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# Rayleigh light scattering in fullerene covered by a spherical argon film—a molecular dynamics study

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## Abstract

We have calculated (by a molecular dynamics method) the interaction-induced polarizability correlation functions and spectra of the depolarized light scattering from fullerene  $C_{60}$  molecules surrounded by an argon ‘atmosphere’ (layer). The calculated correlation functions and spectra of  $(C_{60})Ar_n$  ( $n = 32, 40, 46$ ) clusters show a substantial dependence on the number  $n$  of atoms in the layer.

## 1. Introduction

Since it became possible to produce  $C_{60}$  fullerenes in macroscopic amounts and with high purity [1], the synthesis and study of derived bulk materials have stimulated numerous experimental and theoretical works. In recent years there has been increasing activity in investigating extremely small, finite-size fullerene-based systems, because they are expected to exhibit new chemical and physical properties [2].

Closely connected with the many-body dynamics of the particles in a system is the phenomenon of depolarized (Rayleigh) light scattering, for the bulk atomic liquids already intensively investigated both experimentally and theoretically [4]. Studies of the interaction-induced depolarized Rayleigh spectra of small clusters have so far been limited to  $Ar_{13}$  and  $Xe_{19}$  systems [5, 6]. In this paper we report molecular dynamics simulations of the depolarized Rayleigh spectra of the very interesting conglomerate  $C_{60}Ar_n$ , composed of a  $C_{60}$  molecule coated with  $n$  (a few tens) argon atoms. Because the argon–fullerene attraction is much stronger than the argon–argon one, the Ar atoms form a kind of ‘atmosphere’ surrounding the surface of  $C_{60}$  ‘ball’. One would like to know how the peculiarities of the atomic dynamics in this ultrathin atmosphere influence the light scattering spectra—this is the subject of our computer experiment.

## 2. Simulation details

The interatomic potential between argon atoms is taken to be the usual Lennard-Jones (LJ) potential of the form  $V(r_{ij}) = 4\epsilon[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6]$ , where  $r_{ij}$  is the distance between the

**Table 1.** LJ potential parameters for this simulation.

Atoms	$\varepsilon/k_B$ (K)	$\sigma$ (Å)	$m$ ( $10^{-25}$ kg)
Ar	119.8	3.41	0.664
C	51.2	3.35	0.199

atoms  $i$  and  $j$ ,  $-\varepsilon$  is the minimum of the potential at a distance  $2^{1/6}\sigma$ .  $k_B$  is the Boltzmann constant and the LJ potential parameters  $\varepsilon$  and  $\sigma$  are given in table 1. More sophisticated potentials exist for the argon–argon interaction [7]; however, at the present stage we do not make a comparison with experimental data, so the fine details of the potential are not crucial in this context.

The interatomic potential between argon atoms and  $C_{60}$  molecules ( $V_{C_{60}-Ar}$ ) uses the Girifalco [8] approximation to the fullerene–fullerene potential ( $V_{C_{60}-C_{60}}$ ) of the form

$$V_{C_{60}-C_{60}}(s) = -\alpha \left[ \frac{1}{s(s-1)^3} + \frac{1}{s(s+1)^3} - \frac{2}{s^4} \right] + \gamma \left[ \frac{1}{s(s-1)^9} + \frac{1}{s(s+1)^9} - \frac{2}{s^{10}} \right] \quad (1)$$

where  $s = r/\sigma_{C_{60}}$  and  $\sigma_{C_{60}} = 7.1$  Å is the diameter of the fullerene molecule. Parameters  $\alpha$  and  $\gamma$  are derived from experimental data [9] (table 1). Further theoretical works [10] use the same approximation for the fullerene–rare-gas-atom case and treat this potential as an interaction between a point and a sphere:

$$V_{C_{60}-Ar}(s) = 60 \left[ \frac{c_6}{R^6} F_6(s) + \frac{c_{12}}{R^{12}} F_{12}(s) \right] \quad (2)$$

where  $2R = \sigma_{C_{60}}$ ,  $c_6 = -4\varepsilon_{ArC}\sigma_{ArC}^6$ ,  $c_{12} = +4\varepsilon_{ArC}\sigma_{ArC}^{12}$  and  $F_n(s) = \frac{1}{s(n-2)}[(1-2s)^{2-n} - (1+2s)^{2-n}]$ ,  $s = r/\sigma_{C_{60}}$ . The parameters of the potential between unlike particles A and B are given by Lorentz–Berthelot rules [11]  $\sigma_{AB} = (\sigma_A + \sigma_B)/2$  and  $\varepsilon_{AB} = (\varepsilon_A\varepsilon_B)^{1/2}$ .

