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Collision-induced light scattering spectra of krypton layer confined between graphite slabs – MD simulation

A. Dawid*, D. Wojcieszyk, Z. Gburski

Institute of Physics, University of Silesia, Uniwersytecka 4, 40-007, Katowice, Poland

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ABSTRACT

We have used the molecular dynamics (MD) simulation method to obtain the collision-induced light scattering spectra of the thin krypton layer confined between two parallel graphite slabs. The simulations have been made under constant density, pressure and temperature condition. We have investigated four thin krypton layers of the thickness ranging from 13 to 24 Å. The 2-, 3- and 4-body correlation functions of collision-induced polarizability anisotropy were calculated. The spectra of colliding krypton atoms were simulated as cosine Fourier transform of the total polarizability anisotropy correlation function. The calculated correlation functions and their spectra show substantial dependence on the distance between graphite slabs. The collision-induced light scattering spectrum of krypton bulk sample was also simulated and compared with the krypton layer between graphite walls. The striking differences between these two systems are observed. We have further extended our analysis of krypton movement between graphite slabs by calculating the mean square displacement functions and diffusion coefficients. The decrease of the diffusion of krypton atoms with the increasing distance between graphite walls has been found. The structure of krypton layer has been also investigated by calculating the density profile and pressure tension across the rift. The distance between graphite slabs, for which the highest mobility of krypton's atoms occurred, has been found.

1. Introduction

The noble-gases like argon or krypton due to its low thermal conductivity are used as a filling in modern double glazing windows [1,2]. On the other hand, the thermal conductivity in nanometers slots is very important when it comes to designing of new cooling systems for electronic devices [3]. The dynamics of noble-gas atoms in fluid phase as a classical non-reactive particle were often studied by the computer simulations. At the beginning of computer modeling the researchers concentrated on the small aggregates of atoms, called clusters [4–6]. Further improvement of computer technology allows scientists the simulation of molecular dynamics in bulk samples of noble-gas atoms [7–10]. The dynamics of argon or krypton atoms in small ensemble can be “view” by the collision-induced light scattering (CILS) spectroscopy experiments [11–17]. This phenomenon comes from the fact that the interacting pair of noble-gas atoms induces a short-lived dipole moment that is able to interact with an incident light beam. The interpretation of the results obtained by CILS is a difficult task without taking closer look inside the system. In that case the computer simulations proved their usefulness. For instance, in the small Ar_{13} clusters CILS spectra proved to be sensitive to phase transitions [4]. The dynamics of fluids, confinement in the small space of the size of a few atoms, differs from that for a bulk matter. There are some works about the dynamics of a thin layer of noble-gas atoms adsorbed on fullerene [18–23] and carbon nanotube [24–27]. The formation of krypton layers near the graphite surface has been observed experimentally [28]. The dependence of the phase transition on the number of layers has also been reported [29]. In our previous research [8,10], the noble-gases like argon or xenon between graphite walls, were simulated. Those simulations were performed for varying density inside the slot and showed the increasing mobility of the noble-gas atoms, with the increasing distance between the graphite slabs. In this study we focus on CILS phenomenon in the thin krypton layers confined between graphite slabs, with a constant density of krypton. It means, we change the number of atoms to fill in the volume between graphite slabs.

* Corresponding author.
E-mail address: aleksander.dawid@us.edu.pl (A. Dawid).

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2. Simulation protocol

The modeling of our simulation starts from preparing the graphite wall model. The elementary cell of graphite was constructed from six hexagonal carbon rings with the distance between near carbon atoms equal to 1.42 Å and the angle between two vectors drawn from one atom to nearby atoms equals to 120°. The interlayer distance was set to 3.4 Å. We have assumed that the thickness of graphite walls is much larger than the slot between them, thus the dynamics of krypton atoms has insignificant contribution to the movement of carbon atoms in the wall. In order to simulate this heavy graphite walls we have assumed that carbon atoms are not moving during the simulations. The Lennard-Jones (LJ) potential has been used to model the interaction between krypton–krypton and krypton–carbon pairs.

$$V(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right],$$

where r_{ij} is the distance between atoms, ε_{ij} and σ_{ij} are the LJ potential parameters listed in Table 1. The Lorentz-Berthelot mixing rule was adopted to calculate the parameters between unlike atoms [30]. The simulations were performed with the three dimensional, orthogonal periodic boundary conditions, using the minimum image convention algorithm [31]. The simulation master cell was set to the edge size equal to 28.31 Å in x-direction, 25.73 Å in y-direction and 80 Å in z-direction. The size of cell in z-direction is selected a way to eliminate the periodicity in this direction. The cut-off radius was chosen to be 20 Å. The number of krypton atoms for each slot size was adjusted to fulfill the condition of constant density equal to 2.8876 g/cm^3. The initial positions of krypton atoms were randomly distributed inside the slot. The classical equations of motion were integrated up to 2.5 ns by the velocity Verlet algorithm [32]. The integration time step used in simulation is 2.5 fs which ensures the total energy conservation within 0.01%. We have made our simulations at a constant temperature sets to 117 K. The average temperature was adjusted as desired by a process of velocities scaling using Berendsen algorithm [33]. The system was equilibrated for 2*10^6 MD steps. All simulations of molecular trajectories have been performed using our own simulation software RIGMD [34].

