Sonoluminescence: A theoretical overview

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Abstract

In this paper we present a few of our theoretical attempts to explain the effect of sonoluminescence (SL). These are based on the results for the thermodynamic properties of the gas in the bubble following from the solution of the well known Rayleigh-Plesset equation.

Sonoluminescence (SL) is the emission of light which is sometimes observed when ultrasound is passed through a liquid containing dissolved gases. The effect represents a remarkable degree of energy concentration (as high as 12 orders of magnitude) and consists of easily observable, extremely short (less than 50 ps) bursts of visible light extending into the ultraviolet. These pulses are emitted from strongly modulated gaseous bubbles in liquids with clock-like precision, synchronized to a few parts in 10^{11}. The bubble(s) oscillate with the period of the sound field and for the experimental parameters for which SL pulses are observed, exhibit strongly nonlinear oscillations. Assuming that the gas in the bubble follows the adiabatic law, the temperatures of a few thousand degrees could be expected in the bubble. We present a few models which tend to explain SL based on these results.

1 Collective Effects

The short duration of the SL pulse was our motivation to explore the possibility that some collective effect, like superradiance or superflourescence, could take place.

The cooperative emission from a system of $N >> 1$ atoms is a typical many body effect consisting of an emission proportional to N^2 and a duration proportional to N^{-1}. Superradiance is a cooperative emission from a system excited by a coherent pulse into a "correlated" state which has a macroscopic dipole moment. If we start from the initially uncorrelated excited atoms and the system spontaneously creates correlation, we are talking about the phenomenon of superflourescence. A third "kind" of radiation, also proportional to N^2 is free induction decay, which has to do with the strong inhomogeneous broadening - loss of the coherence through dephasing among atoms with different natural frequencies. For a short time the radiation is enhanced by the coherence, but the energy released is just a small fraction of the total energy. "Short" here refers to the dephasing time - the time needed to destroy the coherence.

The essential ingredient for any collective effect is a highly organized system. How can we expect to have these conditions satisfied in a gaseous cavity under the extreme conditions of high pressures and temperatures? The interaction taken into account in [1]-[3] is between the atoms and the electric field. In our model we assume that there is also an interaction among the atoms in our sample, which could get to be fairly strong. We want to see if we can expect to have some kind of "locking" [4] among the atoms, which can produce a collective state which satisfies the conditions for collective emission.

1.1 Model Hamiltonian

We consider a collection of N atoms (molecules) in thermal equilibrium and model the individual atoms as two-level systems with ground state energy e_0 and excited state energy e_1. We assume the atoms to be close to each other, i.e. that the internuclear separations are small compared with the wavelength of the emitted radiation. Next we add the interaction with the radiation field and the possibility of near field (dipole-dipole) interaction.

The interaction part of the total Hamiltonian we model in a way to correspond to a given atom getting deexcited and resonantly transferring its energy to another atom:

$$H_2 = \sum_{i,j,i\neq j} \Lambda_{ij} \sigma_i^- \sigma_j^+ \tag{1}$$

where Λ_{ij} is the coupling and σ_i^+, σ_i^- are atomic excitation and deexcitation operators, respectively. The total Hamiltonian is

$$H = H_0 + H_{int} + H_2 \tag{2}$$

where

$$H_0 = \sum_{\vec{k}s} \hbar\omega_{\vec{k}s} \left(\hat{a}^+_{\vec{k}s}\ \hat{a}_{\vec{k}s} + \frac{1}{2} \right) \ + \ \sum_{n=0}^{N} \left(\frac{e_0 + e_1}{2} I_n - \frac{\hbar\omega_0}{2} \sigma_n^z \right) \tag{3}$$

and

$$H_{int} = \sum_{\vec{k}si} \gamma_{\vec{k}s} \vec{\mu} \cdot \hat{\epsilon}_{\vec{k}s} \ \left(\hat{a}^+_{\vec{k}s} \sigma_i^- \ + \ \hat{a}_{\vec{k}s} \sigma_i^+ \right) \tag{4}$$

Here $\hat{a}^+_{\vec{k}s}$, $\hat{a}_{\vec{k}s}$ are the creation and the destruction operators for the photon field, $\hat{\epsilon}_{\vec{k}s}$ is the polarization vector, $\{\sigma\}$ are Pauli matrices, $\gamma_{\vec{k}s}$ is given by $\sqrt{2\pi\hbar\omega_{\vec{k}s}/V}$, where V is the quantization volume, ω_0 is defined as $(e_1 - e_0)/\hbar$ and $\vec{\mu}$ is a transition dipole matrix element. This is the Hamiltonian in the dipole and rotating wave approximation. We follow by making some additional approximation in order to see what we can expect from this approach.