The classical equations of motion are integrated up to 10 ns using the velocity Verlet algorithm. The integration time step used in the simulation is 2 fs, which ensures total energy conservation within 0.01%.

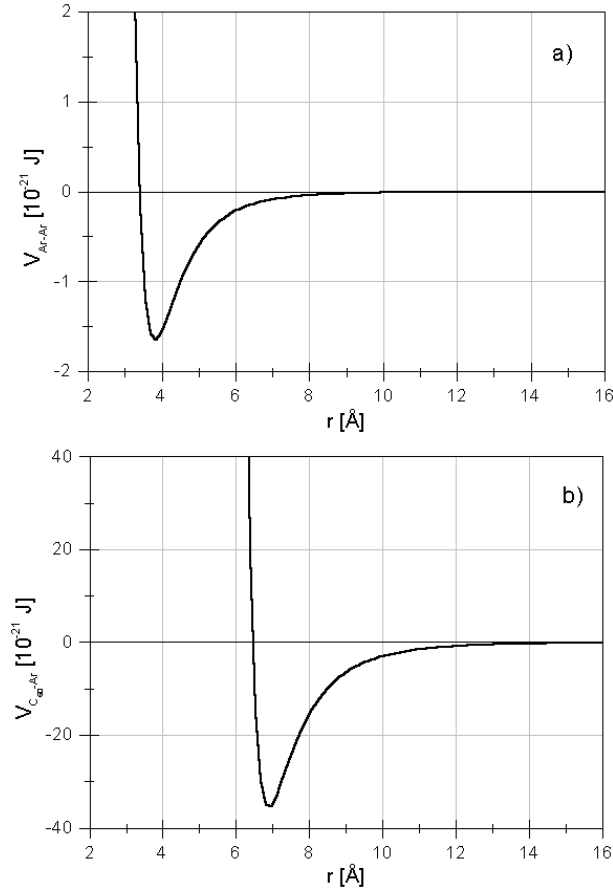
### 3. General relations

The depolarized light scattered by bulk monatomic fluids has been studied for many years. The spectral line shape reflects the time dependence of the polarizability anisotropy of colliding pairs of atoms. The major contribution to the anisotropy is described by the dipole–induced-dipole (DID) mechanism [12]. The DID interactions result from the fact that the incident light beam induces an oscillating dipole on the  $i$ th particle and this dipole generates an oscillating local field at the  $j$ th particle. The DID mechanism is a two-body interaction which gives rise to two-, three- and four-body correlations contributing to the intensity of the scattered light. 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 [12]

$$G(t) \propto \left\langle \sum_{i,j,k,l=1}^N \beta_{ij}(t)\beta_{kl}(0) \right\rangle \quad (3)$$

where  $i, j, k, l$  identify different atoms. The pair anisotropy  $\beta_{ij}$  in the DID limit is [13]

$$\beta_{ij}(t) = \sigma^3 [3x_{ij}(t)z_{ij}(t)/r_{ij}^5(t)] \quad (4)$$



**Figure 1.** The interaction potentials: (a)  $V_{\text{Ar-Ar}}(r)$  and (b)  $V_{\text{C}_{60}\text{-Ar}}(r)$ .

where  $x_{ij}$  and  $z_{ij}$  are components of the separation vector  $r_{ij}$  between the  $i$ th and  $j$ th atoms. The correlation function  $G(t)$  can be decomposed into pair, triplet and quadruplet contributions:

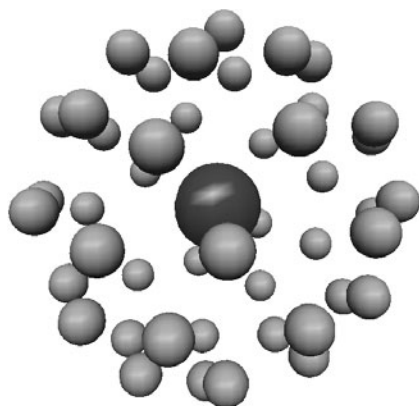
$$G(t) = G_2(t) + G_3(t) + G_4(t) \quad (5)$$

$$G_2(t) \propto \left\langle \sum_{i,j=1}^N \beta_{ij}(t) \beta_{ij}(0) \right\rangle \quad (6)$$

