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Ab initio study of optical properties of shock compressed silica and lithium fluoride

Jean Clérouin[1], Yann Laudernet[1], Vanina Recoules[1] and Stéphane Mazevet[2]

[1] Département de Physique Théorique et Appliquée, CEA/DAM Île-de-France BP12, 91680 Bruyères-le-Châtel Cedex, France
[2] Theoretical Division T4, Los Alamos National Laboratory, NM 87545 New Mexico, USA

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Abstract

The equation of state and optical properties of shocked compressed silica and LiF are investigated using quantum molecular dynamics in a wide range of pressures and temperatures along the principal Hugoniot. For silica, the increase in reflectivity occurs at about 100 Gpa and saturates around 40%. For LiF, a pressure of 600 GPa is needed to observe a significant reflectivity, but no saturation is observed. Our results are in close agreement with the experimental measurements (Hicks D G, Celliers P M, Collins G W, Eggert J H and Moon S J 2003 *Phys. Rev. Lett.* **91** 035502) and a simple fit of the optical index of LiF versus compression is provided.

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(Some figures in this article are in colour only in the electronic version)

1. Introduction

Silica and lithium fluoride are two insulators widely used due to their transparency and physical properties at high pressure. The former is the reference material for building optics and windows able to support high energy fluxes at laser facilities such as the Laser Mega Joule in France or the National ignition Facility in the USA. The latter, LiF, provides optical windows with known optical properties below 1 Mbar [2–4] allowing for high pressure experiments where simultaneous VISAR diagnostics[3] can be performed. Several experimentations have been performed under 1 Mbar but, up to now, little is known on high pressure properties of such materials. Recently, laser-induced shock experiments have been performed on SiO_2 and LiF [1] in the megabar range and have shown the onset of the reflectivity at about 100 GPa for SiO_2 and 600 GPa for LiF. This rise in reflectivity is the sign of a transition from insulator

[3] Velocity interferometer for any reflector.

to a metallic behaviour. Similar experiments have also been performed on water [5], showing the transformation of the target material from transparent to opaque and eventually reflective. This scenario is very general and covers a wide range of thermodynamic conditions along the principal Hugoniot. In order to bridge the gap between low pressure experiments and very high pressure experiments, we performed quantum molecular dynamics (QMD) simulations from the normal density to the highly compressed state. Such high pressure simulations, which involve high temperatures (up to 10 eV) are probably at the extreme limit of capabilities of QMD simulations.

2. Method

QMD simulations were performed using the VASP *ab initio* simulation package developed at the University of Vienna [6], which couples the density functional theory (DFT) for the rapidly evolving electron population, and a classical molecular dynamics for the ions. The electron–ion interactions are treated with the projector augmented wave (PAW) pseudo-potentials [7]. The calculations were performed in the local density approximation (LDA) of DFT as parametrized by Ceperley and Alder [8]. To deal with high temperature regimes (up to a few eV) the simulations were performed using the finite temperature formulation of Mermin [9], and by using partial occupations for the orbitals as low as 10^{-5}. The question of pseudo-potentials was also addressed, for the highest pressures, by including the 1s electrons as valence electrons for the Li pseudo-potential. QMD offers the unique opportunity to compute at the same time the thermodynamical quantities and the transport properties. Pressure, energy and temperature are directly obtained from a simulation and optical properties are deduced from the optical conductivity obtained with the Kubo–Greenwood formulation as described at length in [10].

We followed a two-step process. First, ionic trajectories were produced by a QMD simulation at Γ point and using a minimum number of bands. Afterwards, a full calculation of the transition matrix was done for selected configurations with more k-points (from 2^3 for fluids to 4^3 for solids) and more bands to obtain the optical response in a wide range of energy. From the optical conductivity, dielectric constants, indexes, reflectivities and absorptions are deduced with the usual formulae [11]. The method was checked against experimental optical properties of SiO_2 and LiF at normal conditions. For dielectric constants and optical conductivities, the DFT results strongly underestimate the electronic gaps and ignore the excitonic peaks. Despite these well-known drawbacks, the reflectivities computed at 1 or 2 eV (corresponding to VISAR experiments) are in surprisingly good agreement with experiments (5% computed for SiO_2 instead of 4% exp., and an index of 1.39 at 1 eV for LiF, equal to the experimental value). We can hence trust the optical properties computed in the dense fluid phase, because the effect of the underestimated gap vanishes at these conditions.

3. Equation of state

We checked the equation of state by calculating for a given density, the pressure obtained at a temperature predicted by the SESAME model. For SiO_2, we found an excellent agreement between the pressures and temperatures predicted by the SESAME EOS and QMD averaged quantities (as shown in figure 2(*a*)). In contrast, for LiF, we found pressures and temperatures much lower than those predicted by the SESAME model. By searching the temperature for which, for a given density, the Hugoniot relation is satisfied, we found pressures in better agreement with the QEOS model [12] (figure 2(*b*)).

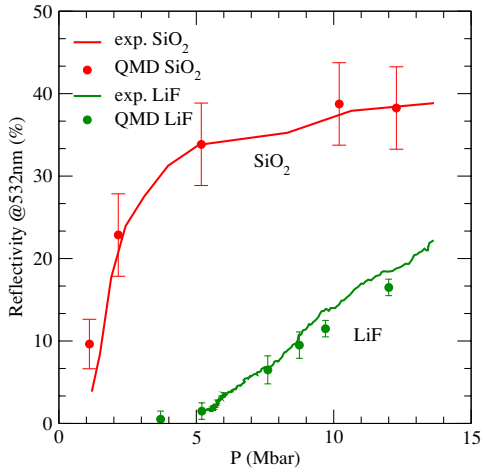

Figure 1. Reflectivity versus pressure for SiO_2 and LiF. Solid lines are laser-induced shock experiments data [1].

