CONSISTENT PATTERNS OF ENCAPSULATING HARD SPHERES IN RESTRICTED VOLUMES: MODELING THE CONFINEMENT OF NANOPARTICLES IN NANOPOROUS MATRICES

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INTRODUCTION

The properties of nanoparticles confined in microscopic spaces within porous materials may differ significantly from those in the free state due to the interface interaction. The attributes of constrained geometries make these structures unique and challenging to study. The chemistry of the molecules in confined phases reveals the effects of geometric constraints on the molecular structure [1-3]. The interest in the study of such systems reflects the ubiquitousness of these materials in technologies, such as heterogeneous catalysis, photocatalysis, or solar energy conversion.

The filling of pores by atoms or molecules is often modeled as arrangements of hard spherical particles into an available space. The control over the density/porosity of a packing and its structural variables, such as the particle size, the coordination number, the radial distribution, the pore diameter, the void structure, etc., is desirable for practical applications [1,4]. The scientific interest is focused on the construction of a packing with given characteristics and its spatial-statistical analysis. This implicates a wide presence of mathematical and computer sciences in material research.

This poster presents some original developments from a computational view point to identify principal trends in the modeling of consistent sphere patterns in restricted volumes.

CONFINED STRUCTURES
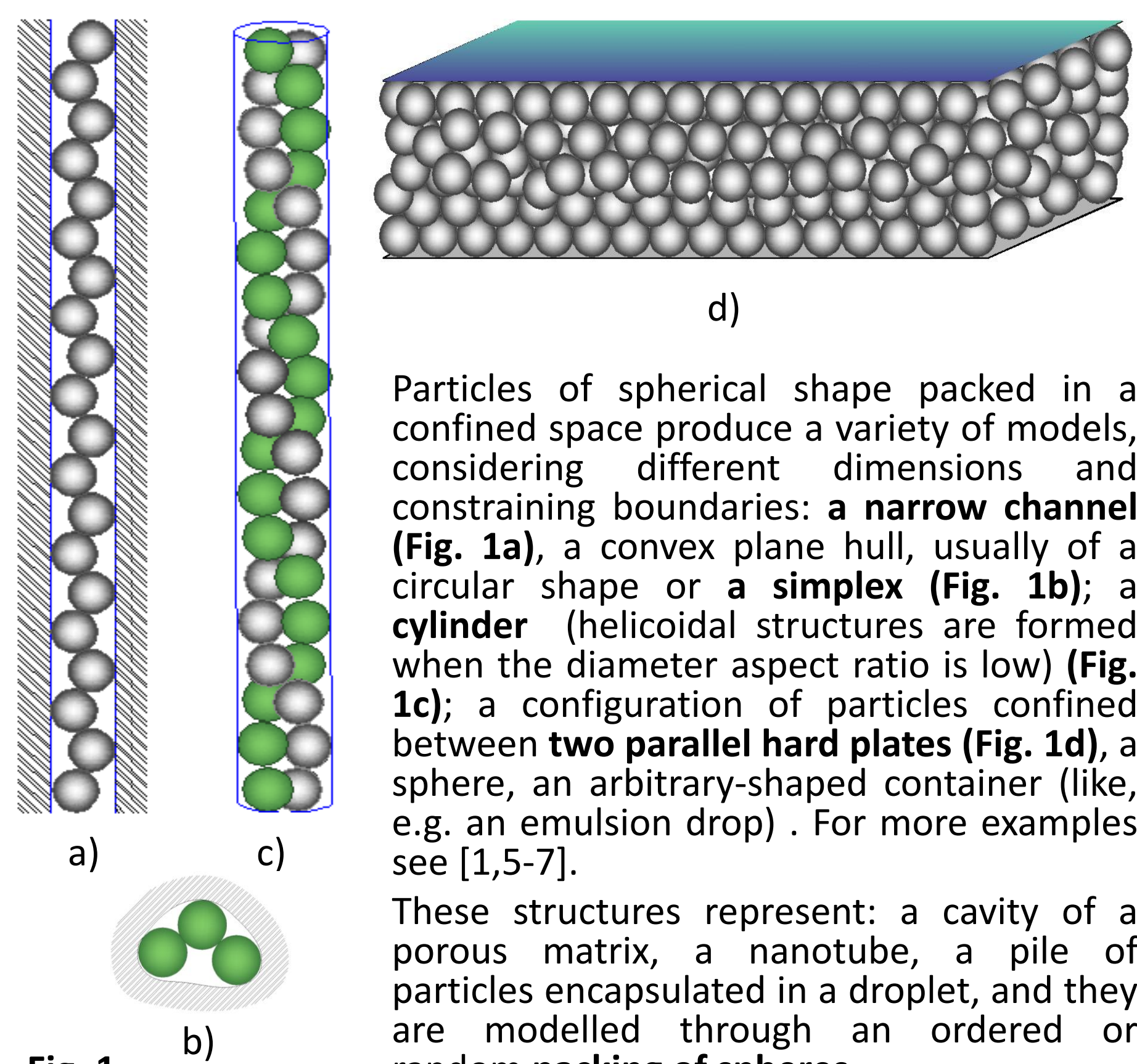
Particles of spherical shape packed in a confined space produce a variety of models, considering different dimensions and constraining boundaries: **a narrow channel (Fig. 1a)**, a convex plane hull, usually of a circular shape or **a simplex (Fig. 1b)**; a **cylinder** (helicoidal structures are formed when the diameter aspect ratio is low) **(Fig. 1c)**; a configuration of particles confined between **two parallel hard plates (Fig. 1d)**, a sphere, an arbitrary-shaped container (like, e.g. an emulsion drop). For more examples see [1,5-7].