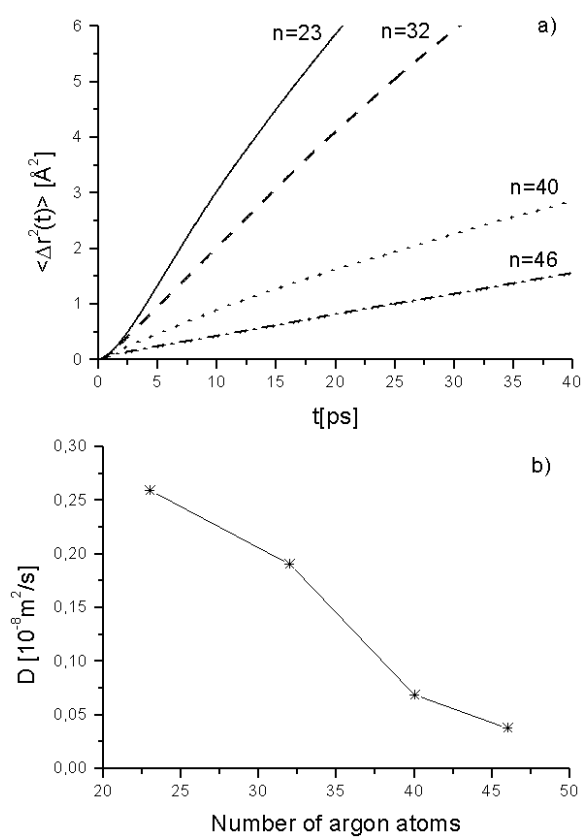
$$G_3(t) \propto \left\langle \sum_{i,j,k=1}^N \beta_{ij}(t) \beta_{ik}(0) \right\rangle \quad (7)$$

$$G_4(t) \propto \left\langle \sum_{i,j,k,l=1}^N \beta_{ij}(t) \beta_{kl}(0) \right\rangle. \quad (8)$$

The first term  $G_2(t)$  in equation (5) is responsible for depolarized light scattering in the low-density limit (the gas phase, where  $G(t) \simeq G_2(t)$ ), while the other two can become important at high density. For the bulk samples at liquid densities, the positive two- and four-body contributions are almost exactly cancelled by the negative three-body term, and the total intensity is much smaller than any of the components [12].



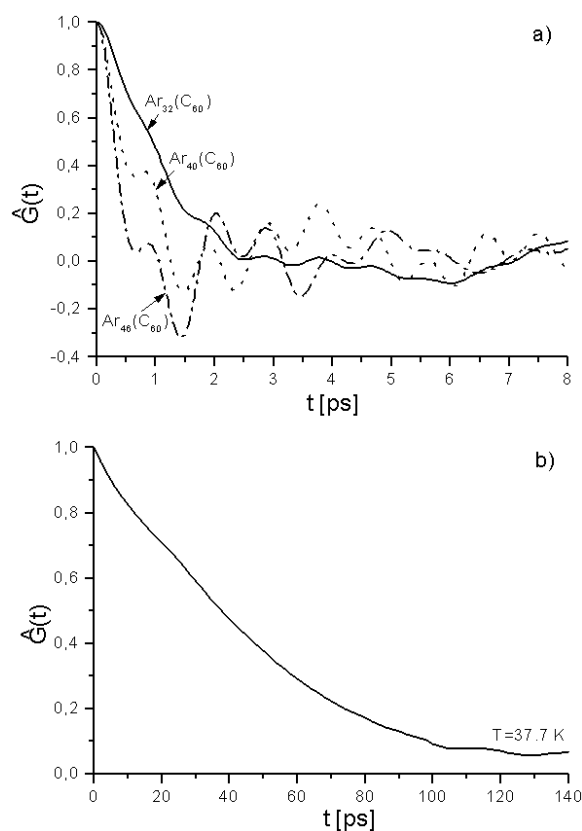
**Figure 2.** A snapshot of the instantaneous configuration of the argon ‘atmosphere’ surrounding the fullerene.



