Eur. Phys. J. D **33**, 315–322 (2005)
DOI: 10.1140/epjd/e2005-00052-6

THE EUROPEAN PHYSICAL JOURNAL D

Theory of light emission in sonoluminescence based upon transitions in confined atoms

L. Fortunato[a] and A. Torrielli[b]

Dipartimento di Fisica "G.Galilei" and Istituto Nazionale di Fisica Nucleare, via Marzolo 8, 35131 Padova, Italy

Received 21 April 2004 / Received in final form 23 June 2004
Published online 3 May 2005 –

Abstract. A theory of light emission in sonoluminescing hydrogen bubbles, based upon transitions in confined atoms, is proposed. Despite the simplicity of the assumptions this model accounts for a number of facts related to sonoluminescence: a broadband spectrum in the correct wavelength window is predicted as well as the number of emitted photons. Taking the temperature at the moment of collapse as a parameter we argue that confined atomic transitions at 4000 K may account for the observed light emission. This result favours a 'cold' interpretation of sonoluminescence in contrast to previous theories. Many considerations are qualitatively extendible to rare gases.

PACS. 43.35.+d Ultrasonics, quantum acoustics, and physical effects of sound

1 Introduction

Sonoluminescence has arisen considerable interest in the scientific community over almost 70 years. It was discovered in the '30 by Frentzel and Schultes and rediscovered in the more appealing form of Single Bubble Sonoluminescence (SBSL) by Gaitan and Crum in the early 1990's [1,2]. This last phenomenon consists in a single bubble of gas trapped in the antinode of a superimposed ultrasound field in a spherical or cylindrical resonator filled with degassed water. The wall of the gas bubble undergoes a strongly non-linear motion that is described by the Rayleigh-Plesset equation. At the very moment in which the bubble is at its maximum compression a burst of light with broadband spectrum in the visible region is seen. Recent reviews on the subject with a complete bibliography may be found in [3].

Our aim is to try to answer a fundamental question like the one that represents the title of a recent article: "Is there a simple theory of sonoluminescence?" [4] by proposing a fully quantum-mechanical light emitting mechanism that explains qualitatively and quantitatively the region of wavelengths and the intensities of sonoluminescence spectra, as well as the broadband nature of the emission.

In the following we will try to relate sonoluminescence to the study of compression in atoms. To summarize before entering into the details, this theory is based on the idea that at the point of maximum compression high temperatures, densities and pressures are present and this modifies the radial form of atomic orbitals. The fact that, in the turn of a very short time, many atoms are forced in a very tiny space and the temperatures are high enough that they cannot form any stable bound state or crystal lead us to use an infinite quantum well to simulate pressure.

Pressure is known to be related to an enhancement of energy levels and to a shrinking of atomic orbitals [5].

Atoms referred to as "confined" quantum systems are not a new issue in physics. Since the famous paper of Sommerfeld and Welker [6] the consolidated theoretical and experimental interest in confined atomic systems ([7] and references therein) is constantly grown thanks to the exciting technological possibilities and to the bulk of work concerning many intriguing systems like atoms enclosed in zeolites, fullerenes [8] or silicon and carbon nanodevices [9], that can be thought as idealized cages. But it is, first of all, stirring the quantum mechanical problem of confined interacting particles, the properties of which are very often different from those of the free ones [10]. Exploiting the features of such a confined atom is, without doubts, a goal to be pursued.

The phenomenon of SBSL has many obscure points and the light emitting mechanism is still not understood even if a plethora of models have been proposed [11]. Our idea is that light is emitted in the very same moment in which the violent collapse of the bubble compresses the gas to such a degree that the notion of hard spheres, that is well-working for the description of the dynamics of the bubble, may turn out to be not a good approximation as far as a light emitting mechanism is concerned. At the beginning all the free atoms are in their ground states, having a Maxwellian distribution of kinetic energies. Then a sudden collapse occurs that we model with

[a] e-mail: fortunat@pd.infn.it
[b] e-mail: torriell@pd.infn.it

the introduction of a square well term in the Hamiltonian. According to the sudden approximation, the occupation probabilities (that at low temperature are 1 for the free ground state and 0 for all the excited states) are reshuffled and the new ones are calculated as overlaps between the old and the new eigenstates: since the angular part of the wavefunctions must also be taken into account and since the spherical symmetry is preserved only states with $\ell = 0$ may be populated in this way, because the overlap integral with the initial s-eigenstate of the free hydrogen atom Hamiltonian and the final state of the compressed hydrogen atom Hamiltonian is separated into a radial and an angular integral and the latter gives $\delta_{0,\ell}$. The lowest state is thus the compressed $2s$ that is populated because of the sudden confinement. The degree of compression is however not the same for all the atoms, but they are compressed according to some distribution that is remnant of the initial one. The interplay of these two simple facts generates a broadband spectrum since the $2s$ state decays to the lower $2p$ one with a confined-confined transition within the right energy interval.

It is an experimental observation that rare gases are optimal to enhance the emitted intensity [12], nonetheless sonoluminescence has been noticed also in gas mixtures and in other chemical species such as hydrogen [13] and the obtained spectrum has a typical extension from red to blue wavelengths with an increasing intensity towards higher energy and a resultant bluish light.

Concerning ourselves to the hydrogen atom, we will discuss the results of Chuu and coworkers [14] about the analytic solution of the Schrödinger equation for that atom in the center of a confining infinite spherical well (Sect. 2). They provide the complete set of eigenfunctions, giving the implicit formula for the eigenenergies.

