Journal of Quantitative Spectroscopy & Radiative Transfer 123 (2013) 23–29

Contents lists available at SciVerse ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

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

Calculations of light scattering matrices for stochastic ensembles of nanosphere clusters

N.F. Bunkin *, A.V. Shkirin, N.V. Suyazov, A.V. Starosvetskiy

A.M. Prokhorov General Physics Institute, Moscow, Vavilova 38, 119991 Russia

ARTICLE INFO

Article history:
Received 29 October 2012
Received in revised form
27 December 2012
Accepted 28 December 2012
Available online 7 January 2013

Keywords:
Nanoparticle clusters
Light scattering matrix
T-matrix
Cluster–cluster aggregation
Fractal dimension

ABSTRACT

Results of the calculation of the light scattering matrices for systems of stochastic nanosphere clusters are presented. A mathematical model of spherical particle clustering with allowance for cluster–cluster aggregation is used. The fractal properties of cluster structures are explored at different values of the model parameter that governs cluster–cluster interaction. General properties of the light scattering matrices of nanosphere-cluster ensembles as dependent on their mean fractal dimension have been found. The scattering-matrix calculations were performed for finite samples of 10^3 random clusters, made up of polydisperse spherical nanoparticles, having lognormal size distribution with the effective radius 50 nm and effective variance 0.02; the mean number of monomers in a cluster and its standard deviation were set to 500 and 70, respectively. The implemented computation environment, modeling the scattering matrices for overall sequences of clusters, is based upon T-matrix program code for a given single cluster of spheres, which was developed in [1]. The ensemble-averaged results have been compared with orientation-averaged ones calculated for individual clusters.

1. Introduction

A great multitude of colloidal systems can be considered as collections of spherical particles. The tendency of colloidal particles to aggregate, taking place to a greater or lesser degree, is a common feature of all colloidal systems and it may result in partial clustering of dispersed particles, especially, if the particles are strongly charged. The clusters, being produced in dispersions, can have various morphologies that are conditioned by the prevailing type of aggregation: "particle to cluster" or "cluster to cluster" aggregation [2]. There exists a problem of retrieving the information about nanoparticle clusters. An effective way of solving this problem is the study of angular dependencies of the scattering matrix elements for the corresponding colloidal system.

The influence of the main parameters of clusters (fractal dimension D of the cluster, the radius r and the number N of its constituent spherical monomers) on the angular dependencies of the scattering matrix elements was studied in a number of works [3–8], where these parameters, being varied widely, took different values but were not distributed randomly. In our view, the important fact is that in real colloidal systems these parameters are not fixed, but they rather are random variables over the ensemble of particle clusters. For this reason the characteristics of light scattering, observed in physical experiments, should be modeled by averaging over the distributions of the random parameters of the scattering clusters. The results of such a simulation using lognormal distributions of parameters N and r are presented in this paper. By varying the exponent of power, denoted by α (see below) in the probability of cluster–cluster aggregation, the change of the fractal dimension of the clusters, obtained from our cluster–cluster aggregation model, was achieved.

* Corresponding author. Tel.: +7 4995038162.
E-mail address: nbunkin@kapella.gpi.ru (N.F. Bunkin).

0022-4073/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jqsrt.2012.12.026

This work was essentially motivated by the problem of the aggregation of ion-stabilized gas nanobubbles in an equilibrium aqueous ionic solution under normal conditions, i.e. at room temperature and atmospheric pressure. The presence of such nanobubbles and their clustering was comprehensively investigated by our group, see, for instance, [9–16]. The kinetics of the nucleation of gas nanobubbles in ionic solutions under normal conditions was considered in [17]. From our theoretic standpoint, see Ref. [16], the ion-stabilized gas nanobubbles contain anions adsorbed at the liquid–gas interface, and therefore are charged negatively. At the same time, the negative charge at the nanobubble interface is balanced by a diffusion cloud of screening counter-ions; the complete compensation of the interface charge is realized at the infinity. It turned out that two types of compound particles (negatively charged gas core surrounded by a dense layer of the diffusion screening cloud) exist in the liquid; these compound particles have inverse charges. This is why such compound particles should coagulate to one another in the field of attractive Coulomb force, i.e. this aggregation is essentially a ballistic one. Thus the problem of the description of clusters resulting from such aggregation is acute. The specified properties of nanobubbles are especially important because they can form micron-sized heterogeneous centers in ionic solutions; such long-living centers play, for instance, a primary role in the interpretation of the ultrasonic cavitation phenomenon, boiling and so on.

