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Methodology of Nanomodified Binder Examination: Experimental and Numerical ab Initio Studies

KOROLEV Evgeniy, INOZEMTCEV Aleksandr, EVSTIGNEEV Alexandr

Yaroslavskoje hw., 26, 129337, Moscow, Russian Federation

info@nocnt.ru

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Abstract. Feasibility of the sulfur-based construction materials is caused by properties, availability and low cost of sulfur. There exist numerous ways to improve the operational properties, including the ways that are based on nanotechnology, and ab initio (quantum chemistry) studies. Unfortunately, both application and verification of numerical simulation within the same research are quite complex. In the present case study we present typical scheme of survey involving both experimental and numerical studies. As a test subject we have selected orthorhombic sulfur crystals grown from the solution in toluene. It was clearly shown that good correspondence between experimental and numerical results can be achieved for offered methodology; Raman shifts for isolated S_8 molecule mostly correspond to the shifts of sulfur crystal. Computed frequencies for all primary modes are close to the experimental data. Similar correspondences can serve as proofs of conformity between unknown molecular structures in nanomodified sulfur-based material and selected structural models.

Introduction

There are permanent demands in modern construction for new materials with specific operational properties. Both structure and properties of any constructional composite are in great dependence on type of matrix material. Among other promising matrices for composites there are sulfur-based and sulfur-modified ones.

Applications of nanotechnology in constructional material science and civil engineering are numerous, ranging from admixture of carbon nanotubes into concrete composites to molecular design of advanced hyperplasicizers [1, 2]. At present, there are also formulated principles general enough to allow implementation of nanotechnology in construction in stable, consistent manner [3].

There exist numerous ways to improve the operational properties of concretes based on sulfur. By means of application of polymers distributed on the surface of fine filler it is possible to outcome several drawbacks of the traditional material with thermoplastic matrix [4,5]. Obviously, nanoscale layer of high-molecular substance significantly alters structure forming process near the phase boundary. According to [6], elemental sulfur is at the same time one of the best investigated chemical elements and one of the most complex systems; peculiar behavior on allotropes causes necessity of investigation by as many types of spectroscopy as possible. Thus, despite the progress in the understanding of the sulfur-based materials, material of sulfur and sulfur-enhanced composites is still with several “white spots” [7].

The research work in constructional material science can be advanced to the next level with help of system analysis [5,8,9]. The key point for successful application of system analysis in material science is the determination of bounds for spatial scales of interest and corresponding list of possible interactions – which, in turn, define applicable research methods [9]. The aim of the work is to present an example of application of such methods for nanoscale spatial level.

Modeling in material science

For decades, numerical experiments are used for design and analysis of structures in civil engineering. At the same time, development of building materials is mainly based on experimental studies combined with regression analysis (so-called “statistical modeling”). Such situation is a

natural consequence of complex character of building materials [9]. Due to demand of building materials with unique complex of properties (including materials with controllable service lifetime [10]) research efforts are currently focusing on modern methods of nanotechnology [11]. The reduction of resource consumption during research and development is possible in case of changing the direction towards modeling and simulation.

Constructional material science takes advantages of plethora of models, algorithms and software tools already developed in other branches of science. The application of phenomenological models [12-14] is also efficient; such methods can be used for modeling of polymer nanocomposites [14].

The modeling process involves system analysis as a sound foundation. The examination of complex system is the decomposition process. The system is decomposed in parts; then, both number of parts and number of cross-dependencies between them are minimized. Yet before decomposition can be started the bounds for spatial scales of interest and corresponding list of applicable modeling methods should be considered.

The selection of methods, algorithms and simulation software tools depends on characteristic scale of the system under examination. There can be several distinctive scales – from nanometer scale up to macroscopic level, and there are corresponding modeling methods (representing primary interactions between elements) most suitable for these scales. Depending on the characteristic size of the test system, different techniques of numerical analysis can be applied – methods based on quantum and classical mechanics; geometry and probability theory; continuum mechanics [9].

The coarse-grained structure of constructional mixtures and materials is mainly forming under influence of gravity; this level commonly referred as *macrostructure*. The structure of fine-grained part (binder, water and fine filler in case of cement composites; binder and fine filler in case of materials with polymer, bitumen and sulfur matrices) evolved under influence of forces caused by surface effects and surface energies. This level usually referred as *microstructure*. Exact spatial boundary between macro- and microstructure is not defined, but it is near 100 um.