We then imagine the physical situation in which the atom undergoes a transition between confined states. We use hydrogen as a model to carry on calculations, since its compressed wavefunctions are known, with the purpose to achieve a good description of the spectrum from a qualitatively point of view as well as to estimate the order of magnitude of the most important quantities. Hydrogen and rare gases have a striking similarity for what concern their level scheme: the first excited state lies at very high excitation energy (at least about 10 eV). This is a feature that is not met in other gases (such as pure N_2 or pure O_2) that do not yield light emitting bubbles.

In Section 3, we make a simple model for a transition near the sudden confinement. The electromagnetic matrix elements for purely free hydrogenic atoms have been usually calculated in dipole approximation (see Bethe and Salpeter [15] for a detailed review) but have also been derived exactly in a very elegant way by Moses [16] and Seke [17]. We will carry on a complete calculation without recurring to the dipole approximation because dipole approximation may fail as long as the dimension of the system are changed, and we would like to get rid of this possible problem from the beginning. This does not introduce a greater degree of complication in the numerical calculations.

In Section 4, our ideas about sonoluminescence are discussed and in Section 5, we show the electromagnetic matrix elements, transition probabilities and emitted power, as a function of the degree of compression (either expressible as the radius of the confining well or as the wavevector of the emitted light, as we explain later). The origin of the broadband spectrum is treated in Section 6 and we give numerical estimates for relevant quantities. We conclude with a few remarks on the *pro et contra* and on the possible ways of improvement.

A somewhat similar model was introduced some years ago by Bernstein and Zakin [18]. They considered emission from electrons bound in interatomic cavities. In our model both electon and atomic nucleus are included in some sort of cavity (that comes from the presence of other surrounding atoms), in which are both confined.

2 Confined hydrogen

The Hamiltonian of a non relativistic hydrogenic atom without spin correction and with an infinite mass nucleus, to avoid the complications arising from the motion of the center of mass, situated at the center of an infinite spherical potential well reads:

$$H = \underbrace{\frac{-\hbar^2\nabla^2}{2\mu} - \frac{Ze^2}{\epsilon r}}_{H_0} + V(r). \tag{2.1}$$

Here μ, Z and ϵ are the effective mass, electric core charge and dielectric constant. We assume that the potential well has a radius R_0 and it can be expressed as

$$V(r) = \begin{cases} 0 & \text{if } r < R_0 \\ \infty & \text{if } r > R_0. \end{cases} \tag{2.2}$$

This potential gives rise to boundary conditions at the extremes and implies that the wavefunctions of the system are identically zero for $r > R_0$.

We refer the reader to the already cited work of Chuu et al. for the details and we merely discuss their results. Being the confining potential infinite, the spectrum contains discrete states only, both for negative and positive energies. They find the wavefunctions for those two cases, for a given total angular momentum $J = L$ (since spin is not included), in terms of Whittaker and Coulomb functions respectively:

$$R_L(r) = \mathcal{N}_C\ e^{-(\alpha r)/2}(\alpha r)^L \times {}_1F_1\big(1 + L - \eta, 2L + 2, \alpha r\big) \tag{2.3}$$

for $E < 0$, with $\alpha^2 = -8\mu E/\hbar^2 > 0$, $\eta = 2\mu Ze^2/\epsilon\hbar^2\alpha$ and

$$R_L(r) = \mathcal{N}_C'\ e^{-(i\tilde{\alpha} r)}(\tilde{\alpha} r)^L \times {}_1F_1\big(1 + L - i\tilde{\eta}, 2L + 2, 2i\tilde{\alpha} r\big) \tag{2.4}$$

for $E > 0$, with $\tilde{\alpha}^2 = +2\mu E/\hbar^2 > 0$[1], and $\tilde{\eta} = -\mu Z e^2/\epsilon\hbar^2\tilde{\alpha}$. The normalization constants $\mathcal{N}_C$ and $\mathcal{N}'_C$ are very important since they depend on alpha's and have to be calculated numerically.

In both cases the boundary condition is $R_L(R_0) = 0$, that is equivalent to the problem of the values of the zeros of the confluent hypergeometric function. Considering for example the former case one may write:

$$ {}_1F_1\big(\underbrace{1+L-\eta}_{-a}, \underbrace{2L+2}_{c}, \alpha R_0\big) = 0, \tag{2.5} $$

where $a \in \mathbb{R}^+$ in order to yield positive zeros. This equation is usually solved numerically in η. The energy of the system may be expressed as

$$ E = -\frac{\mu Z^2 e^4}{2\epsilon^2\hbar^2}\frac{1}{\eta^2}. \tag{2.6} $$

We note that when the first parameter of the hypergeometric is $n_r < a < n_r + 1$, with $n_r \in \mathbb{N}$ there are n_r nodes in the radial wavefunction. For consistency with the free hydrogenic atom notation the nodes in the two extremes $r = 0$ and $r = R_0$ are not considered. Rewriting the relation between a and η in a more transparent way, as $\eta = 1 + L + a \in \mathbb{R}$, we immediately find that η plays the same role as the principal quantum number n. In the free case the levels are degenerate with respect to the angular quantum number and they only depends upon the principal quantum number, while in the confined case some dependence on L is expected. The optimum would be to solve analytically equation (2.5) but, to our knowledge, only fairly approximated formulae [20,21] have been reported so far for the zeros of the confluent hypergeometric functions.

