE INFO

Keywords:
Colloidal suspensions
Freezing
Particle self-assembly
In-situ revealing

ABSTRACT

In the field of freezing colloidal suspensions, it is important to understand the particle-scale behavior of particle packing. Here, we reveal the dynamics of particle packing by identifying the behavior of each single particle in situ. The typical pattern consists of locally ordered clusters and amorphous defects. The microscopic mechanism of pattern formation is ascribed to the non-equilibrium particle-packing process on the particle scale, described with the dimensionless Péclet number. The macroscopic migration of a particle layer is also revealed by an analytical model involving parameters of freezing speed and initial volume fraction of particles.

1. Introduction

Freezing of colloidal suspensions is ubiquitous in nature and technology [1]. It is an important factor in many research areas, such as ice templating of porous ceramics [2], polymers and composites [3], bone tissue engineering [4], science of soft matter [5,6], geophysical

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http://dx.doi.org/10.1016/j.colsurfa.2017.07.073
Received 22 May 2017; Received in revised form 24 July 2017; Accepted 25 July 2017
Available online 26 July 2017

science [7], thermal energy storage [8], crystal growth [9], cryobiology [10], etc. In all of these cases, the segregation of particles from the growing ice and the consequent increase of particle concentration in the fluid regions are vital. In particular, the arrangement of segregated particles on the scale of single particles is important, because the particle-scale structure is the key to understanding the rejection of particles and hence predicting the large-scale structure [11].

During freezing of a suspension, particles are expelled from ice [12,13], forming a close-packed layer in front of the freezing interface. This process can cause self-assembly of the particles [14] similar to that caused by drying [15,16] or sedimentation [17] of colloidal suspensions. Similarities between these patterns suggest that the physics underlying the colloidal behavior may be similar, though the driving forces in each case differ. Therefore, knowledge gained from studying particle packing in freezing colloidal suspensions may be applicable to colloidal suspensions in diverse circumstances, such as drying or sedimentation of colloidal suspensions.

Researchers have tried to reveal dynamic particle packing during freezing colloidal suspensions through theoretical models [18], experiments [11,14,19–27] and simulations [28], but are still far from a complete understanding of the phenomenon [26,27]. Presently, there is no theory that can fully predict the morphology or detailed characteristics of particle packing. Previous theories assume that the particles in the condensed layer form a random close packing [18], and the condensed layer is considered uniform with an average particle density. However, the detailed structure and dynamics of the condensed layer has not previously been identified by experiments on the scale of individual particles. Most studies involve a posteriori analysis of samples after fixing the particle structure [22–25]. They provided only static information about the final arrangement of particles. Some experiments have tried to resolve the dynamic behavior of particle layers by using X-ray radiography and tomography [19–21,26,27] as well as small-angle X-ray scattering [11]. X-ray techniques can probe inside visibly opaque materials. X-ray tomography can even provide a full three-dimensional reconstruction of the samples. However, none of these techniques provided information about the dynamic packing status on the scale of individual particles due to limited spatial resolution ($^{>}$ 1 μm) in fast X-ray tomography (temporal resolution $<$ 1 s) [29]. Molecular dynamics simulations [28] have been also used to investigate dynamic particle packing during freezing suspensions, which stimulates us to conduct laboratory experiments to gain information about how real systems behave.

In this Letter, we present in-situ observation of dynamic particle packing on the scale of individual particles made during directional freezing in carefully controlled experiments. A uniform thermal gradient and a constant pulling speed are controlled independently [30]. The typical pattern in the close-packed particle layer consists of locally ordered clusters and amorphous defects. The microscopic mechanism of pattern formation is investigated by particle packing process on the particle scale. Finally, the mechanisms of macroscopic particle layer migration are quantified by an analytical model involving parameters of freezing speed and initial volume fraction of particles.

