



Clustering in binary mixtures of axial multipoles confined to a two-dimensional plane



Manjori Mukherjee, Sanat Kumar, Pankaj Mishra *

Department of Applied Physics, Indian School of Mines, Dhanbad- 826004, India

HIGHLIGHTS

- Clustering in 2D binary mixtures of multipolar colloidal particles is studied.
- Analysis of pair structures reveals partial clustering in all the cases.
- Dipoles show larger clusters which decreases successively for quadrupoles and octupoles.
- Cluster extent changes with interaction strength, asymmetry and composition.

ARTICLE INFO

Article history:

Received 17 April 2014

Received in revised form 27 June 2014

Available online 8 September 2014

Keywords:

Colloids

Binary mixture

Multipoles

Clustering

ABSTRACT

Structures in the binary mixtures of model charged colloidal particles resembling axial multipoles confined to a two-dimensional plane have been studied with special attention to clustering, using hypernetted chain integral equation theory. The multipolar symmetric axes of the particles are assumed to be directed along the normal to the plane of confinement. Particles in the mixtures interact via purely repulsive potential proportional to the $(2l+1)$ -th power of the inverse interparticle separation. Corresponding to the values of l being equal to 1, 2 and 3, we have three different binary mixtures comprising dipoles, quadrupoles, and octupoles respectively. We observe that the structural features of the three systems are distinct from each other and changes significantly with the variation in the characterizing parameters of the mixture. Smaller particles of the mixture are found to form clusters marked by the emergence of a prepeak preceding the principal peak of their partial structure factors of all the three systems. Size of the clusters is found to be largest for the dipoles, and decreases successively for the quadrupoles and octupoles. Simultaneously we notice that the clusters are most diffused for the dipolar system but become sharp with well defined boundaries as we move to the mixtures of higher order multipoles. Cluster size and its sharpness are found to depend on the interaction strength, particle asymmetry and the composition of the mixtures. Fluid phase of the mixtures remains macroscopically homogeneous and no phase separation is observed.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

A system of large number of mesoscopic particles, having characteristic diameter in the range of $10\text{--}10^3$ nm, dispersed in a suspending fluid is known as a colloidal suspension [1,2]. The scientific interest in such systems stems from the fact that unlike ordinary molecular systems, where the underlying interactions are generally complex and predefined, the inter-particle

* Corresponding author. Tel.: +91 9470194401.

E-mail address: mpankaj@gmail.com (P. Mishra).

interaction potentials in colloidal systems are in general much simpler and easier to control or modify externally [3,4]. Owing to their small size and the forces exerted upon them through the dispersive media [3,5–7], colloidal particles have the ability to self assemble into a diverse set of structures [8–18]. Self assembling is a dynamic reverse process towards thermodynamic minimum-energy structure, controlled by a complex balance of essentially many body attractive and repulsive interactions [19]. This process is of key relevance for the construction of devices with desired mechanical, rheological and optical properties having applications ranging from drugs to dairy products. Since the colloidal forces dictate the suspension stability along with the self-assembled structure quality, a clear understanding of the effect of various types of interactions on the structural behavior of colloidal suspensions is essential.

In recent years, the investigation of colloidal particles trapped at fluid interfaces which form effectively a two-dimensional system has gained much interest [20–37]. As the behavior and structural properties of the condensed matter depend sensitively on the spatial dimension, these model systems offer a rich spectrum of phenomena which are rather distinct from three-dimensional (3D) bulk properties. For example, depending upon the interaction potential, 2D systems are reported to show heterogeneous structures with aggregated particles [38], formation of homogeneous colloidal films with different degrees of order [39,40] and structures with mesoscopic order [41–43] for which there are no equivalent structures in 3D. Additionally, the longer range of interparticle interaction and fundamentally different character of melting transitions [44–47] are some important features which distinguish 2D from 3D.