The aggregation processes of inversely charged particles in dispersed systems are basically modeled by the ballistic mechanism with zero aiming distance. The two aggregation regimes are possible here: "ballistic particle to cluster" (BPCA) or "ballistic cluster to cluster" (BCCA) [7,8,18]. In our previous study [19], we analyzed the scattering properties of ensembles of BPCA clusters. Since the ballistic aggregates of nanobubbles, arising from the coagulation of charged compound particles, also possess noncompensated electrical charge, such separate aggregates are able to coagulate to one another. The subject of the present study is, therefore, the investigation of light scattering by systems, composed of BCCA nanobubble clusters.

2. Aggregation model

As was indicated in [15,16], the radius of ion-stabilized bubble is a random value lying in the range (10–100) nm. Thus the problem consists in modeling the structure of clusters composed of spherical monomers, having a certain distribution over their sizes. We have modified the hierarchic model for the clustering of spherical particles [18]. In our model, we iteratively generated sequences of clusters, starting with N separate spherical particles. The values of radii of these spheres are just the realizations of the stochastic process with a specified distribution. At each step of the iteration routine, two clusters is randomly chosen; these clusters aggregate to one another forming thus a new cluster. The probability P of choosing the given cluster obeys the power law in the form $P=C\cdot V^{-\alpha}$, where V is the cluster volume, α is the parameter of the model (this parameter qualitatively accounts for the attraction of clustered particles, which invokes the ballistic aggregation), and C is the normalizing factor. Numerical algorithm of coupling the chosen clusters is as follows (Fig. 1):

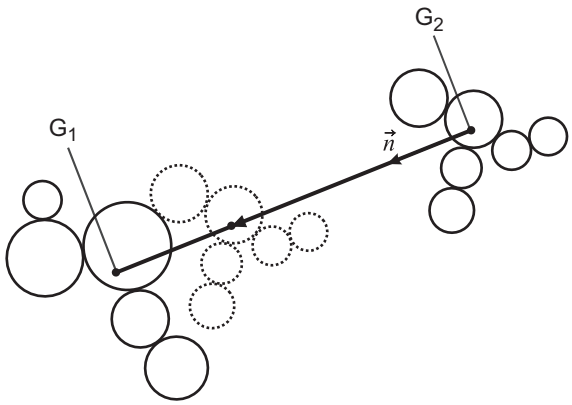

Fig. 1. Schematic of the aggregation of two clusters.

(1) A cluster (1) is implied to be immobile, and the reference system is associated with the center of gravity of this cluster (the point G_1).
(2) A cluster (2) turns around its center of gravity G_2 randomly in the space (this corresponds to a random rotation of the cluster (2) during its motion prior to collision).
(3) A point H, located randomly at the surface of a large enough sphere with the center in the point G_1 is chosen. Thus the direction HG_1 of falling the cluster (2) upon the cluster (1) is specified (we denote this direction by a unit vector $\vec{n}$). Here it is not necessary to take into account the random rotation of the cluster (1) around the point G_1, since it is automatically involved by the random choice of the direction of falling (Fig. 1).
(4) The point of the collision of two clusters is determined; it is implied that the cluster (2) starts moving along the vector $\vec{n}$. In the case where the collision point is absent, the previous step 3 is repeated.
(5) The aggregation of two clusters results in the formation of a new cluster, which replaces this pair of clusters in the generated consecution of clusters.
(6) The routine proceeds until the single cluster, consisting of N spheres, is built.

In this hierarchic cluster–cluster aggregation model, the average fractal dimension $\langle D\rangle$ of generated ensembles of the clusters has a dependence upon the parameter α. Furthermore, we can discern an interval, where the average fractal dimension varies quite noticeably and monotonically from the minimum to maximum values, corresponding to the boundary points of the interval. This parameter is just a new "degree of freedom" that allows us to bring the angular profile of the scattering indicatrix (the element $F_{11}(\theta)$) into the maximum proximity with experimental data; this feature can be