3 Electromagnetic interaction

The electromagnetic interaction, neglecting the second order terms in the vector potential, is

$$ H_{em} = i\frac{e\hbar}{\mu c}\mathbf{A}\cdot\nabla. \tag{3.7} $$

The exact matrix elements for the free atom are calculated by Moses [16].

In our case we want to derive the matrix elements between states of the system modified by the presence of the confining potential. We have two possible versions of the system: the free atom, the Hamiltonian of which is the well-known one, that we have called H_0, and the confined atom, with Hamiltonian $H_0 + V(r)$. Each one has its own basis of eigenstates and corresponding eigenenergies.

Imagine the situation in which the atom is, in the far past, in an eigenstate of one of the two Hamiltonians, say, to fix the ideas, the free Hamiltonian, and then abruptly at a certain time the atom is caged by the infinite potential well. It is worth mentioning that the initial free state now becomes an admixture of the basis states of the caged atom, *without radiating any photon* (this is commonly referred to as the "sudden approximation", well explained in [22]). This is an important part of the phenomenon that we are discussing since the sudden occurrence of the barrier has two consequences: first the occupation probability are redistributed in such a way that any excited state with the same angular momentum of the initial state has a non-zero population and second the wave functions are modified by the presence of the barrier. Now we imagine an electromagnetic transition between two confined stationary states, in which a spontaneous photon emission occurs. We recall the standard treatment of spontaneous emission by classical analogy (see for example [23]): correct formulas for the transition probability are obtained replacing the current density characterizing the classical radiating charge-current distribution by a quantum analogous, consisting of the matrix element of the gradient operator between two states, an initial upper eigenstate and a final lower one with a change λ in the total angular momentum. The same arguments made in [23] for free hydrogen atom apply here for the compressed eigenfunctions. We want to extend this analogy to the present case.

We will consider the complete multipolar expansion of the electromagnetic Hamiltonian for the sake of generality. We will indicate with $R^C_{\{A'\}}$ the radial wave function of the state of the confined hydrogen atom. Here $\{A\}$ is the set of quantum numbers $\{n, j, l, m\}$ (but $j = l$ here, since we have no spin). The elegant result of Moses expresses the electric and magnetic matrix elements for the transition between an initial state $|1\rangle$, for which there is no photon and the atom is described by the quantum numbers $\{n_1, j_1, m_1\}$, and the final state $|2\rangle$, for which there is a photon with quantum numbers $\{E, j, m, \Lambda\}$ (where the last is the helicity) and the atom is in the state $\{n_2, j_2, m_2\}$. For the convenience of the reader, we report here his general result for $j + j_1 + j_2$ even (electric-type transition), but with our modification to the upper boundary of the integrals:

$$ \begin{aligned} \langle 1|H_{em}|2\rangle_E &= e^2 a_0(\alpha_{f.s.}/8)^{1/2} i^j (-1)^{m_1}\Lambda \\ &\times\left(\frac{(2j+1)(2j_1+1)(2j_2+1)}{\pi j(j+1)}\right)^{1/2}\begin{pmatrix} j & j_1 & j_2 \\ m & -m_1 & m_2\end{pmatrix}\begin{pmatrix} j & j_1 & j_2 \\ 0 & 0 & 0\end{pmatrix} \\ &\times\Bigg[\Big(j(j+1)+\Delta(W+1)\Big)\underbrace{\int_0^{R_0} j_j(kr)R_1^{C^*}(r)\Big(\frac{\partial}{\partial r}R_2^C(r)\Big)rdr}_{I_{E1}} \\ &+\Big(-j(j+1)+\Delta(W+1)\Big)\underbrace{\int_0^{R_0} j_j(kr)\Big(\frac{\partial}{\partial r}R_1^{C^*}(r)\Big)R_2^C(r)rdr}_{I_{E2}}\Bigg], \end{aligned} \tag{3.8} $$

[1] We have had confirmation by the authors [19] that in [14] there were some typos regarding the sign of $\tilde{\alpha}^2$. Notice that we have slightly changed notation adding a tilde in order to avoid confusion.

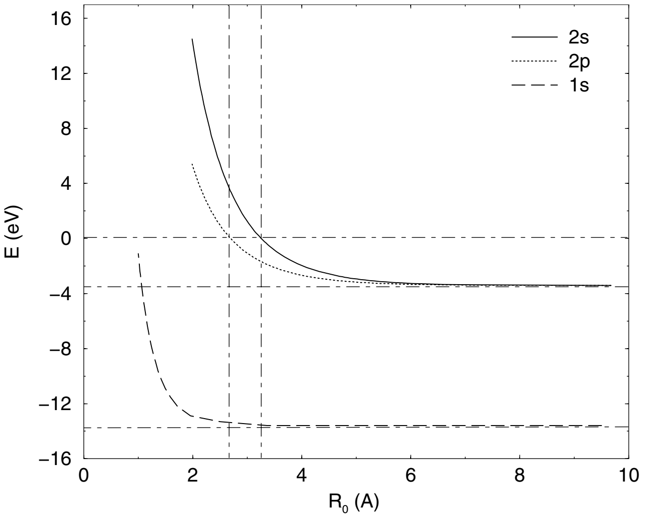

Fig. 1. Energy level scheme as a function of the confining barrier R_0. The two lower dot-dashed lines represent the energies of the free hydrogen $n = 1$ and $n = 2$ states, while the upper is the threshold at $E = 0$. The vertical lines placed at $R_0 \sim 2.69$ Å and $R_0 \sim 3.24$ Å divide the figure in three regions (see text). Notice that the energy gap depends on the radius of the confining barrier.

where $\Delta = j_1 - j_2$ and $W = j_1 + j_2$, a_0 is the Bohr radius and $\alpha_{f.s.}$ is the fine structure constant. For the Wigner 3-j symbols the reader could refer to [24].