**Figure 3.** The mean square displacement (a) and the diffusion coefficient (b) of argon in  $\text{C}_{60}\text{Ar}_n$  clusters at  $T \simeq 100$  K as a function of the number  $n$  of atoms.

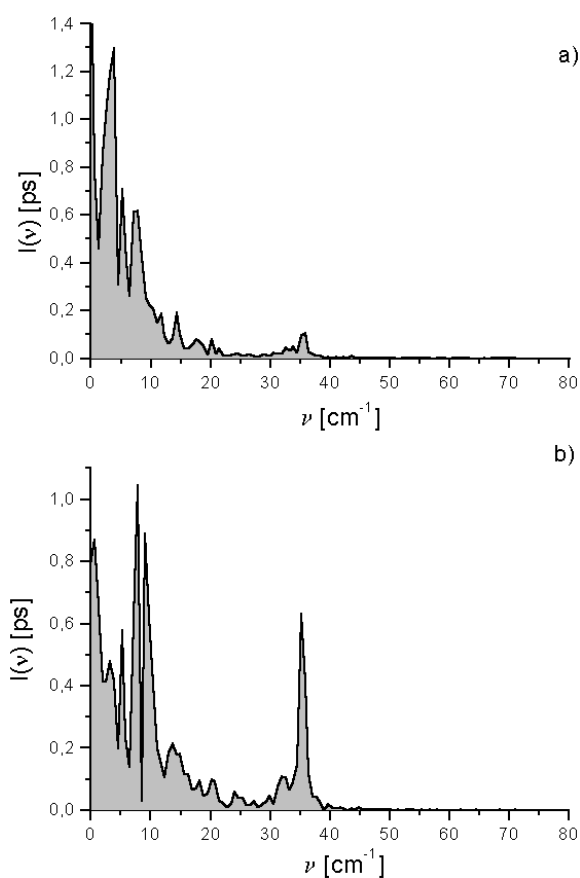
#### 4. Results

As we see in figure 1, the minimum of the  $V_{\text{C}_{60}-\text{Ar}}(r)$  potential is much deeper than that of  $V_{\text{Ar}-\text{Ar}}(r)$ ; therefore covering the fullerene molecule with an increasing number  $n$  of Ar atoms



**Figure 4.** (a) The normalized anisotropy correlation function  $\hat{G}(t)$  for  $\text{C}_{60}\text{Ar}_n$  ( $n = 32, 40, 46$ ) at  $T \simeq 100$  K; (b)  $\hat{G}(t)$  for a pure  $\text{Ar}_{46}$  cluster at  $T \simeq 37.7$  K (liquid phase).