1.2 Atom - Atom Interaction

For the time being, we assume that Λ_{ij} is a constant (the equal coupling approximation) and drop the radiation coupling. The argument for the last approximation is that we want to explore the effect of coupling among atoms through the "near field". The radiation coupling will be considered later. So, the Hamiltonian becomes

$$H = -\frac{\hbar\omega_0}{2}\,\sigma^z \;+\Lambda\,\sigma^-\sigma^+ \tag{5}$$

where the σ operators are defined as

$$\vec{\sigma} = \sum_{n=1}^{N}\;\vec{\sigma}^i \tag{6}$$

We calculate the spectral distribution of the emitted radiation using

$$I(\omega) = \int_{-\infty}^{\infty} e^{-\imath\omega t}\;Tr[\rho\;\sigma^+(t)\;\sigma^-(0)]\;dt \tag{7}$$

where ρ is the density matrix, given by

$$\rho = \frac{e^{-\beta H}}{Tre^{-\beta H}} \tag{8}$$

We use the fact that the system of N atoms can be represented as a system having a quasi-angular momentum $N/2$ [1]-[6]. Using the Dicke notation we represent our basis states with two quantum numbers j, m (j is so called "cooperation number"), satisfying the condition $|m| \leq j \leq N/2$.

The final result for the radiation intensity is

$$I(\omega) = 2\pi\frac{\sum_{m=-N/2}^{N/2}\delta(\omega_0-\omega+\frac{2m\Lambda}{\hbar})\,e^{\beta\hbar\omega_0 m-\beta\Lambda m(1-m)}\;\mathcal{F}(N,m)}{\sum_{m=-N/2}^{N/2}e^{\beta\hbar\omega_0 m-\beta\Lambda m(1-m)}\sum_{j=|m|}^{N/2}g_j\;e^{-\beta\Lambda j(j+1)}} \tag{9}$$

where

$$\mathcal{F}(N,m) = \sum_{j=|m|}^{N/2} g_j\,e^{-\beta\Lambda j(j+1)}j(j+1) - m(m+1)\sum_{j=|m|}^{N/2} e^{-\beta\Lambda j(j+1)} \tag{10}$$

and g_j is the degeneracy of a state with a given j

$$g_j = \frac{N!\,(2j+1)}{(\frac{N}{2}+j+1)!\,(\frac{N}{2}-j)!} \tag{11}$$

By examination of the results for the intensity versus number m, or frequency radiated, for different numbers of atoms, we notice that the width Γ (full width at half maximum) grows sublinearly with the number of atoms (time scale for the pulse emitted is $\Delta t \propto 1/\Gamma$). In order to check the dependence of the total emitted radiation (if we do not resolve individual lines) on the number of atoms, we calculate the total intensity as $I = \int I(\omega)d\omega$ and the results also show sublinear growth. Thus, it turns out that with these approximations of our model, we do not get evidence that a cooperative effect takes place.

1.3 Atom - Field Interaction

In the previous section, the interaction of the atoms with the radiation field was neglected. In what follows, we will try to explore the possibility of obtaining a population inversion through this interaction.

We consider a simplified Hamiltonian, corresponding to $H_0 + H_{int}$, given by Eqs. (3, 4)

$$H = \frac{\hbar\omega_0}{2}\sigma^z \;+\; \alpha(t)\,\sigma^-\hat{a}^+ \;+\; \alpha^*(t)\,\sigma^+\hat{a}^- \tag{12}$$

The time dependence in α, α^* comes from the exponential factor in the electric field and also from the time dependence of the temperature and other parameters which depend of the bubble radius $R(t)$. Furthermore, we generalize this Hamiltonian by adding phenomenological relaxation times T_1 and T_2. Using the density matrix formalism and expressing the density matrix in terms of a Bloch vector $\vec{P}$

$$\rho = \frac{1}{2}[I + \vec{P}\cdot\vec{\sigma}] \tag{13}$$

we obtain the following expression for the components of $\vec{P}$

$$\dot{P}_z = -\frac{2\imath}{\hbar}[\alpha P_+ - \alpha^* P_-] \; - \; \frac{1}{T_1}[P_z - P_z^0] \tag{14}$$

$$\dot{P}_- = -\imath\omega_0 P_- \; - \; \frac{P_-}{T_2} \; + \; \frac{4\imath\alpha^*}{\hbar}P_z \tag{15}$$

$$\dot{P}_+ = \; \imath\omega_0 P_+ \; - \; \frac{P_+}{T_2} \; - \; \frac{4\imath\alpha^*}{\hbar}P_z \tag{16}$$

Here P_z^0 is the initial condition, following from

$$\rho^0 = \frac{1}{Z}\begin{pmatrix} e^{-\beta e_1} & 0 \\ 0 & e^{-\beta e_0} \end{pmatrix} \tag{17}$$

where Z is the partition function. The above equations were obtained using the Heisenberg equations of motion for the components of the density matrix. Here e_1 and e_0 are defined as before. The initial value P_z^0 is always less than 0 [1]. Now, solving the equation for $\dot{P}_z$ in the limit where T_2 is short, we see that the evolution of the system is constrained by the condition $P_z(t) < 0$ for every t. That means that, as the result of our simplified approach, we cannot expect a population inversion to be created.

Conclusion

Our approximate approach does not provide evidence that collective effects are important for the process of sonoluminescence. Of course, only by solving the complete problem, with the Hamiltonian given by Eqs. (1-4), would we obtain a rigorous theoretical answer to this question.

[1] From the definition of P_z we see that $P_z > 0$ means negative temperatures.

2 Trapping of Light

Here we explore the optical properties of the gas in the bubble. The basic idea is that the extreme conditions in the bubble might be expected to lead to high values of the dielectric constant of the gas and eventual trapping of radiation in the bubble.