For $j + j_1 + j_2$ odd (magnetic type transition) one obtains an analogous formula. We can see that, apart from physical constants and numerical factors, due to angular integration, the hurdle to overcome here is the integral, that we will nevertheless calculate numerically. We work with the exact form of Bessel function, without recurring to the usual dipole approximation because the difference of implementation is minimal and in this way we get rid of any possible failure as long as the atom is shrinked to a size that may make the dipole approximation useless.

4 Outline of the physical case of SBSL

Now we are prepared to the discussion of sonoluminescence from a quantum mechanical point of view.

The idea underlying the model is summarized in Figure 1. One solves the Schrödinger equation with respect to the parameter R_0 that is the radius of the infinite spherical well, obtaining the level scheme and the eigenfunctions.

The free hydrogen atom (without spin corrections), that here is recovered in the $R_0 \to \infty$ limit, has the 1s state at -13.6 eV, the degenerate $2s$ and $2p$ states at -3.4 eV and a threshold (corresponding to $n = \infty$) at zero energy. We have drawn three horizontal dot-dashed lines in correspondence to these three values. When the barrier comes closer to the position of the nucleus the energy levels begin to rise their energies according to the prescriptions in [5] and at the same time the degeneration in energy between states with different angular momentum quantum numbers is lost: the state with lower ℓ raises more. We have divided the figure in three regions by means of vertical lines placed at $R_0 \sim 2.69$ Å and $R_0 \sim 3.24$ Å. These radii correspond respectively to the points at which the energy of the $2p$ or of the $2s$ state crosses the threshold. These cases require an individual analysis since in the right region both wavefunctions are of the type (2.3), in the central region the $2p$ wavefunction is of the type (2.3), while the $2s$ one is of a (2.4) type and in the left region they are both of a (2.4) type.

Imagine now that we have a population (we will discuss later the way in which it is achieved) of the $n = 2$ states (both $\ell = s$ and $\ell = p$) at some fixed R_0. The possible electric dipole transitions are:

$$\begin{aligned} 2p &\to 1s \qquad 10.2 \text{ eV} < E_\gamma < \infty \\ 2s &\to 2p \qquad 0.0 \text{ eV} < E_\gamma < \infty. \end{aligned}$$

The energy of the first one must be bigger that 10.2 eV and it may be ruled out by the absorption of water at this frequencies, while the second, may have every energy gap. It turns out that in the region around 2–3 Å the energy is between 2–6 eV. This is the range of the confining radii that gives energies in accordance with the experiments. If one solves the Rayleigh-Plesset equation with some equation of state (from isothermal to adiabatic) with heat-exchange, and divides the volume of the bubble at its minimum for a typical value of number of atoms in the bubble, one may notice that the radius of the specific volume that surrounds each atom is in the range between 1 Å to some 4 Å. Thus the fact that these two ranges are consistent seems a clue that suggests that this phenomenon may be a candidate to explain SBSL. This statement will be reinforced by the calculation of the spectral intensities in the next sections. We mention that the specific volume decreases accordingly to the radius of the cavity, because in our model the wavefunctions are limited by the wall of the potential well and the expectation value of r^2 depends therefore on the extent of compression. The same reasoning may in principle be applied to the spectra of all the rare gases since there is always a big gap between the ground state and the first excited state.

5 Results for the transition between compressed 2s and 2p states

The matrix element for the transition between a compresses $2s$ orbital and a compressed $2p$ with the emission of a photon with wave vector k, given helicity Λ and given third component of the angular momentum m reads:

$$\begin{aligned} \langle 2s^C, 0ph | H_{em} | 2p^C, 1ph \rangle_{\Lambda,m} &= i e^2 a_0 \sqrt{\frac{\alpha_{f.s.}}{\pi}} \Lambda \\ &\times \int_0^{R_0} j_1(kr) \left(\frac{\partial R_{2s}^{C*}(r)}{\partial r} \right) R_{2p}^C(r) \; r \; dr, \quad (5.9) \end{aligned}$$

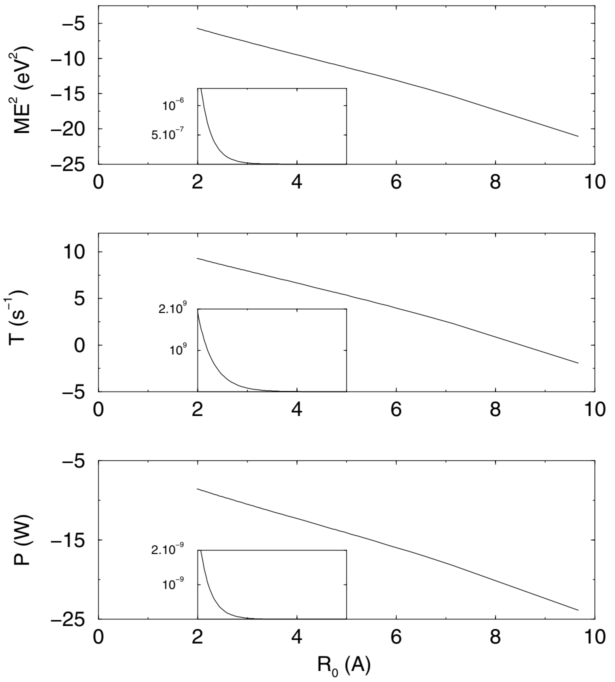

Fig. 2. Square of the matrix elements (in eV^2), transition probability (in s^{-1}) and emitted power (in W) as a function of the confining radius (in Å). The vertical scales are logarithmic and only the exponents of 10 have been explicitly written. The three insertions present the same data but in a linear vertical scale, for a limited interval ranging from 2 to 5 Å.