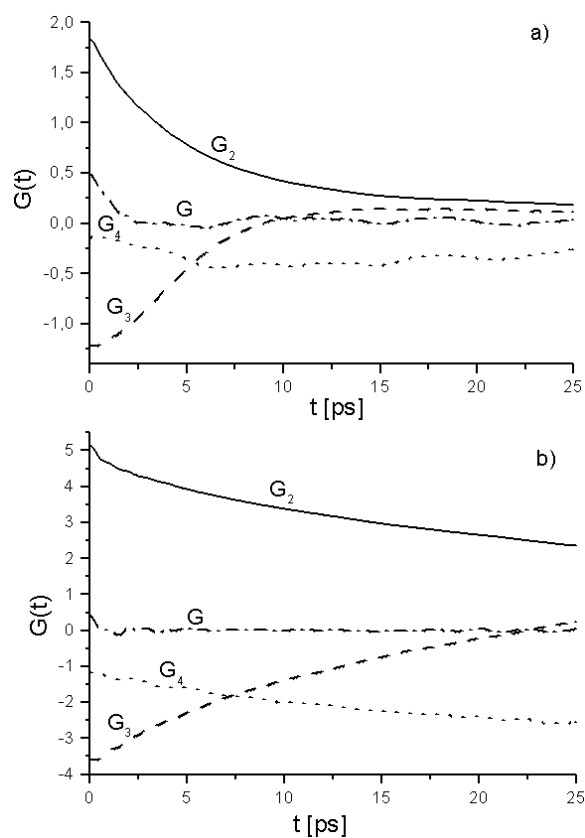
leads to the development of an argon shell or ‘atmosphere’ surrounding the  $\text{C}_{60}$  buckyball. The argons spread out quite evenly over the  $\text{C}_{60}$  surface, forming a spherically shaped monatomic layer (see the snapshot in figure 2). We have found that at a given temperature, the dynamical properties of the layer depend on the number  $n$  of its constituents. The simulated mean square displacement  $\langle \Delta r^2(t) \rangle$  and the translational diffusion coefficient  $D$  of argon in  $\text{C}_{60}\text{Ar}_n$  at  $T \simeq 100$  K ( $n = 32, 40, 46$ ) are presented in figure 3. The more atoms there are in a layer, the closer the packing is, the smaller the space for movement is and the smaller the diffusion coefficient is. The effect of layer ‘packing’ is also very clearly seen in the plot of the normalized polarizability anisotropy correlation function  $\hat{G}(t) = G(t)/G(0)$  of the argons. The function  $G(t)$  strongly depends on the number of atoms (figure 4(a)). It decays almost featurelessly for  $n = 32$  (low density), whereas for  $n = 40, 46$  it performs fast and clumped oscillations, characteristic for dense matter. We think that it is also interesting to show the difference between the depolarized light scattering in the pure argon cluster  $\text{Ar}_{46}$  (no fullerene, figure 4(b)) and in the spherically shaped argon layer ( $n = 46$ ) which covers the  $\text{C}_{60}$  (figure 4(a)). Note the substantially different timescale for the decay of  $\hat{G}(t)$ : it takes a few picoseconds for  $\text{C}_{60}\text{Ar}_{46}$  but a hundred picoseconds in the case of the  $\text{Ar}_{46}$  cluster. In the next figure (figure 5) we show the calculated depolarized light scattering intensity  $I(\nu) = \int_0^\infty dt \hat{G}(t) \cos(2\pi\nu t)$ . Note that the intensity peak  $I(\nu)$  at  $\nu \simeq 35$   $\text{cm}^{-1}$ , which is very small for  $n = 32$  (figure 5(a)), increases substantially when more argons are added (see figure 5(b),  $n = 40$ ); this can be associated with



**Figure 5.** The intensities  $I(\nu) = \int_0^\infty dt \hat{G}(t) \cos(2\pi \nu t)$  of the depolarized light scattering spectra at  $T \simeq 100$  K for (a)  $C_{60}Ar_{32}$  and (b)  $C_{60}Ar_{40}$ .

the increasing number of atomic collisions in the argon layers when  $n$  increases. For the bulk materials, the separate two-, three- and four-body correlation functions  $G_i(t)$  ( $i = 2, 3, 4$ ) are sometimes discussed [4, 12], in addition to the total function  $G(t)$ . An example showing the separately calculated  $G_i(t)$  for  $C_{60}Ar_n$  in low-density ( $n = 32$ ) and high-density ( $n = 46$ ) layers at  $T \simeq 100$  K appears in figure 6. For the low density,  $G_4(t)$  is almost negligible and the cancellation effect of negative  $G_3(t)$  with positive  $G_2(t)$  is clearly seen. For the closely packed layer (high density), the cancellation effect of negative  $G_4(t)$ ,  $G_3(t)$  and positive  $G_2(t)$  is even more pronounced. The decay of the two-body correlation function  $G_2(t)$  in a dilute layer is much faster than that in a dense one. This may be associated with the faster diffusion of less constrained argons over the sphere (figure 3).

In this paper we do not attempt to analyse the computer experiment data obtained in terms of theoretical models, because the theoretical treatment of interaction-induced light scattering in extremely small and ultrathin layers is not yet fully developed. The same remark applies to comparison with ‘real-life’ experiments; to our knowledge, experimental data (light scattering) for fullerene covered with an ultrathin argon layer are not yet available. The preliminary study reported here may serve as a comparison for future experimental and theoretical research on the interaction-induced light scattering in finite-size, coated fullerene systems.



**Figure 6.** Decomposition of the  $G(t)$  correlation function into two-, three-, four-body contributions for (a)  $C_{60}Ar_{32}$  and (b)  $C_{60}Ar_{46}$  clusters at  $T \approx 100$  K.

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