Since at the macroscopic level the main type of interaction is the interaction caused by gravity force, the motion equations for elements of the system are simple. These are equations of classical mechanics. In constructional material science, the transient problem of structure formation process reflects technology of preparation and laying of constructional mix. If this problem is out of scope for the research, then modeling is often preformed only to determine the final configuration of coarse aggregates. The corresponding problems are theoretical examination and Monte Carlo simulation of dense packing in polydisperse systems, as well as percolation problems for frame of aggregates.

Modeling of the microstructure is more complicated in comparison with modeling of the upper structural level. To adequately represent the disperse system with fine filler, not only gravity force must be taken into account. The primary forces caused by surface properties of the disperse phase and free energies on the inter-phase boundaries. Forces caused by surface effects and by external compaction pressure may be of the same order of magnitude.

Atomistic scale is the domain of quantum mechanics: there are no particles; there are only waves and probability. Time-independent Schrödinger equation is very simple in form – it only states that valid energy E must be eigenvalue of Hamiltonian H, and corresponding to this energy "shape of electron" ("shape" of electron orbital) should be square $\psi\psi^*$ of the eigenfunction ψ (wave function of electrons). The "solution" of the Schrödinger equation – even in time-independent case – is not simple, though. The numerical methods, specifically designed for solution of Schrödinger equation, are implemented in software. The methods themselves often referred as quantum chemistry methods, and corresponding software is called quantum chemistry software.

Among other open source packages (e.g. [15], [16]) for quantum chemistry there is a General Atomic and Molecular Electronic Structure System (GAMESS) [17]. The code base of GAMESS was served as basis for some derivatives. Methods of quantum mechanics are also implemented in various multi-purpose commercial packages, notably *Biovia* (former *Accelrys*) *Materials Studio*.

The nanoscale level of constructional composite was firstly defined in [9]: it is the spatial level where properties of material are considerably affected by size effects. Software tools for neighbor

spatial scales can be utilized during investigation of nanostructure. For instance, modeling based on the analysis of the ensemble geometry is universal and can be applied on any structural level. In particular, authors of [18] had used this method in combination with Monte Carlo method for solution of percolation problem at nanoscale level. The obtained results concerning value of percolation threshold can successfully be used during development of building materials on upper spatial levels.

Notes on methodology

During implementation of nanotechnology in material science the methodology of research can be different; it depends not only on "practical" goals of the research (development of the building material with required values of operational properties), but also on allowed time and resource consumption, requirements for precision and reproducibility, demands for new scientific data with high predictive potential.

It is common in practice in real research work to combine some parts from different survey schemes [9]. Some methods (both experimental and theoretic) provide a lot of "scientific" information (IR-, Raman and NMR spectroscopy, adsorptive porometry, XRD, quantum chemistry methods based on density functional theory) which is hard to utilize entirely during applied research. Such methods are often used as a source of data for verification. Outcomes of other methods may be single scalar values (viscosimetry, X-ray scattering, simulation methods based on thermodynamics). Such methods are mostly suitable for routine work, and values obtained are subjects for verification by means of other methods.

Cross-verification of the results obtained with help of different methods is, obviously, a necessary part of any research. Many methods can be verified in more then one way – for example, results of Raman spectroscopy can be verified by means of density functional theory (DFT) and molecular dynamics (MD) calculations, with different basis, type of self-consistent field and different pair-wise potentials. In particular, it is evident that both DFT and MD simulation can be used during verification of Raman spectra; but these methods can also be used for verification of IR spectra and – in case of MD – even for macroscopic properties of the building materials [13,19].

Raman spectroscopy and quantum chemistry: case study

The feasibility of the sulfur-based construction materials is caused by properties, availability and low cost of sulfur. In Russia, there are many sulfur dumps near the oil industry enterprises. Such dumps consumes a lot of area which otherwise could be occupied by vegetation, contributing to the improvement of the environmental situation. Incorporation of sulfur in bulk building materials contributes to decrease of load to the environment [20].

During our research, extensive examination of the influence of different nanostructuring agents on the properties of sulfur was preceded by preparation of reference orthorhombic sulfur. The crystals (Fig. 1) were grown from the solution in toluene. To select the treatment regime corresponding to complete evaporation of the solvent, we analyze the Raman spectra of the prepared crystals. Suitability of this method is due to high Raman activity of sulfur allotropes and sulfur-based compounds. The experimentally obtained spectra are shown on Fig. 2.