These structures represent: a cavity of a porous matrix, a nanotube, a pile of particles encapsulated in a droplet, and they are modelled through an ordered or random **packing of spheres**.

Fig. 1.

MODELING APPROACHES

There are **three principal approaches** to model a packing of spheres in a bounded space:

1) Computer simulation - Monte Carlo method, Discrete element method, Molecular dynamics, among others [1,2,6];

2) Mathematical tessellation (Fig. 2) of a packing using Voronoi diagrams. It is a fundamental method for modeling of a packing [2,8];

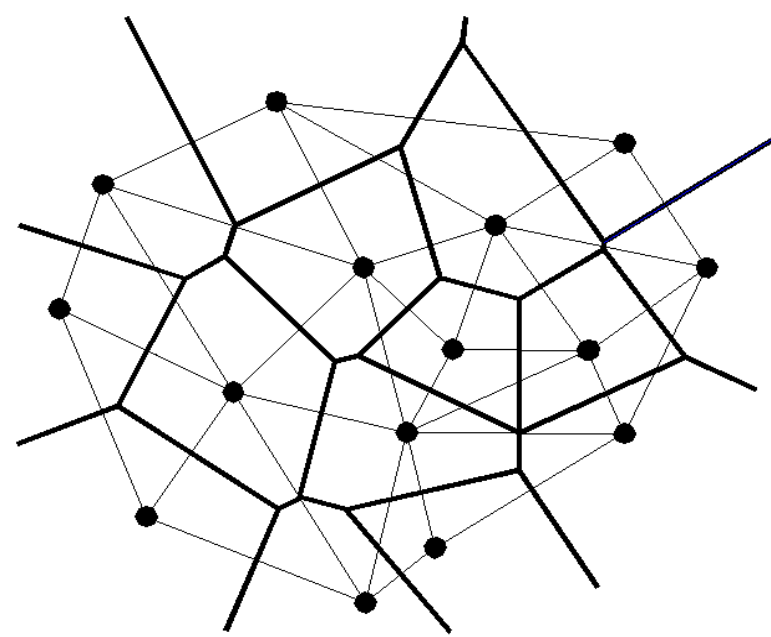**3) Mathematical programming** [9,10].
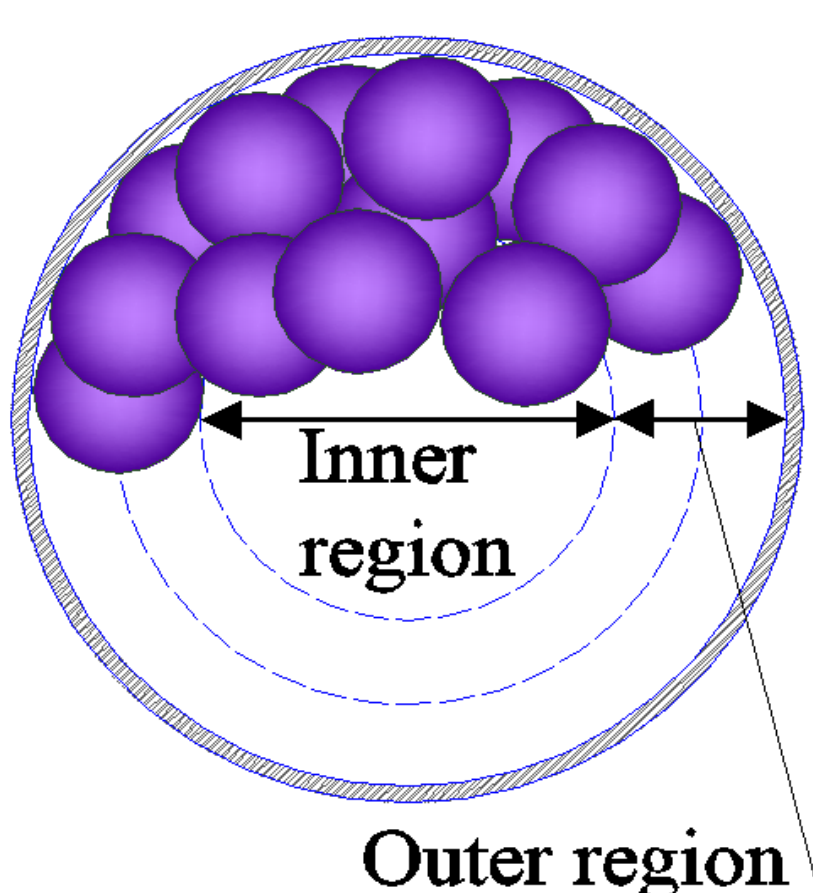