The extreme conditions which exist in a collapsing gaseous bubble in a liquid might lead to high values of dielectric constant, and even to the possibility that the dielectric constant of the gas ϵ_1 will be larger than the dielectric constant of water ϵ_2, which is 1.77 at high frequencies. In Fig. 1 we see that, if really $\epsilon_1 > \epsilon_2$, there is a possibility of total internal reflection. The critical angle of incidence for this phenomenon to occur is given by

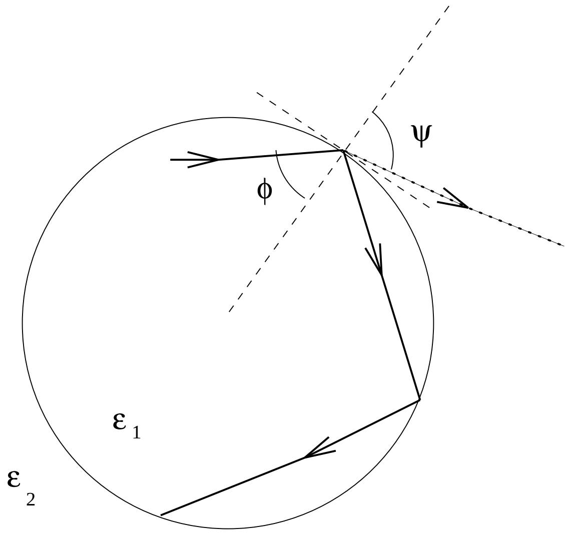

Figure 1: *The possibility of total internal reflection for the radiation produced in the bubble. Total internal reflection happens if the angle of incidence ϕ is larger than the critical angle ϕ_c, which is defined in text.*

$\phi_c = \sin^{-1}(\sqrt{\epsilon_2/\epsilon_1})$. Assuming a uniform distribution of radiators, simple geometric arguments give that the trapped part of the total radiation emitted is given by

$$f = \Theta(\epsilon_1 - \epsilon_2)\ \left(\frac{\epsilon_1 - \epsilon_2}{\epsilon_2}\right)^{\frac{3}{2}} \tag{18}$$

The question is, of course, could the possibility of this high dielectric constant of the gas be expected. The Clausius-Mossotti equation gives the following result for the dielectric constant

$$\epsilon(\omega) = \frac{1 + \frac{8\pi n}{3}\,\alpha(\omega)}{1 - \frac{4\pi n}{3}\,\alpha(\omega)} \tag{19}$$

where n is the gas density and $\alpha(\omega)$ is molecular (atomic) polarizability, given as a Lorentz oscillator

$$\alpha(\omega) = \frac{q^2}{M}\ \frac{1}{\omega_0^2 - \omega^2} \tag{20}$$

where q is the electron charge, M is the molecular mass, and ω_0 is the natural electronic frequency. We see from Eq. (18) that ϵ depends not only on the frequency, but also on the density of the gas. What is encouraging about this approach is that it favors blue light (as reported in the experiment [7]) over other frequencies (following from Eq. (20)). The light could be eventually liberated by the expansion of the bubble.

The idea itself is simple, but the calculation of ϵ_1, is not. The initial expression for the dielectric constant could be questioned, because the necessary compression ratio[2] is larger than 10 (in order for the dielectric constant of the gas to be larger than for the liquid), and at this ratio the densities involved are already those of liquidified or even solidified gases. The index of refraction of these substances is smaller than that of water. On the other hand, effects like the production of free electrons, or the eventual alignment of the gaseous molecules can produce a large change in dielectric constant.

[2]Defined as equilibrium over minimum radius.

The other physical situation which could leads to the trapping of light in the bubble would be the existence of a spatial gradient of the thermodynamic quantities of the gas in the bubble (temperature, pressure, density) and a corresponding gradient in the dielectric constant, So, let us explore what the space dependence of the dielectric constant should be to produce light trapping inside the bubble (assuming a spatial nonuniformity of the gas in the bubble). For this purpose we employ geometrical optics. Using the Eikonal equation [8]

$$\nabla n = \frac{d}{ds}\left(n\,\frac{d\vec{r}}{ds}\right) \tag{21}$$

(following from the Fermat principle), we get following expression

$$\frac{dr}{d\theta} = \pm r\,\sqrt{\left(\frac{nr}{A}\right)^2 - 1} \tag{22}$$

where A is a constant, $n = n(r)$ is the index of refraction of the gas and r, θ are spherical polar coordinates. We see that, in order to have, for example, circular orbits ($dr/d\theta = 0$), n should be proportional to r^{-1}. That gives a r^{-2} dependence of dielectric constant.

It is hard to see why a spatial profile of this sort would exist in the bubble. Since some experimental results imply that the production of shock waves might be expected in the bubble, we tried to analyze this idea and how it can lead to the emission of short pulses of light. The evolution of the shock wave in bubble is presented in Fig. 2. Before shock production, the index of refraction in the bubble n_a is smaller than that of water n_w, so no trapping is possible. As the shock propagates in the bubble the density of air behind the shock front will be greater than the density in front of the shock front. Correspondingly, we will expect that $n_a < n_1 < n_w$, so again no optical trapping is possible. After the shock front collapse to radius zero, it