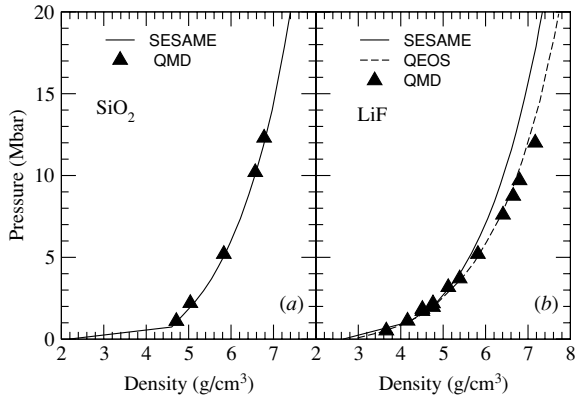

Figure 2. Pressures versus density along the Hugoniots for: (*a*) SiO_2 and (*b*) LiF compared with QMD simulations.

4. Reflectivities

Reflectivities are computed from the real n and imaginary part k of indexes

$$r(\omega) = \frac{[n_0(\omega) - n(\omega)]^2 + [k_0(\omega) - k(\omega)]^2}{[n_0(\omega) + n(\omega)]^2 + [k_0(\omega) + k(\omega)]^2}, \tag{1}$$

in which, for VISAR experiments, n_0 must be taken as the index of the unperturbed material before the shock. Figure 1 shows that the QMD reflectivities are in excellent agreement with experiments. We note that the reflectivity of SiO_2 is significant at a much lower pressure than LiF, but saturates while the reflectivity of LiF is seen to increase continuously. The rapid increase for SiO_2 is linked with the dissociation of Si–O bonds as revealed by the computation of the pair distribution function. For LiF, which is a strong ionic system, we observe a total charge transfer of one electron from lithium towards the fluor atom. The increase of reflectivity of LiF is probably associated with the gradual ionization of fluor with temperature.

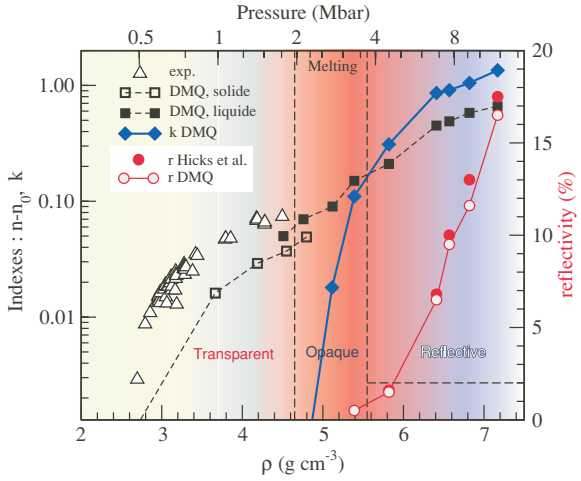

Figure 3. Left axis: indices (triangles: experiments; squares: QMD) and absorption coefficient (blue line with diamonds) and right axis: reflectivities (open circles: QMD; full circles: experiments) versus density.

5. LiF optical properties

Figure 3 presents a global scenario for LiF following the observed change in optical properties from transparent to opaque and eventually reflective along the principal Hugoniot. Temperatures are not shown, but correspond to QEOS predictions. The optical properties data are evaluated at a frequency of 2 eV (532 nm), twice the frequency of a Nd-glass laser to allow for comparisons with VISAR diagnostics. Experimental data are given for a broadband light between 1 and 4 eV. Between normal density and below 4.76 g cm^{-3} ($P = 2.2$ Mbar, $T = 5250$ K), LiF is transparent and the QMD simulations yield an index of refraction, $n(\omega)$ slightly underestimated when compared to the experimental values. In this state, the imaginary index, $k(\omega)$, and the reflectivity are negligible, and below the numerical accuracy of the method.

For densities between 4.76 and 5.82 g cm^{-3}, corresponding, respectively, to pressures of 2.2 and 5.2 Mbar, the imaginary index, $k(\omega)$, rises by four orders of magnitude (blue line with diamonds on figure 3). In this density range, the reflectivity also starts increasing but remains negligible while the real part of the index of refraction, $n(\omega)$, varies from a value of 1.39–1.6. This state corresponds to an opaque state recently characterized in VISAR experiments, and to the melting of the LiF crystal.

In the third region, beyond 5.8 g cm^{-3} (5 Mbar), LiF is in a fluid state and gets warmer (T goes up to 40000K). The Li ions diffuse and ionization sets in. The imaginary index continues to increase but saturates at about 1, with a reflectivity that rapidly increases but with no signs of saturation in agreement with the experiment.

6. Conclusion

We have shown that the QMD *ab initio* approach, despite some well-identified limitations in the solid phase, provides a continuous description of the optical properties of insulators from the solid phase to the dense plasma phase. In particular, the computed reflectivities for both materials in the high pressure conducting phase are in perfect agreement with experiments.

The method is also able to discriminate between different models of equation of state. For LiF we have also proposed a fit of the index versus compression that should help to interpret high pressure experiments using LiF window[4].

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[4] We propose the following quadratic expansion which accounts for both the experimental data below $\sigma = \rho/\rho_0 = 2$ and the QMD simulations results, above $\sigma = 2$:

$$n = n_0 + 0.1x + ax^2 + bx^4$$

with $a = -0.0133$, $b = 0.06895$, $n_0 = 1.39$ and $x = \rho/\rho_0 - 1$, with $\rho_0 = 2.638$.