where the angular part has already been calculated. The integral in the expression above, containing the radial wavefunctions of the mentioned states, may be computed numerically. The nontrivial dependence of the normalization constant of compressed states upon the wavevector has been carefully considered and attention has been brought to take into account the proper values. We plot in the combined Figure 2 the square of the matrix element summed over the two possible helicity and three values of m (amounting to a total factor of 6) expressed in shorthand notation as $ME^2 = \sum_{\Lambda,m} |\langle - | - | - \rangle|^2$, the transition probability $T = \frac{2\pi}{\hbar}\frac{ME^2}{\hbar\omega}$ and the emitted power $P = \hbar\omega T$ with respect to the radius of the confining barrier. Each point in the figures represents the value of matrix elements, transition probability or emitted power that an atom will exhibit when shrinked to a well defined value of the confining radius that, in turn, results in a well defined value for the wave vector of the emitted photon. The modifications that we have found are interesting and one should expect that, if a transition between an initial confined $2s$ and a final $2p$ compressed state is produced, the signature in the spectrum must be seen clearly. To summarize we argue that sudden compression of hydrogen atoms will result in a transition to a lower state with the following features:

– good energy gap from (free limit) 0 eV to few eV's, resulting in visible light emission;
– sizeable growth of matrix elements, transition probability and emitted power;

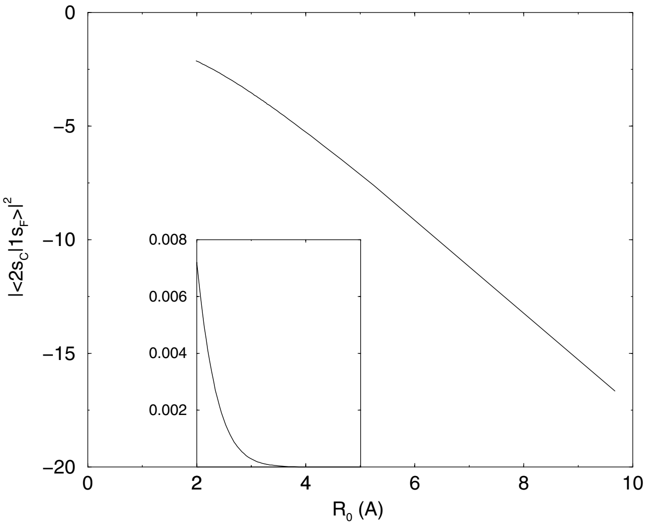

Fig. 3. Squared overlap between the $1s$ free wavefunction and the $2s$ compressed wavefunction as a function of the confining radius (in Å). The vertical scale is logarithmic. The insertion presents the same data but in a linear vertical scale, for the interval of interest ranging from 2 to 5 Å.

– population of $n = 2$ states due only to the sudden confinement (to be discussed in the following paragraph).

Our calculations depend on the infinite square well approximation that we have employed, nevertheless we expect that this model captures the essential features that a more realistic potential would yield. In particular, assuming a typical value for the acoustic pressure applied to the bubble and a typical volume change, one can calculate the compressional energy transferred to the gas. Distributing such energy among the atoms, one can see that on the average each of them gets enough compressional energy to reach the region of small R_0's (in Fig. 3), needed for our model to give a correct spectrum.

6 Discussion of the origin of the broadband spectrum

Many theories are available on the stock to describe the dynamics and thermodynamics of the bubble to a more or less refined degree. We do not attempt here a detailed enumeration of these approaches, but we refer the reader to the appropriate bibliography [3]. Despite the early attempts to give an estimate for the maximum temperature reached at the collapse that ended with predictions of very high temperatures, it seems that nowadays various groups have reached a common range of values, from few thousands Kelvin to, at maximum, 20 thousands. These temperatures are consistent with blackbody fits of the spectra, which look rather successful, but still lack a robust physical explanation. The gas inside the bubble follows the well-known laws of gases in the most part of the SBSL cycle, that is with the exception of the last part of the quick compression. At the moment of collapse a simple adiabatic equation of state is too crude an approximation. Instead of the many elaborated treatments that can be found in literature we will propose simple arguments. Without the need of specifying the details of the collapse, we argue that, at the end of the shrinking process, the bubble contains a high density fluid and the compressed atoms, that *on the average are at rest*, have a distribution of specific radii (i.e. the radius of the volume that each atom may occupy) that is remnant of the initial energy distribution: it turns out from experimental data, as noticed by many authors, that the specific atomic volume may be smaller or of the same order of magnitude of the free atomic volume. Reshaping these consideration within the physics of compressed atomic orbitals implies that each atom is trapped in a cage small enough to modify its orbitals and the radii of the various cages may be different, according to some distribution. We take the Maxwellian distribution as an approximation for the distribution of kinetic energies inside the bubble *before* the collapse. The kinetic energy is transformed into potential energy *after* the collapse resulting in an enhancement of the energy levels. Assuming this hypothesis one can write a distribution in confining radii that depends only on the temperature:

$$H(R_0)dR_0 = \frac{2}{\sqrt{\pi}}\Big(\frac{1}{kT}\Big)^{3/2} \times \sqrt{E_\gamma(R_0)}e^{E_\gamma(R_0)/kT}\frac{dE_\gamma}{dR_0}dR_0, \quad (6.10)$$

where E_γ is the energy of the $2s$-$2p$ transition at a given R_0. Hence the fraction of atoms that emit light is

$$\tilde{N}_\gamma(R_0)dR_0 = \frac{N_\gamma(R_0)dR_0}{N_{atoms}} = |\langle 2s^C|1s^F\rangle|^2 H(R_0)dR_0 = |\langle 2s^C|1s^F\rangle|^2 H(\lambda)\left|\frac{dR_0}{d\lambda}\right|d\lambda, \quad (6.11)$$

where $N_\gamma(R_0)$ is the number of emitters, while N_{atoms} is the total number of atoms in the bubble. This fraction is displayed in Figure 4 as a function of the confining radius for a given temperature of 4000 K (see below for a detailed discussion). As a side remark we notice that any other reasonable choice for the radii distribution, i.e. showing a peak in the correct window of radii and decreasing quickly at zero and infinity, should give at this stage similar results. In particular, relaxing the hypothesis of an infinite hard-core potential, one may expect a distribution of potential energies, that should be properly taken into account in the present reasoning. It seems to us that the use of infinite square well includes the essential part of the physics, and only details can be modified using a more sophisticated modellization.

We show in Figure 5 the predictions for the specific spectral radiance (defined as the spectral radiance divided by the total number of atoms in the bubble). It reads

$$\tilde{R}(\lambda)d\lambda = \frac{R(\lambda)d\lambda}{N_{atoms}} = |\langle 2s^C|1s^F\rangle|^2 P(\lambda)H(\lambda)\left|\frac{dR_0}{d\lambda}\right|d\lambda, \quad (6.12)$$

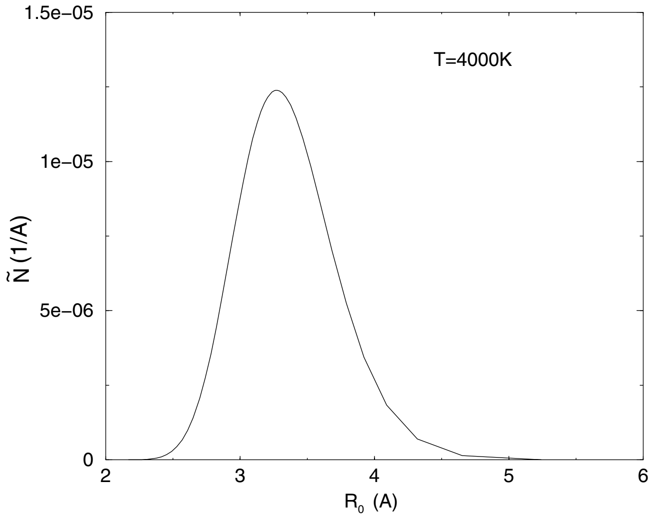

Fig. 4. Distribution of the number of emitters as a function of R_0 at 4000 K divided by the total number of atoms in the bubble. The integral is about 10^{-5} which, combined with the typical number (10^9) of atoms in the bubble, gives a reasonable estimate (10^4) for the number of emitted photons.

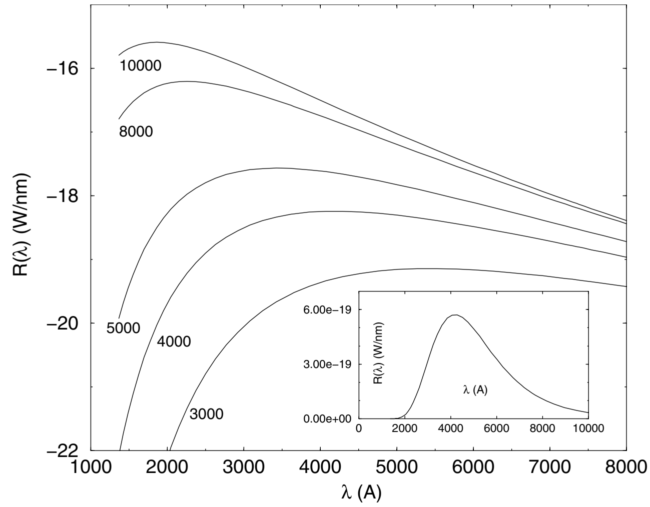

Fig. 5. Spectral radiance for one atom (logarithmic vertical scale) in W/nm as a function of the wavelength of the emitted light (in Å) for various temperatures indicated in Kelvin near each curve. To obtain the spectrum one has to multiply these curves for the total number of atoms in the bubble since the fraction of them that occupies the 2*s* is already been taken into account (see text). The inset shows the 4000 K curve in a vertical linear scale.

where $P(\lambda)$ is the emitted power (equal to $\hbar\omega T$, see previous section) as a function of the wavelength of the emitted light. It already contains the occupation probability of the $2s$ state that is the square modulus of the overlap integral.