2. Experiments

In our experiments, a narrow-gapped sample cell was designed to obtain quasi-two-dimensional, mono-layer suspensions of micron-sized spherical particles in which the packing behavior of individual particles could be identified. The manufacturing and operation of the colloidal-monolayer sample cells is identical to Ref [31]. The glass surfaces were rigorously cleaned by chromic acid and deionized water for three times, so that particles did not stick to the walls. The colloidal suspensions were brushed onto a glass slide and another glass slide was used to seal the suspensions. Finally, edges of the slides were glued together with epoxy adhesives to form a sample cell of fixed thickness. The gap ($\approx$2.6 μm) between the slides was a little larger than the diameter ($\approx$1.73 μm) of the particles to allow Brownian motion of the monolayer of particles. The particles floated around midplane of the cell because the density of particles (1.03 g/cm^3) matches with water (1 g/cm^3) very well. A high-precision, directional-solidification apparatus was used to freeze the colloidal suspensions. The details of the apparatus are given in the Supplementary Material. The part of temperature gradient which is of great importance on the whole apparatus is with high linearity on both static and dynamic cases [30]. A CCD camera with 2580 × 1944 sensitive elements on a time-lapse video recorder (one frame per second) was used to make continuous recordings [30]. The large optical contrasts between the areas of ice, close-packed particles and suspensions allowed a simple image-analysis technique to be employed. We used suspensions of polystyrene microspheres (PS) approximating hard-sphere interactions, which is an ideal system to investigate the freezing of colloidal suspensions [32]. The mean diameter of PS particles used was d = 1.73 μm, with poly-dispersity smaller than 5% (Bangs Lab, USA). The thickness of the sample cell was around 2.6 μm, which is confirmed by Supplementary Movie S1. The general criterion of the thickness is the out-plane fluctuation along the direction of thickness [31]. The length and width of the sample cell were approximately 80 mm and 20 mm respectively, which are about four orders of magnitude larger than the thickness. The particle packing density n, defined as particle number per μm^2 (i.e., two-dimensional area number density), in the quasi two-dimensional thin-film suspensions, is used to represent the volume fraction of particles.

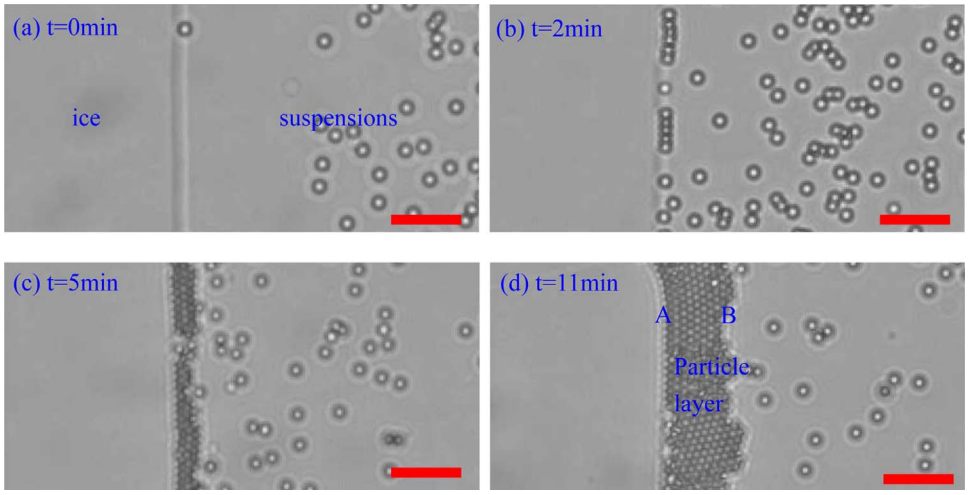

Fig. 1. Dynamic creation of a close-packed particle layer during directional freezing of colloidal suspensions with a thermal gradient G = 9.24 K/cm and pulling speed V = 0.4 μm/s from right to left. The left side of the sample is the cooling zone, while the right side of the sample is the heating zone. A is freezing interface of ice and B is packing interface of particles. The scale bars are 10 μm.