It has been observed that the Van der Waals forces and hydrophobic interactions in colloidal suspensions lead primarily to close packed structures such as colloidal crystals when the assembly is performed in the bulk fluid [48–50] and to particle aggregates or clusters when the assembly process is confined to the interior of an emulsion droplet or to a liquid–liquid interface [11,51]. Equilibrium clusters have been observed in systems of particles interacting via the competition between a short-ranged attraction and a long-ranged repulsion [52,53]. Clustering occurs even in the complete absence of attractions, provided that the repulsive potential is bounded and decays rapidly to zero at large interparticle distances [54]. Hoffmann et al. [29] have studied a binary mixture of superparamagnetic colloidal particles confined to a 2D water–air interface interacting via repulsive dipole–dipole interparticle potential and have observed partial clustering of small particles in the voids created by unclustered big particles. Similar results of the clustering of small particles in two dimensional binary mixture of point dipoles have been demonstrated experimentally by König et al. [55] and using Monte-Carlo simulation by Hajnal et al. [56]. The heterogeneity of the systems due to partial clustering is the key for glass transitions in above 2D colloidal system [34]. It has also been shown that partial clustering prevents solidification into energetically preferred crystalline or poly-crystalline morphologies in a binary 2D colloidal glass former [57,31,58].

Recently Randall M. Erb et al. [59] developed a self assembly process which gives rise to highly reproducible, rotationally symmetric arrangements resembling electrostatic charge configuration such as axial quadrupoles and axial octupoles. The pair interaction potential between two such axial multipoles can be purely repulsive if the symmetric axes of the particles are directed along the normal to the plane of confinement. Here in this paper our objective is to study and compare the pair structures in three different 2D binary mixtures of charged colloidal particles resembling above axial electric multipoles namely dipoles, quadrupoles and octupoles. Special attention has been given to the distinctive feature of cluster formation characterized by the emergence of prepeak in the structure factor curve. Pair correlation functions which give structural information of the fluid has been calculated by solving Hypernetted Chain (HNC) integral equation theory at the grid of characterizing parameters (defined in Section 2) of the mixture. We observe significant changes in the structural features of the mixtures along with the associated changes in the size and sharpness of the boundaries of the cluster with the variation in the characterizing parameters.

The paper is organized as follows: In Section 2 we discuss the form of multipolar interaction potentials through which particles of the mixtures interact. We also describe the details of our model in this section. Subsequently we discuss the details of liquid integral equation theory in Section 3. Our results have been presented and discussed in Section 4. We finally conclude in Section 5.

2. Interaction potential and the model

2.1. Multipolar interaction potentials

The total electrostatic interaction energy of any two rigid charge clouds is given as $U = \sum_{ij} q_i q_j / r_{ij}$ where i and j run over the charges of distributions 1 and 2 respectively, and r_{ij} is the separation between charges q_i and q_j . In case when the two charge distributions do not overlap, we can resolve U into multipole–multipole constituents $u_{l_1 l_2}$, in which the multipole of order l_1 of distribution 1 interacts with the multipole of order l_2 of distribution 2. In other words $u_{l_1 l_2}$ is the electrostatic interaction energy between the multipoles of orders l_1 and l_2 of charge distributions 1 and 2 respectively. Using the space fixed spherical harmonic expansion of $1/r_{ij} = 1/(|\vec{r}_j - \vec{r}_i|)$, the total interaction energy between the charge distributions can be written as [60,61]

$$\begin{aligned} U &= \sum_{l_1 l_2} u_{l_1 l_2}(r) \\ &= \sum_{l_1 l_2} (A_{l_1 l_2} / r^{l_1 + l_2}) \sum_{m_1 m_2 m} C_g(l_1 l_2 l; m_1 m_2 m) Q_{l_1 m_1} Q_{l_2 m_2} Y_{lm}^*(\omega) \end{aligned} \quad (1)$$

Download English Version:

<https://daneshyari.com/en/article/7379659>

Download Persian Version:

<https://daneshyari.com/article/7379659>

[Daneshyari.com](https://daneshyari.com)