In this figure we give many curves corresponding to different temperatures in a logarithmic scale (and in the inset we display the curve at 4000 K in a vertical linear scale). The lineshape of the experimental spectrum given in reference [12] (which updated older ones, see references therein for details) is thus reproduced considerably well for a temperature that ranges between 3000 K and 4000 K, that gives the peak in the right windows of λ's. However to obtain the total spectrum we still have to multiply by the *total* number of hydrogen atoms inside the bubble. It turns out that a factor of about 10^6–10^7 is needed to reach a few 10^{-13} W/nm. This factor is two or three order of magnitude smaller than the typical value for the number of atoms inside an hydrogen bubble trapped with a partial pressure of 3 torr: with $R_0 = 3$ μm and $f = 33$ kHz at room temperature one expects at maximum some 10^9 atoms. If one insists in using this value, one obtains a spectral radiance that is bigger than the experimental values. Standing the various approximations that our model contains and the rough estimates that we have employed in our previous considerations, the results seem nevertheless to point in the right direction. Moreover integrating the distribution in Figure 4 and multiplying for the total number of atoms (say 10^9), one can obtain for the total number of emitters (that corresponds to the total number of photons) an estimate of about 10^4. This value is about 1/10 of the typical value of photons emitted from an air bubble in water at room temperature. This seems to go in the same directions of the measurements of SL in hydrogen bubble that also indicates that this gas yields dim bubbles [13], although it is still unclear to what extent water vapor might play a role both in the bubble dynamics and in the emission mechanism (for example it may modify the interaction potentials, i.e. contribute to the compression with a differently shaped potential well and/or change the concentration of emitting atoms). Another good point is that the slopes of the two tails are in good agreement with the typical trends found experimentally: the sharp cutoff near the maximum at high energies (low wavelengths) is a natural consequence of the convolution of the power (Fig. 2, third panel) with the distribution of the specific radii, while the mild falloff at low energies is also consistent with the available data (from the peak position to 8000 Å it typically decreases of less than one order of magnitude).

7 Summary and conclusions

The main outcome of the present work has been to furnish a completely novel quantum mechanical mechanism to explain, at least in a qualitative way, the observed broadband light emission in single bubble sonoluminescence. This theory is based on the natural extension of electromagnetic transitions in confined atoms, that we think may play a crucial role in the solution of the SBSL puzzle. After setting the model we have specialized the calculations in the case of hydrogen, giving some numerical support to this view.

We think that our theory does not include the following points:

- we have not found the width of the light pulse (that is considered a test-quantity [3]). This is due to the fact that the 'real' phenomenon has an evolution with time that we left out introducing the Maxwellian distribution of radii, that in turn relies on the equivalence between kinetic energies before and compressional energies after the quick collapse: a refined way to treat this would be to implement a two-channels system with back and forth transitions;
- we have focussed on the light emitting mechanism leaving aside the study of the dynamics of the bubble (a topic that has been extensively covered until now). A complete theory of sonoluminescence needs to join these two aspects;
- we have not yet included transient type of light emission (unstable SL) in the present context.

Nevertheless, starting from quantum mechanical exact calculations and making use only of reasonable approximations, such as the simulation of the quantum effect of pressure with an infinite square well and the derivation of a 'Maxwellian' distribution for the radii at the collapse, this theory explains in a simple and attractive way many observations:

- the broadband spectrum is obtained without introduction of any parameter except temperature (that is not known so far). Choosing a temperature that is considerably lower than the ones proposed in the past, the process gives enough visible light to reproduce the peak and the shape of the spectrum. The fact that this theory may explain the observed intensities at a temperature that is lower than the ones needed or proposed in other models should be considered a strong argument;
- two main explanations of the absence of line emission in sonoluminescence were often given: or the pressure broadening spreads the discrete lines forming a continuum or the continuum radiation (due to some mechanism) is more intense that the line emission that thus remains invisible. Our mechanism furnishes a natural alternative to the absence of line emission explaining the spectrum as a collection of discrete transitions with different energies. In fact experimental data like Figures 18 and 19 in the work of Brenner et al. [3] have a simple qualitative interpretation at the light of our model. Notice that Figure 18 in the cited work is for argon, while Figure 19 is for organic fluids: both organic molecules and water, that was considered a "friendly" environment for SL (see Barber et al. [3]), contain hydrogen. After a few cycles (perhaps just one) these molecules are likely to be broken, as explained, and they provide a source of free hydrogen, that is at the very center of our present speculations;
- the number of photons comes out naturally from our scheme, if we choose a reasonable estimate for the total number of hydrogen atoms inside the bubble;
- the particular role of hydrogen and rare gases is found to rely in the big gap that they present in the level scheme. For these particular gases the reshuffling is effective only for s states due to the orthogonality of the wavefunctions with different ℓ (as we already explained) and the occupation probabilities are smaller for higher lying states. In principle one should take

into account all the $Ns - (N-1)p$ transitions, but the lowest possible is the strongest. Other gases with a different electronic structure with respect to noble gases (that are expected to give rise to more complex situations) may populate low-lying states by collisions before reaching an appreciable degree of compression;
- a clue to the explanation of the dramatic dependence of the total emitted power upon the ambient conditions is suggested: a variation of the initial conditions affects the final temperature of the bubble and the intensity of the spectrum strongly depends upon this temperature as seen in the last figure;
- the lowering of ionization potentials and appearance of electronic band structure may be also explained qualitatively. In our simple model the use of an infinite well prevents to speak about a meaningful ionization potential, nevertheless with a finite well the behaviour would have been the same, though milder, and in that case the energy needed for ionization would have decreased accordingly to the radius of the confining well. Thus electrons free from their original atoms, but still bound by the cavity would give rise to electronic band-like behaviour;
- even if we have not introduced the effects of a dense gas on the propagation of light in an accurate way, a semi-classical argument is in order to support our idea: if the emitter is in the center of the bubble and the photon has to go straight through the bubble at its maximum compression (say 0.2 μm), the order of magnitude of the number of atoms that it may encounter is $\sim 2 \times 10^3$. The distribution of the number of emitters/absorbers is given in Figure 4. In the most unfavourable situation the photon is emitted by an atom whose cage is the most abundant, and the probability to find another atom with the same cage is at maximum some $\sim 10^{-5}$. The probability for the absorption of such a photon is thus roughly $\sim 2 \times 10^{-2}$, that may be easily neglegted.