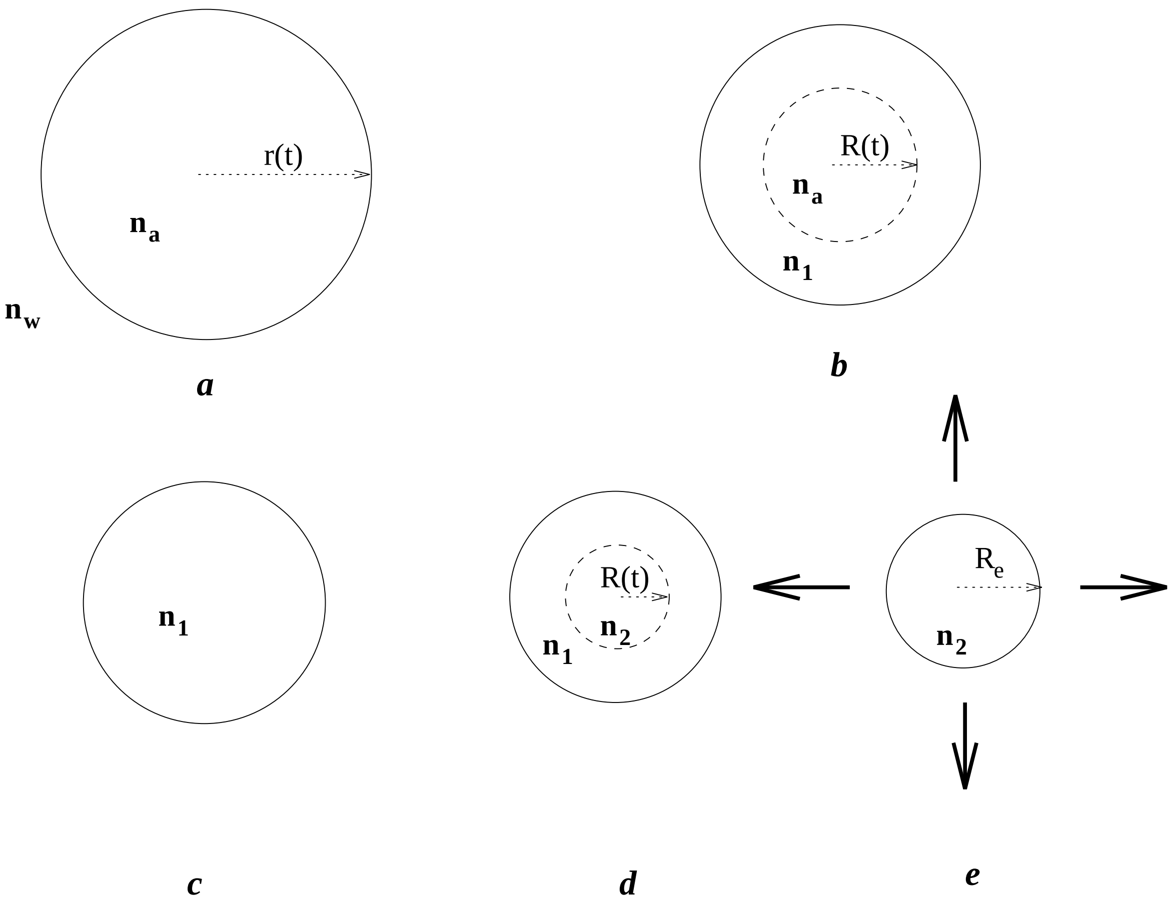

Figure 2: *Different stages of bubble collapse and shock propagation. The bubble collapse just before it reaches the minimum radius is shown. A converging shock $R(t)$ is shown in part b. In part c, the shock converged completely. In part d, the rebounding shock wave propagates outwards. In part e the shock wave reaches the bubble wall, and at that point the trapped radiation may be emitted.*

starts expanding outward, and it is known (self-similar approach, cf. [9]) that the density behind the shock front is considerably larger than the density in front of the shock front (by about a factor of 23). We therefore now have the inequality $n_1 < n_2$. Light trapping is possible behind the expanding shock front. This situation lasts until we arrive at case "e" in Fig. 2, where the expanding shock collides with the bubble surface. The trapped light is now free to escape into the surrounding liquid and will come out as a sudden burst of light.

The problem with this approach is that the shock radius at the point where the temperature is high is very small - smaller or of comparable size to the wavelength of the radiation which is eventually trapped, so the use of the geometric optics equations is very questionable. In addition there is the penetration of the electrical field into the region in front of the shock. The phenomenon of frustrated total internal reflection would occur and this would spread out the duration of the light pulse.

Conclusion

The mechanisms which we considered in this section do not give a precise answer about the duration of the SL pulse or about the shape of the spectrum of the emitted radiation. Still, many effects were not taken into account in our simplified approach. Let us mention some of them:

- The size of the region of interest is comparable to the wavelength of the emitted radiation. Correspondingly, physical optics should be used rather than geometrical optics;
- Physical and chemical processes in the gas in the bubble are not clearly understood [10]-[14]. Some of them could strongly influence the results

for the dielectric constant of the gas in the bubble;

- There is the question if it is correct to consider the liquid layer around the bubble as structurless; some of our preliminary results show that if high pressures and temperatures are developed, there can be some ice-like structure in this layer [14, 15];

- There is a possibility (we will not go into the details in this work) that some charge could be expected to be transferred to the bubble from the liquid. The charging of the bubble would involve large changes in the dielectric constant and even calls to question the correctness of the macroscopic dielectric theory that we are using here (cf. [16]-[18]).