There are no peaks corresponding to the used aromatic solvent on the Fig. 2 (no toluene peak near 510 cm^{-1} is observed); thus, during the treatment there was complete evaporation of the solvent.

Analysis of the influence of different nanostructuring agents includes comparative studies on data obtained in real and numerical experiments. On the initial stage, the outcome is basically a decisions concerning applicability of the methods and software tools; several practical conclusions can also be made.

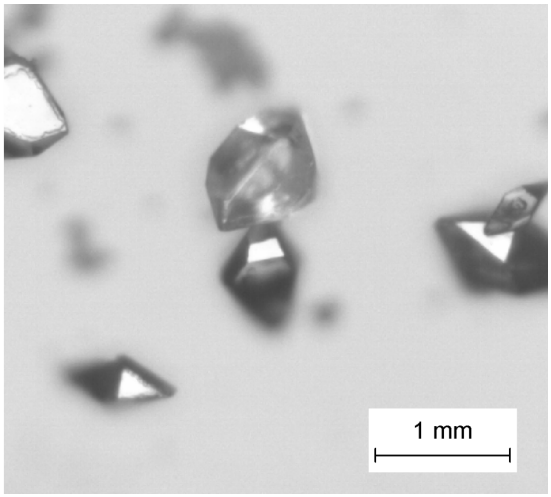

Figure 1. Test subjects for spectroscopy

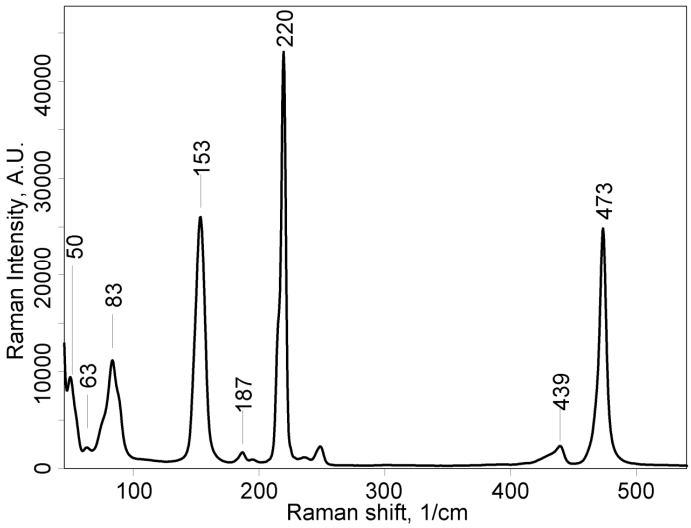

Figure 2. Raman spectrum of reference sample

As a rule, open source quantum chemistry software (including [17]) is designed with so-called "UNIX Way" in mind – only one specific task is implemented. The GAMESS is pure quantum chemistry solver which must be controlled from command line, with text input files of specific format. Pre- and post-processing tasks have to be solved with different tools. This can be difficult at first, and often requires deep knowledge of POSIX operating systems. Nevertheless, such an approach for numerical simulation is broadly accepted in science.

Selection of accompanying tools is the matter of choice and individual preferences. The Jmol [21] is a tool which can be used for visualization of molecular structures. The PyMOL [21] molecular graphics system can be both for visualization and for molecular editing.

Gabedit [23] and Avogadro [24] (Fig. 3) quantum chemistry software tools are very useful because of implementation of preprocessing functionality for GAMESS.