Fig. 2.

CONFINING WALLS

Fig. 3.

Randomly packed spheres near the confining walls form more ordered structures than those in the internal region and should be taken into account in modeling (**Fig. 3**, see also **Fig. 1c**) [1,2,7]. This effect propagates from two to four sphere diameters into the bulk and influences the local density near the walls making the **structural properties** of the material near the wall different from the internal area. It is observed on all confined structures, but it has a more pronounced effect on "small" packings, such as cylinders with low diameter aspect ratio [6,7,11].

DIAMETER ASPECT RATIO
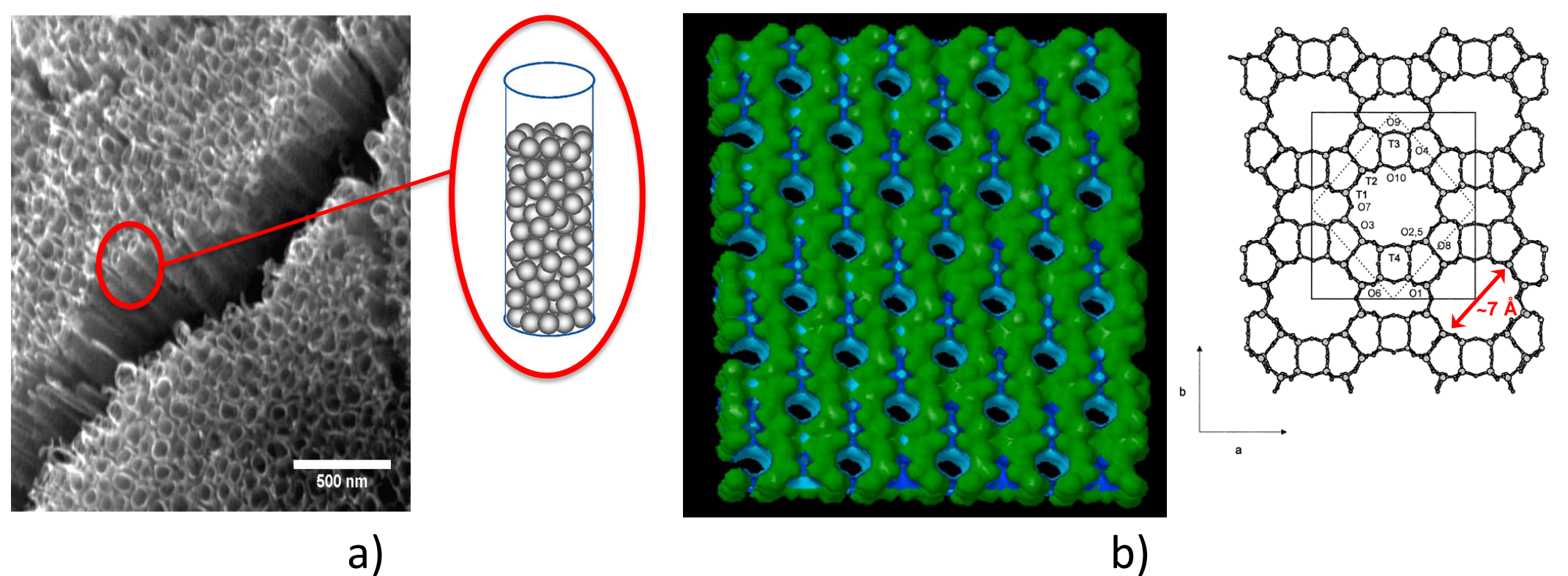

a)   b)