3 "Electrical" Models

In this section, we formulate a few models where we explore the consequences of the high temperatures in the bubble on its electrical properties. These models examine the possibility of charge separation in the bubble, or in the bubble-liquid system.

Introduction

We have already seen that the temperature in a bubble can reach very high values even for the case of an adiabatic compression. Assuming that the temperature in the liquid just next to the bubble is high as well, we would have a high percentage of dissociated water molecules (dissociation energy is $0.5 - 0.6\ eV$ [19]). The natural question to ask is can we expect that this, or some electrical phenomena, play an important role in producing the light signal. Actually, it has been shown in the literature [20, 21] that the production of a surface charge on the bubble-liquid boundary will occur even for a stationary bubble. This is a result of the Poisson - Boltzmann equation.

We consider here a few possible mechanisms for the formation of free charge in (or on) the bubble and explore the possibility that these effects lead to the sonoluminescent radiation. Here we show that some of the electrical effects might be expected to take place, but it seems that they do not give an explanation for sonoluminescence.

3.1 Electrification of the Liquid

Here we would like to calculate the electric field in the liquid just outside the bubble and also the amount of charge in the bubble. We do not expect H^+ ions to deposit themselves in the bubble; the energy needed for that is about $16\,eV$ [15], but the energy for evaporation of OH^- is just about $4\,eV$. The other mechanism for the transfer of negative charges to the bubble is by collisions of positive gaseous (or water vapor) ions M^+ with the bubble wall, by a process like $M^+ + H_2O \leftrightarrow M + H_2O^+$.

The electric current of the positive charges in the liquid consists of conduction, diffusion and convection term and is given by

$$\vec{J}_+ = \frac{\sigma_+}{e}\vec{E} - D_+ \nabla n_+ + n_+ \vec{u} \tag{23}$$

with a similar expression for the negative charges. Here $\vec{u}$ is the velocity of a particle in the liquid, the conductivity is given by $\sigma_+ = n_+ e^2 \tau_+ / M_+$ and the diffusion constant can be expressed by the Einstein relation $D_+ = \tau_+ k_B T / M_+$, where n_+ is the concentration of + charges, τ_+ is their mean collision time and e, M_+ are the charge and the mass of the proton, respectively. Here the Soret effect was neglected.

These currents (J_+, J_-) satisfy the continuity equations and the electric field follows from Gauss law. The charge concentrations n_+ and n_- result from the process $H_2O \leftrightarrow H^+ + OH^-$ with production rates k', k for the backward and forward directions. These constants were calculated from the vibrational frequencies of the water molecule [15]. The fact that some of the OH^- charges evaporate into the bubble should be included as well. The probability of evaporation of OH^- radicals strongly depends on the temperature and solvation energy. The solvation energy can be found using the Born solvation scheme to be $U_s = -e^2/2a \cdot (1 - 1/\epsilon)$, where a is the size of the solvation shell. This energy is small if ϵ is taken to be the dielectric constant of the gas, following from the Clausius-Mossotti equation. This is correct even at high densities which we expect in the bubble. In the course of the research it was found, interestingly enough, that this energy is much larger if OH^- is solvated at the wall (within a solvation hemisphere). The value of the solvation energy is close to the value for solvation in water (about $0.5\,eV$).

The temperature in the liquid next to the wall is to be found[3] from the heat conservation equation

$$\nabla \cdot \vec{J}_q + \frac{\partial q}{\partial t} = 0 \tag{24}$$

with

$$\vec{J}_q = -K\nabla T + q\vec{u} \tag{25}$$

and

$$\nabla q = C\ \nabla t \tag{26}$$

where we assume that K (thermal conductivity) and C (heat capacity) are temperature independent (Peltier effect was neglected). This equation was

[3]This is true if we assume that the temperature just next to the bubble wall in the liquid is the same as in the bubble. The constant evaporation of water vapor from the liquid surface probably lowers this temperature.

solved using the POST-package [22]. The result for the temperature gradient in the liquid, just next to the bubble wall, is of the order of $10^7\ K/cm$. The electric field resulting from this gradient (thermopower of water) is of the order of $10^4\ V/cm$, which, as we will see later, is not a very important contribution.

Finally, with the solved temperature and bubble equations, we are left with the following system of equations. The continuity equation for positive charges is

$$\frac{\partial n_+}{\partial t} - D_+\nabla^2 n_+ + \vec{u}\,\nabla n_+ = -\beta e D_+\left[\vec{E}\,\nabla n_+ + \frac{4\pi e}{\epsilon}(n_+ - n_-)\,n_+\right] \quad (27)$$

The equation for the negative charges has the same form

$$\frac{\partial n_-}{\partial t} - D_-\nabla^2 n_- + \vec{u}\,\nabla n_- = \beta e D_-\left[\vec{E}\,\nabla n_- + \frac{4\pi e}{\epsilon}(n_+ - n_-)\,n_-\right] \quad (28)$$

