Ab initio simulation of effects of structural singularities in aerogel absorption potential

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Abstract. In the present work simulation of Van der Waals potential between helium atom and part of silica aerogel strand by means of \textit{ab initio} methods was performed. Cell with alpha quartz structure was used as building block of aerogel strand, because it is the most stable structure at low temperature, and only the surface layer of aerogel has been considered. For modeling absorption potential field in plane, summation of potential from individual building blocks has been provided. Two dimensional Van der Waals energy field was calculated for different geometries of aerogel strands. A rather deep potential well has been found in the corner formed due to aerogel strand crossing.

1. Introduction

A material is, by definition, the combination of a matter and a geometry. With the emerging field of nanotechnologies the geometry and the structure of the matter seem to be more important for innovation than the nature of the matter itself. Consequently, the characterization and the comprehension of organization at the molecular scale is the key of future technologies. For more than twenty years \cite{1} the question of aerogels structure appeared as a crucial point to allow us to use practically all features of this extremely porous structure. It is a really very promising material for the functionalized surface technologies. Aerogels are nowadays well known for their unique mechanical, chemical, thermal and optical properties \cite{2}, their density is close to only three times that of the air. This amazing combination of properties is mainly due to the unique structure of aerogels, characterized by their continuous solid network.

For studying material with such complex internal geometry very tiny and sensible “probe” should be used. At the role of such probe one can propose quantum liquids like \textsuperscript{3}He or \textsuperscript{4}He because atom size of helium is very small and it can penetrate in very narrow nanochannels and nanopores inside aerogel. In superfluid phase these liquids show unusual behavior due to appearance of macroscopic collective wave function of all helium atoms which results in coherent motion. A new “degree of freedom” is emerged. For example in superfluid in addition to pressure oscillation (first sound) one has temperature oscillation \cite{3}. In the case of \textsuperscript{3}He atoms we have additional magnetic degrees of freedom, relaxation of which inside aerogel porous structure can give us essential information about internal structure of latter.

Aerogels represent a system of inhomogenously distributed impurities for quantum liquids like \textsuperscript{3}He and \textsuperscript{4}He. The influence of these impurities on the magnetic relaxation of liquid \textsuperscript{3}He in normal
and superfluid phases was the subject of numerous studies in the recent years, but the complete understanding has not yet been reached. Recently the model of inhomogeneous potential absorption has been proposed to explain the observed temperature and field dependencies of spin-lattice relaxation times of liquid $^3$He inside aerogel at temperatures about 1.5 K [4].

In the present work simulation of Van der Waals potential between helium atom and part of silica aerogel strand by means of \textit{ab initio} and semi-empirical methods was performed.

2. Aerogel model

The fabrication of aerogel is always divided into three steps: hydrolysis, condensation and supercritical extraction. It is crucial to mention that every step of the fabrication process has an impact on the final aerogel structure. But the global chemical nature of aerogel is still the same. It should be mentioned that aerogel has the fractal structure at a scale length from 10 to 100 nm [5]. The fractal construction takes place during the formation of aerogel because of the percolation phenomena. In present work we will consider silica aerogel, which consist from agglomerated particles of SiO$_2$.

For running the energy calculation at the nanoscopic scale the quartz $\alpha$-crystal structure appeared to be the most appropriate. This model does not match perfectly with all possible structure of silica aerogel but it is the most stable for low temperature. But, the entire surface of aerogel is covered by hydroxide groups which determine its hydrophilic nature. One can see on Fig. 1 that different hydroxide group configuration may appear, depending on the cutting direction. If we assume that all reactions are finished, then for computer modelling it is reasonable "to cut" the quartz $\alpha$ cell along the surface 2 because only one hydroxide group will remain.

To minimize the calculation time, we found the two dimension elementary cell on this plane. From this elementary cell, we are able to reconstruct the entire three dimensional structure. From the optimized crystal structure the model of aerogel building block at low temperature has been extracted. The two hydroxide group have been added to represent the remaining hydrophilic layer.
3. *Ab initio* calculations of aerogel-helium potential

The calculation model has been chosen to afford us to calculate really precise interaction for all possible three dimensional geometries. As the first approximation, only the aerogel surface layer has been used because the influence of the lower layers is assumed to be negligible.