Fig. 4. a) The diameter of the titania tube with respect to the atom size is relatively big. A packing leads to a confinement without a clear structure.

b) Crystal structure of mordenite zeolite. It has channels with a diameter of 0.7 nm. Depending on the selected material (atoms of Li, Na, K, Rb and Cs have the diameters 0.31, 0.38, 0.47, 0.50 and 0.54 nm, respectively), the D/d ratio varies significantly, so the properties of these metals confined in a mordenite matrix will differ considerably. On the other hand, between more than 220 different zeolite structures, we can find channel ones with slightly different diameters; so the same metal (for example Na) forms a structure with distinctly different tube-to-particle aspect ratios, in this way drastically changing the properties of the final samples.
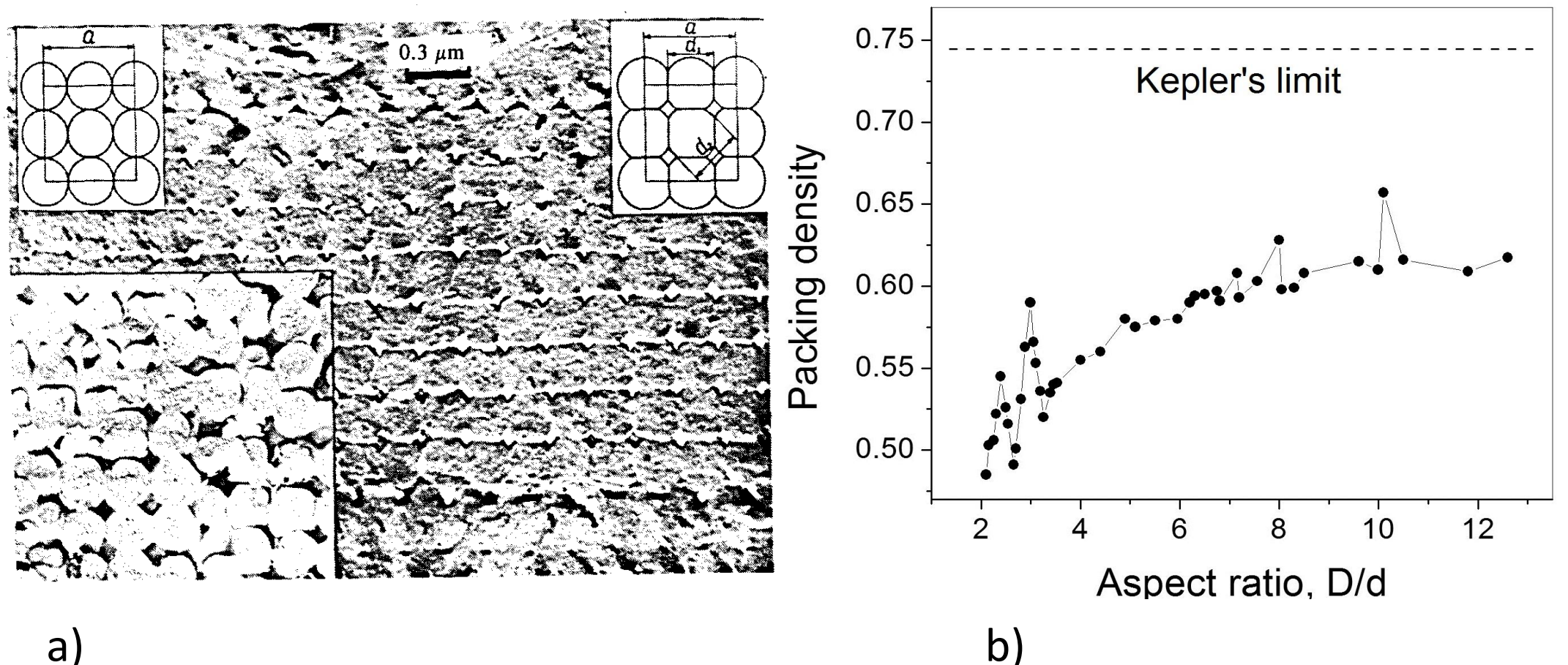

a)   b)