The equation for electric field $\vec{E}$ follows from Gauss's law

$$\nabla \cdot \vec{E} = \frac{4\pi e}{\epsilon}(n_+ - n_-) \quad (29)$$

In order to specify the boundary conditions, we have to estimate the charge transfer between the bubble and the liquid. If we label the fraction of the collisions of the positive ions with the bubble wall, leading to ionization, as σ, the effective transfer of charge due to collisions is given by $\Gamma = \sigma\, n_{M^+} < v > /4$. Here $< v >$ is the average ionic thermal velocity. Finally, the current density satisfies

$$\hat{r} \cdot \vec{J}_+(R_-(t), t) = \Gamma(t) \quad (30)$$

and

$$\hat{r} \cdot \vec{J}_-(R_-(t), t) = 0 \quad (31)$$

The adsorption of electrons from the bubble is neglected. The boundary condition for the electric field is given by

$$\left[\hat{r} \cdot \vec{E}\,\right]_{r=R_+(t)} = -\frac{4\pi e}{\epsilon} N_- \tag{32}$$

following from the continuity equation for the radial component of the electric field. Here N_- is the number of negative charges in the bubble. The additional boundary conditions are that the ion density should return to its equilibrium value ($pH = 7$) far from the bubble and the electric field should approach zero there.

The system of the equations, Eqs. (27-29) is fairly complicated, especially taking into account the fact that the boundary conditions are time dependent because of the motion of the bubble wall. Anyway, by estimating the relative size of the different terms in these equations, we conclude that the diffusion term is probably the most important. So, by neglecting convection and conduction terms in Eq. (27), and also by eliminating the nonlinear terms on the right hand side of this equation, we get the decoupled equation for the concentration of positive charges in the liquid, just next to the bubble wall. After change of variables $\xi \equiv r^3 - R(t)^3$, $\tau \equiv t$, this equation becomes

$$\frac{\partial n_+}{\partial \tau} = 9D_+ \frac{\partial}{\partial \xi} \left(\xi^3 - R(\tau)^3\right)^{4/3} \frac{\partial n_+}{\partial \xi} \tag{33}$$

with the boundary conditions

$$\left[-3D_+ R(\tau)^2 \frac{\partial n_+}{\partial \xi}\right]_{\xi=0} = \Gamma(\tau) \tag{34}$$

$$[n_+]_{\xi \to \infty} \longrightarrow 0 \tag{35}$$

A further change of variables

$$s(\tau) \equiv 9D_+ \int_0^\tau R(\tau')^4 \, d\tau' \tag{36}$$

allows expressing the solution in the following form

$$n_+(\xi, s) = \frac{3R_{min}^2 \Gamma_0}{\sqrt{\pi}} \sum_{n=0}^{\infty} \frac{\Theta(s - ns_a)}{\sqrt{s - ns_a}} \exp\left(-\frac{\xi^2}{4\,|s - ns_a|}\right) \qquad (37)$$

where $s_a = s(\tau = \tau_a)$ and τ_a is the acoustic period. Here R_{min} is the minimum bubble radius and the ionization rate $\Gamma(\tau)$ is modeled as $\Gamma(\tau) = \Gamma_0 \sum_{n=0}^{\infty} \delta(\tau - n\tau_a)$.

From the result for the concentration of the positive charges, Eq. (37), we are able to estimate the electric field in the liquid and the total electromagnetic energy contained in the system consisting of the negatively charged bubble and the liquid layer around the bubble. The rough estimate gives that this field might be strong enough to lead to the emission of the high energy photons observed in SL experiments. However, the short duration of the pulse does not follow from this model. The other possibility would be that the emission of radiation happens as a result of a recombination process during the expansion part of bubble cycle (immediately after the bubble reaches its minimum radius). But, it is observed experimentally that the SL pulse is emitted shortly *before* the bubble reaches its minimum radius, in contradiction to this idea.

3.2 Polarization Model

One of the assumptions of the previous model was that there is a considerable number of free electrons in the bubble close to its final stages of collapse. This result follows from the Saha equation, which predicts that there are $10^5 - 10^6$ free electrons in the bubble[4]. Some flow of negative charge from the

[4] This estimate is strongly dependent on thermodynamic parameters in the bubble, especially temperature. The high temperatures which develop if a shock wave is produced would lead to an even larger number of electrons.

surrounding liquid might be expected as well. Let us analyze the interaction of the electrons in the bubble with each other and with the liquid. The ion distribution, being spherically symmetric, sets up a constant potential inside the bubble. Suppose for the moment that all the electrons are on the surface of a sphere of radius r' and allow r' to vary. We start with the usual power series for a potential which is finite (except at point charges) and goes to zero for infinite r. After including the boundary conditions of continuity for the potential and the radial component of the $\vec{D}$ field at $r = R(t)$, we get following expression for the total electrostatic energy of the system

$$U = \frac{q^2}{2r'} \sum_{ij,i\neq j} \frac{1}{|\hat{r}_i - \hat{r}_j|} - \frac{q^2}{2R} \sum_l \frac{(\epsilon - 1)(l+1)}{l + \epsilon(l+1)} \left(\frac{r'}{R}\right)^{2l} \sum_{ij,i\neq j} P_l(\hat{r}_i \cdot \hat{r}_j) \quad (38)$$

for $r' < R$. The analogous solution for $r' > R$ is

$$U = \frac{q^2}{2}(1-\epsilon) \sum_l \frac{l}{l+\epsilon(l+1)} \frac{R^{2l+1}}{(r')^{2l+2}} \sum_{ij,i\neq j} P_l(\hat{r}_i \cdot \hat{r}_j) + \frac{q^2}{2\epsilon r'} \sum_{ij,i\neq j} \frac{1}{|\vec{r}_i - \vec{r}_j|} \quad (39)$$