3. CILS model

When two atoms collide, the temporary anisotropy in the polarizability of colliding atoms appears. The collision-induced light scattering spectrum is related to the polarizability anisotropy of colliding pairs of atoms. The formation of polarizability anisotropy in symmetric noble-gas atoms can be described by the dipole-induced-dipole mechanism (DID) [35–40]. The phenomenon comes from the fact that incident light beam induces an oscillating dipole in a given atom which in turn induces a dipole in a neighboring atom These oscillations generally are not aligned with the polarization of incident light. As the result, we have depolarized light scattering phenomenon. DID mechanism in the sense of computer simulation can be described by pair anisotropy $\beta_{ij}(t) = \sigma^3[3x_{ij}(t)z_{ij}(t)/r_{ij}^5(t)]$ [21], where x_{ij} and z_{ij} are components of the separation vector r_{ij} between the ith and jth atoms and σ is the LJ potential parameter. The depolarized Rayleigh spectrum is the Fourier transform of the polarizability anisotropy autocorrelation function G(t), which for a monatomic sample of N atoms is

$$G(t) \propto \left\langle \sum_{i,j,k,l=1, i\neq j, k\neq l}^{N} \beta_{ij}(t)\beta_{kl}(0) \right\rangle,$$

where i, j, k, l identify different atoms. Although DID mechanism is a two-body interaction, it can be decomposed into pair, triplet, and quadruplet contributions $G(t) = G_2(t) + G_3(t) + G_4(t)$, where

$$G_2(t) \propto \left\langle \sum_{\substack{i,j=1,\\ i\neq j}}^{N} \beta_{ij}(t)\beta_{ij}(0) \right\rangle$$

$$G_3(t) \propto \left\langle \sum_{\substack{i,j,k=1,\\ i\neq j, i\neq k, j\neq k}}^{N} \beta_{ij}(t)\beta_{ik}(0) \right\rangle$$

Table 1
Lennard-Jones potential parameters taken from Ref. [42].

Atom	ε [meV]	σ [Å]
Carbon	2.412873	3.40
Krypton	10.341	3.63

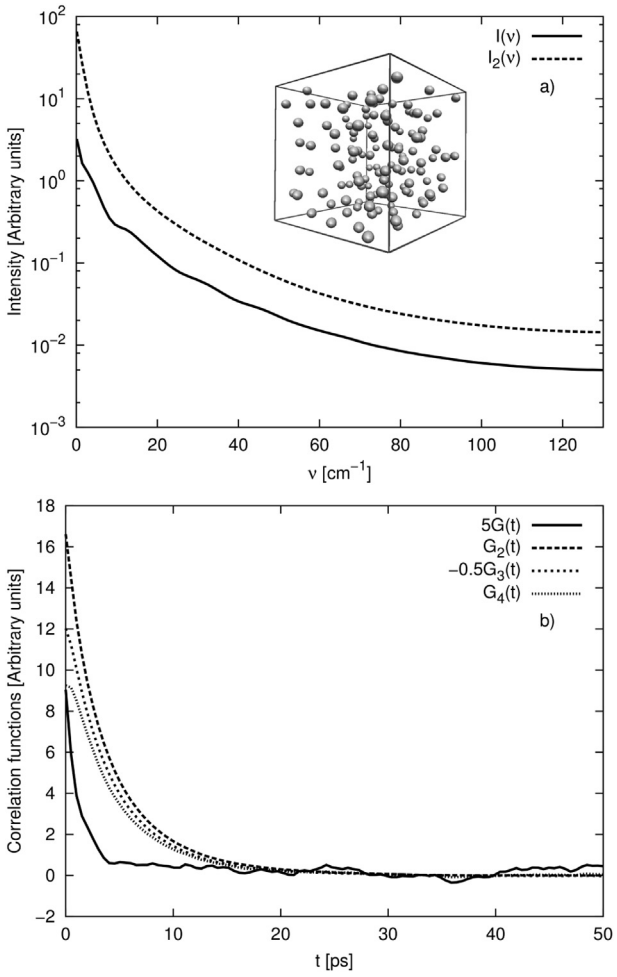

Fig. 1. The CILS of krypton in bulk sample. a) total I(ν) and pair correlation $I_2(\nu)$ spectra, b) The polarizability anisotropy correlation functions of two-body $G_2(t)$, three-body $G_3(t)$ multiplied by −0.5, four-body $G_4(t)$ and total $G(t) = G_2(t)+G_3(t)+G_4(t)$ multiplied by 5.

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