At the first stage, Gaussian code [6] has been used to calculate the adsorption potential in one direction. To obtain a more precise adsorption potential field, the total energy has been calculated for three different points, see Fig. 2. Some silicon atoms from aerogel building block have been removed to avoid double counting during the calculation of the potential field. From each point, the total energy of both the chosen model and the helium atom has been calculated for range of distances in one direction, see Fig. 2. At least 350 calculation have been performed with Gaussian code using the B3LYP functional and 6-31++G basis set on the interval from 1 to 90 Å. To obtain interaction energy (Van der Waals energy component) the following expression has been used

\[ E_{\text{VdW}} = E_{\text{Total}} - E_{\text{Aerogel}} - E_{\text{Helium}}, \]

where \( E_{\text{Total}} \) denotes energy of system on Fig. 2, \( E_{\text{Aerogel}} \) and \( E_{\text{Helium}} \) are energies of the used aerogel building block and helium atom respectively. The three curves obtained are depicted on Fig. 3.

![Figure 2.](image)

**Figure 2.** (color online) Calculations of energy have been performed along the direction perpendicular to surface plane for every chosen point

One can note the oscillations of interaction energy for all three reference points in length range from 2 to 25 Å. This seems to be in contrast with results of Ref. [7], where authors obtained non oscillation curve for helium ad-atom adsorption potential in nonplanar geometry. But this publication is completely based on potential curves calculated only for two atoms. In another Ref. [8] one can find results similar to our ones - the calculated with use the Lennard-Jones potential energy of a particle adsorbed by an infinite wall shows oscillations. So the result given by the *ab initio* method can be considered as a reliable result.

4. Two dimensional adsorption potential

It was mentioned above that the used in calculations the block of aerogel is just a piece of a complete aerogel strand. To obtain full adsorption potential in a given point near aerogel strand there exist two possible solutions: using a direct *ab initio* calculations for the whole strand or
van der Waals energy dependencies on distance for three reference points providing the summation of already calculated potentials for blocks. The second method has been chosen because the calculation time for a complete molecular structure by means of the first method is enormously high.

We have calculated two dimensional Van der Waals energy field for two different types of aerogel strands geometry: two crossing strands and pore inside a silica ring (Fig. 4 and 5). One can observe the appearance of a deep potential wall generated by the geometric singularity - crossing point. At the same time the depth of potential wall in the case of the ring is homogeneous one.

The minimum energy is always located at the distance 20Å from each aerogel strands. To analyze the influence of the strands length and the intersection angle between strands onto near-surface adsorption potential well we have calculated the interaction energy for several models. From these calculations one can conclude that depth of well decreases with length of strand (or number of silica molecules in strands). Close geometry like a pore reduces the depth in comparison to the straight strand. So any irregular geometry with some singularities generates a rather deep potential well just near this singularity, and this observation support the proposed model of inhomogeneous adsorption potential [4].

5. Conclusion
We have provided ab initio calculations of the adsorption potential well for helium atom near silica aerogel strands. One can improve calculation accuracy by increasing the number of points and directions for interaction potential. Also it is possible to use the post-Hartree Fock perturbation method MP2 with improved basis set 6-31++G(2d) to describe Van der Waals interactions better. But all these improvements will have an effect on the depth of potential well but not cancel the main result - the appearance of a rather deep potential well for helium atom near geometry singularity (strands intersection, for example). It supports the model of inhomogeneous adsorption potential proposed in [4] to explain very short spin relaxation times for 3He atoms adsorbed on the silica aerogel surface.
Figure 4. Two dimensional Van der Waals energy field for two intersected strands with the crossing angle $\pi/3$ ($x, y$ in Å; $z$ in a.u.)

Figure 5. Two dimensional Van der Waals energy field for silica ring with radius 48 Å ($x, y$ in Å; $z$ in a.u.)

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