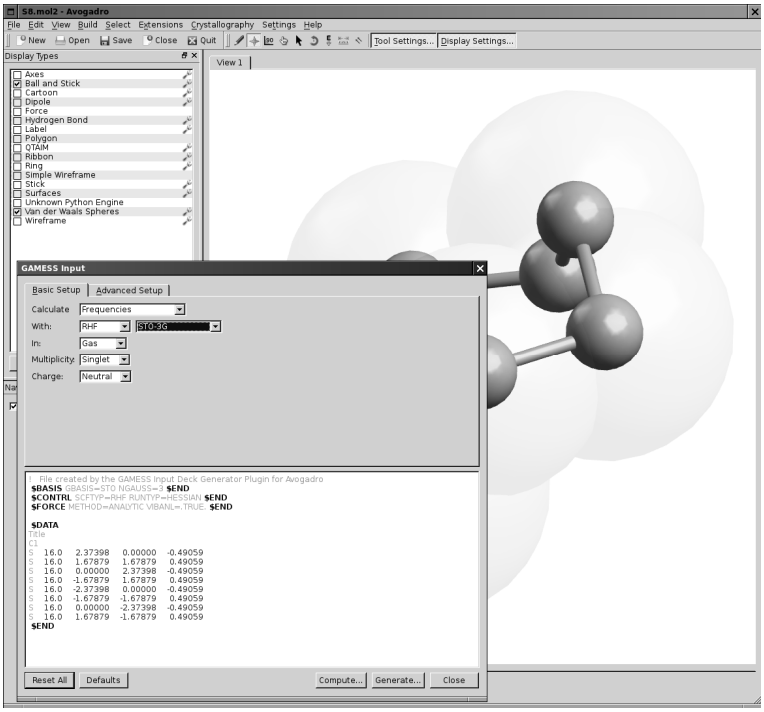

Figure 3. Avogadro main window with dialog for GAMESS input file creation

Numerical determination of the Raman spectrum with GAMESS is usually performed in several steps. If the geometry is build manually, the geometry optimization step is required. Then, hessian

matrix have to be obtained during “RUNTYP=Hessian” computation pass. The final stage is “RUNTYP=Raman” pass for input file with “$HESS” matrix extracted from previous output. The results of quantum chemistry calculations of Raman intensity for isolated S_8 molecule are shown on Fig. 4.

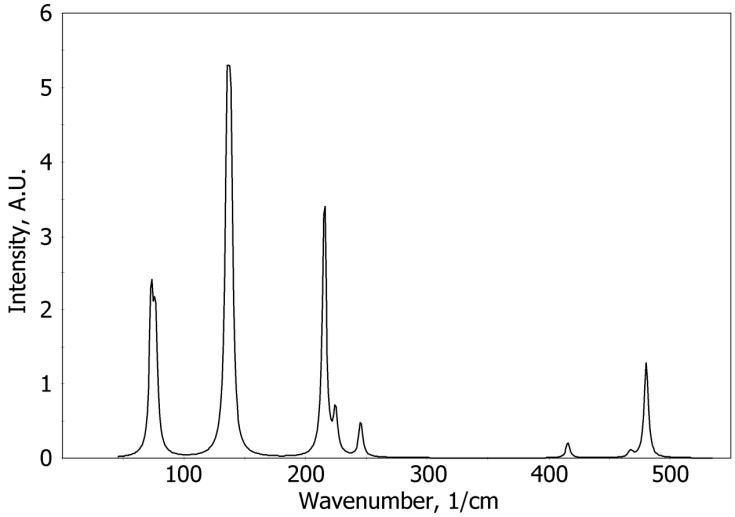

Figure 4. Computed Raman spectrum of S8 molecule

As it follows from Fig. 4, the values of Raman shifts for isolated S_8 molecule mostly correspond to the shifts of sulfur crystal. The computed frequencies for all four primary modes are close to the experimental data. Intensities of some modes also roughly correspond to the intensities of real spectrum. Such correspondences (along with XRD data) are important proofs of conformities between unknown molecular structure of nanomodified sulfur material and model of the lattice which is used during quantum chemistry simulation.

Conclusion

While there are a lot of progress in development of modeling methods and software, the numerous particular problems arising during R&D in constructional material science and nanotechnology of construction still require adequate solution. The system approach to the analysis of problem, followed by selection of proper modeling methods, algorithms and software tools, is the key for design of new efficient building materials.

Cross-verification of the results obtained with help of different methods is, obviously, a necessary part of any research. While the Raman spectroscopy, which is widely used for chemical analysis in materials science, can be directly verifies by ab initio calculation, the process of such calculation is quite complex. It is necessary for the investigator to select appropriate basis set, type of self-consistent field etc.; choice of simulation software is also non-trivial.

As an example, in the present case study we presented typical scheme of survey, involving both experimental and numerical ab initio studies. It was shown that for selected software tools good correspondence can be achieved between experimental and numerical results. Such correspondence can be important proof of conformity between unknown molecular structure of nanomodified sulfur material and selected structural model.

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