The dielectric constant for the surrounding liquid is ϵ, where $\epsilon >> 1$. The terms with $i = j$ give rise to the image interaction with the wall of the cavity. The other terms describe the direct and indirect Coulomb interaction of the charges with each other. These formulae were programmed and the output is in agreement with what we get from a continuum limit (which is more than justified if we have $10^5 - 10^6$ electrons in the bubble). The result from the continuum approximation is

$$U = \begin{cases} \frac{q^2 N^2}{2(r'-R)} - \frac{q^2 N}{2R} \frac{1}{1-(\frac{r'}{R})^2} + O(\frac{1}{\epsilon}) & if\ r' < R \\ \frac{q^2 N^2}{2\epsilon r'} \left(1 - \frac{1}{\sqrt{N}}\right) + \frac{q^2 N}{2\epsilon R} \left[\frac{R^2}{r'-R^2} + \ln\left(1 - \frac{R^2}{r'^2}\right)\right] + O(\frac{1}{\epsilon^2}) & if\ r' > R \end{cases} \quad (40)$$

where only leading terms in $1/\epsilon$ are kept. Examination of these formulae shows that the total electrostatic energy is positive for small r', becomes negative and approaches $-\infty$ as r' approaches R from below, falls from $+\infty$ above R and eventually falls to zero. Of course, the presence of the positive ions, which were neglected here, would cause the energy to get smaller as r' gets larger.

We conclude that for negative energy the system is likely to find itself with the electrons inside the bubble near $r' = R$. For positive energy, however, the system is unstable and the r' would like to expand to infinity. The image potential poses a barrier to this expansion and a tunneling event or a thermal excursion must happen in order for this to occur.

For the moment, we approximate our potential energy for $r' > R$ to be infinite, so it does not allow for tunneling. Furthermore, we assume a two-dimensional electron gas trapped on the wall and use the variational method to get the energy of the electrons. Without going into details, we get what is expected: for a large number of electrons, the Fermi energy is positive. This critical number is of order 10^6. To the Fermi energy we have to add the Coulomb energy of repulsion of the electrons. This energy again depends on the number of electrons in the layer.

The conclusion is that for a high number of electrons, at the final stages of collapse, the total energy of the electrons can be positive and fairly large. These electrons are trapped inside the bubble next to the bubble wall. On the other hand, we know that there is a certain concentration of positive ions in the liquid next to the bubble wall. Here we explore the possibility that this configuration could produce radiation.

Since the energy of the electrons becomes elevated as the bubble contracts (Coulomb repulsion), one would expect that the bubble discharges at some point. The question is why should this discharging occur on so short time scale? A hypothetical answer to this question could be that discharging at one point of the bubble produces a big change of the electric field at some other points on the bubble wall. If this were true then we can expect that one of two things happen: either this change of the electric field is large enough to considerably increase the probability for tunnelling, or this additional field is strong enough to produce an electrical breakdown.

In order to get some qualitative results, we formulated a model in which we assumed a polarization layer formed on the bubble. We assumed that polarization is given by

$$\vec{P}(\hat{r},\omega) = \hat{r}P(\hat{r},\omega)\,\delta(r-a) \tag{41}$$

As a result of this polarization, the power radiated is

$$P = 2\pi ck^2R^2\sum_{lm} l(l+1)|P_{lm}(\omega)|^2 j_l^2(kR) \tag{42}$$

where P_{lm} is lm coefficient in the expansion of the polarization in a series of spherical harmonics and $R(t)$ is the radius of the bubble. We see, as expected, that no radiation is emitted for the $l=0$ spherically symmetric mode.

By solving the field equation for this model, we get a simple and interesting result:

$$\hat{r}\cdot\vec{E}(\vec{r},t) = \frac{1}{a}\,\mathcal{L}^2\int\frac{P\left(\hat{r}',t-\frac{a}{c}|\hat{r}-\hat{r}'|\right)}{|\hat{r}-\hat{r}'|}\,d\hat{r}' \tag{43}$$

where $\vec{\mathcal{L}} = -\imath\,\hat{r}\times\nabla$ is proportional to the angular part of Laplacian.

So, the electric field at a time t depends on the polarization at previous times t'. Efforts have been made to solve this equation self-consistently (the polarization itself depends on the electric field), but at this moment we have to use a more intuitive argument which tells us that we will have large electric field at some points. First we establish an equivalence between our result for the electric field of a polarized layer and the result for the dipole field given, for example, in [23]

$$\vec{E}(\omega) = k^2[\hat{n} \times \vec{\mu}(\omega)] \times \hat{n}\frac{e^{\imath \vec{k}\vec{r}}}{r} + [3\hat{n}\hat{n} \cdot \vec{\mu}(\omega) - \vec{\mu}(\omega)]\left[\frac{1}{r^3} - \frac{\imath k}{r^2}\right] e^{\imath \vec{k}\vec{r}} \qquad (44)$$

in the continuum approximation. In "near field limit", we see that the switching of one of the dipoles will produce a weaker field for others, but this is not true in general; at some points the field will be larger. We checked this point by doing explicit calculations for a system of two dipoles, four dipoles at the vertices of a tetrahedron and for eight dipoles at the corners of a cube. The conclusion was that if one dipole decays fast enough, it can produce a switching of other dipoles (the condition is that $\beta > Ka/c$, where β is a decay constant for the exponential decay of a dipole and K is a number of order one). Our next step is to assume that, first, this additional electric field is large enough to produce tunnelling or breakdown and, second, that the decay happens immediately (tunneling is a very fast process).