We feel that a better level of approximation may lead to precise quantitative results, but the rough features of the phenomenon are under control. Further theoretical investigations on SBSL must clarify if a relaxation of the hypothesis of sudden approximation leads to different results. In negative case, this theory seems to support a cold interpretation of SL spectra (where with 'cold' we mean colder that the current interval that ranges from 8000 K to higher temperatures). Thus any 'hotter' theory should take into account the contribution given from confined-confined transitions to the total spectrum.

One may wonder that in real SL the bubbles are filled with molecular hydrogen, H_2 and not with atomic hydrogen. If one confines an H_2 molecule inside the cavity and shrinks the radius, the behaviour of the systems is similar: for a certain compression the molecular ground states crosses the threshold and the molecule is no more bound: this anyway happens for much larger radii because the molecule is much less bound than the atom. This may be a line of refinement of our model.

We also mention that an effort to repeat and refine these calculations with other gases (using variational wavefunctions, for instance) is required and that the last word should be searched in experiments, specifically designed to measure the temperature of the bubble, that has insofar eluded any experimental effort.

References

1. D.F. Gaitan, Ph.D. thesis, Un. of Missisippi (1990)
2. L.A. Crum, Phys. Today **47**, 22 (1994)
3. M.P. Brenner, S. Hilgenfeldt, D. Lohse, Rev. Mod. Phys. **74**, 425 (2002); D. Hammer, L. Frommhold, J. Mod. Opt. **48**, 239 (2001); B.P. Barber et al., Phys. Rep. **281**, 65 (1997)
4. S. Putterman, Nature **409**, 782 (2001)
5. J.P. Connerade et al., J. Phys. B **33**, L847 (2000); J.P. Connerade et al., J. Phys. B **33**, 251 (2000)
6. A. Sommerfeld, H. Welker, Ann. Phys. **32**, 56 (1938)
7. W. Jaskólsky, Phys. Rep. **271**, 1 (1996)
8. A. Baltenkov, J. Phys. B **32**, 2745 (1999)
9. M. Knupfer, Surf. Sc. Rep. **42**, 1 (2001)
10. J.P. Connerade et al., J. Phys. B **32**, L239 (1999); J.L. Zhu, Phys. Rev. B **39**, 8780 (1989); J.L. Zhu et al., Phys. Rev. B **41**, 6001 (1990); Y.P. Varshni, J. Phys. B **31**, 2849 (1998); Y.P. Varshni, J. Phys. B **30**, L589 (1997); E. Ley-Koo, S. Rubinstein, J. Chem. Phys. **71**, 351 (1979)
11. K. Yasui, Phys. Rev. E **60**, 1754 (1999); B.D. Storey, A. Szeri, Phys. Rev. Lett. **88**, 074302 (1992); C. Eberlein, Phys. Rev. Lett. **76**, 3842 (1996); L. Frommhold, A.A. Atchley, Phys. Rev. Lett. **73**, 2883 (1994); M.J. Moran, D. Sweider, Phys. Rev. Lett. **80**, 4987 (1998); W.C. Moss et al., Phys. Rev. E **59**, 2986 (1999)
12. R.A. Hiller, S. Putterman, Phys. Rev. Lett. **77**, 2345 (1999); R.A. Hiller, S. Putterman, Phys. Rev. Lett. **75**, 3549 (1995)
13. G. Vasquez et al., Phys. Rev. Lett. **88**, 197402-1 (2002)
14. D.S. Chuu, C.M. Hsiao, W.N. Mei, Phys. Rev. B **46**, 3898 (1992)
15. H.A. Bethe, E.E. Salpeter, *Quantum Mechanics of One- and Two-Electron Systems* in *Hanbuch der Physik*, edited by S. Flügge (Springer-Verlag), Vol. **35**, 345ff., 1954
16. H.E. Moses, Phys. Rev. A **8**, 1710 (1973)
17. J. Seke, Physica A **203**, 269 (1994)
18. L.S. Bernstein, M. Zakin, J. Phys. Chem **99**, 14619 (1995)
19. D.S. Chuu, private communication
20. *Bateman manuscript project: higher transcendental functions*, edited by A. Erdély et al. (Mc-Graw-Hill book company, Inc., 1995)
21. F. Tricomi, Ann. Mat. Pura Appl. (IV) **26**, 141 (1947)
22. B.H. Bransden, C.J. Joachain, *Quantum Mechanics*, 2nd edn. (Prentice Hall, 2000), p. 458
23. L. Shiff, *Quantum Mechanics* (Mc-Graw-Hill book company, Inc., 1968), p. 413ff
24. *Atomic, Molecular & Optical Physics Handbook*, edited by G. Drake (AIP, New York, 1996)