Fig. 5. a) TEM image of an opal structure from [4]. The voids of the opal structure can be obtained in a wide range of sizes; and they can be considered as excellent containers for injected substances, giving rise of photonic crystals. b) Modelling of packing densities in the range of D/d from 2 to 12 [11].
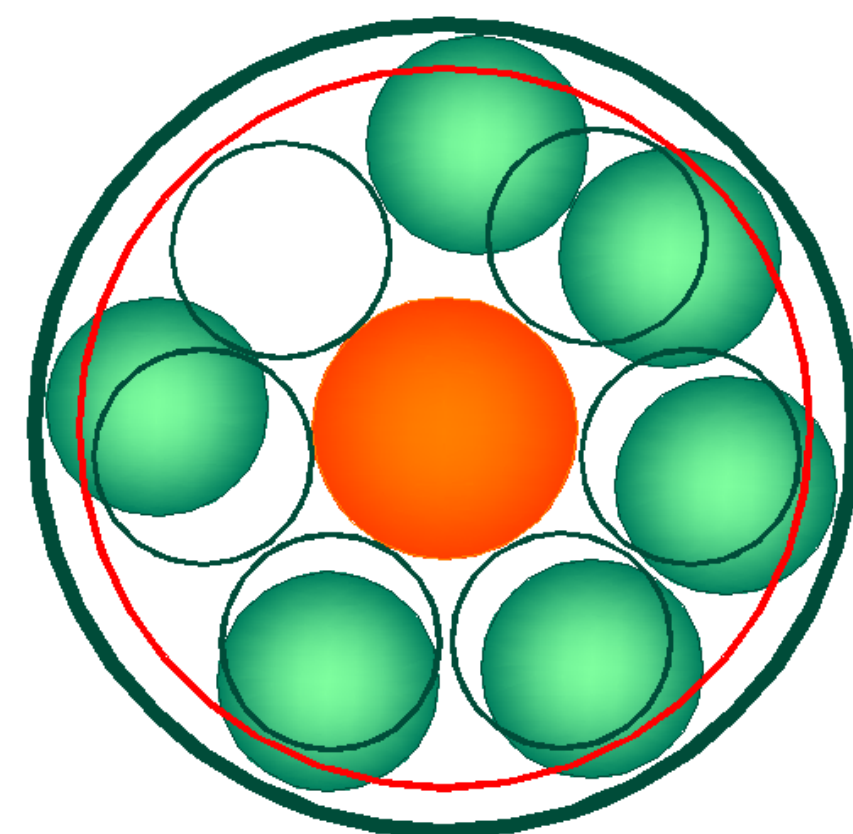
OPTIMIZATION PROBLEMS

Fig. 6.

Packing belongs to the optimization problems of discrete and computational geometry, and it is known to be **NP-hard** even for restricted versions with identical regular-shaped objects and domains of low-dimensional space, therefore approximate solutions are appropriate [12].

Related optimization problems should be classified into two main groups:

• Finding of the maximal packing density;
• Optimization of a structural parameter.

The problem of a minimal height of a bounded cylindrical channel [9] (**Fig. 4a**, right) and the problem of the minimal radius of a sphere containing a set of congruent spheres (with a central sphere) (**Fig. 6**) belong to the 1st group. The latter problem deals with the optimization of the structure of a cluster, and it is also interpreted as a packing in a circular hull [10]. Both problems are known to be NP-hard and are treated by **non-linear programming methods.**

The problem of minimal total interaction energy, which is obtained varying the size of spheres into a spherical pore [2], is an example of the 2nd group. It was resolved by applying a **simulated annealing metaheuristic**.

CONCLUSIONS

The development of methods for the synthesis of complex nanomaterials requires the establishment of an appropriate mathematical apparatus for targeted searches. Long-term efforts to develop a mathematical formalism describing the packing in unlimited volumes were started by J. Kepler. Now, they move to the stage of finding adequate methods to describe the packing in limited nano-volumes, where boundary effects begin to play a decisive role. In the present study, we collected data on some existing and incoming methods and tools and analyzed their ability to describe different phenomena in such a kind of structures.

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