We developed a few models for "decay" of the polarization layer which models our physical system. The result is that neither of these models was able to reproduce the observed SL pulse, especially the observed spectrum, which is black-body like. We conclude that there is not enough evidence that the sudden decay of the polarization layer is responsible for the emission of radiation which is observed in the form of sonoluminescence. (It is worth comparing the approach here (based on classical electrodynamics) with the quantum approach developed in the first section.)

4 Plasma radiation

The high temperatures which develop in the bubble naturally lead to the idea that a plasma could form in the bubble close to its minimum radius.

Relatively high temperatures are required, so this assumption is based on the formation of shock waves in the bubble or the adiabatic collapse of the bubble with a large compression ratio.

The Saha equation gives that multiple ionization happens at temperatures of a few tens of thousands of degrees, leading to a large number of free electrons. These thermally energized electrons randomly scatter off the ions, eventually leading to radiation.

In order to explore this possibility in a more precise manner, we assume that our system consists of N fluctuating dipoles

$$\vec{\mu}_i(t) = -e\left(\vec{r}_i(t) - \vec{R}_i\right) \tag{45}$$

where $\vec{r}_i$ gives the position of i^{th} electron, and $\vec{R}_i$ is the position of i^{th} ion. The thermal motion of electrons is much faster than that of ions, which are assumed to be stationary. Correspondingly, the time rate of change of a dipole is given by

$$\dot{\vec{\mu}}_i = -e\vec{v}_i(t) \tag{46}$$

where $\vec{v}_i(t)$ is the velocity of i^{th} electron. The power radiated by such a dipole can be calculated using the Larmour formula

$$P_i(t) = \frac{2}{3}\frac{\left|\ddot{\vec{\mu}}_i\right|^2}{c^3} \tag{47}$$

Assuming no interaction between the electrons we postulate an exponential model for the velocity autocorrelation

$$< \vec{v}_i(t) \cdot \vec{v}_j(t') > = < v^2 > \delta_{ij} \exp\left[-\frac{|t-t'|}{\tau}\right] \tag{48}$$

Here the average is over an ensemble and τ is the autocorrelation time, assumed to be identical to the inverse of the collision rate of the electrons with the ions.

In calculating the radiated energy, it is useful to realize that there are two time scales in the problem: A fast scale, characterized by the electron motion and a slow scale, characterized by the ion motion or the time the bubble spends close to its minimum radius. So, if we calculate the energy radiated during one "frame" of slow motion, we can assume that the ions are stationary, and that the conditions (i.e. temperature) in the bubble do not change significantly. Correspondingly, the energy radiated during the time characterized by the slow time scale t_s is given by

$$W_i = \int_0^{t_s} P_i(t)\, dt = \frac{2}{3c^3} \int_0^{t_s} \left|\ddot{\vec{\mu}}_i\right|^2 \tag{49}$$

and Eq. (46) can be employed. The calculations were done in frequency space and the result for the spectral power radiated is

$$P_i(\omega) = \frac{4e^2}{3\pi c^3} \frac{< v_i^2 >}{\tau} \frac{\omega^2}{\omega^2 + \frac{1}{\tau^2}} \tag{50}$$

We get the average electron velocity from the electron thermal energy (assuming thermal equilibrium). Furthermore, the result for the spectral power radiated should be corrected because of the presence of the rest of the plasma. This correction factor is explained in more detail elsewhere [24]. The final result for the spectral power radiated from N electrons is

$$P(\omega) = \frac{4e^2}{\pi m c^3} \frac{N k_B T}{\tau} \frac{\omega^2}{\omega^2 + \frac{1}{\tau^2}} \left| \frac{3}{2 + \epsilon(\omega)} \right|^2 \tag{51}$$

where $\epsilon(\omega)$ is the frequency dependent plasma dielectric constant. The total number of electrons N was calculated using the Saha equation. Finally, the electron collision time was assumed to follow from $1/\tau = n_e v \sigma_c$, where n_e is the electron density, and σ_c is the Coulomb cross section. The typical result for the collision time is $\tau \sim 10^{-14} s$.

Since our final goal is to compare the results with experiment, we want to check what radiation spectrum results from this approach. By fitting the result of our approach to the experimental spectrum, and using τ as a fitting parameter, we get a fairly good correspondence with experiment for a value of the electron collision time of $\tau = 1.3 \times 10^{-16}\, s$.

One cannot understand why the collision time should be so short. We tried to improve our model, by including more sophisticated effects, like screening, which lowers the ionization energy. Still, we are not able to reproduce so short a collision time. Also, the result for the duration of the SL pulse turned out to be much longer than experimentally observed ($50\, ps$). These results indicated that the mechanism for SL radiation should be given on the basis of some other model for the hot gas in the SL bubble.

Conclusion

We presented a few theoretical models with the goal of trying to understand SL. It is found that a better understanding of the thermodynamic properties of the gas is required in order to fully understand the effect of sonoluminescence. That is going to be the subject of our future work.

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