

Argon Rectification and the Cause of Light Emission in Single-Bubble Sonoluminescence

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In single-bubble sonoluminescence, repeated brief flashes of light are produced in a gas bubble strongly driven by a periodic acoustic field. A startling hypothesis has been made by Lohse and co-workers [Phys. Rev. Lett. **78**, 1359 (1997)] that the non-noble gases in an air bubble undergo chemical reaction into soluble products, leaving only argon. In the present work, this dissociation hypothesis is supported by simulations, although the associated temperatures of about 7000 K seem too low for bremsstrahlung, which has been proposed as the dominant light emission mechanism. This suggests that emission from water vapor and its reaction products, heretofore not included, may play an important role.

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In single-bubble sonoluminescence (SBSL), repeated brief flashes of light are produced in a gas bubble strongly driven by a periodic acoustic field. A startling hypothesis that the non-noble gases in an air bubble undergo chemical reaction into soluble products, leaving only argon [1], has found support in recent experiments [2,3]. There remains uncertainty regarding the source of the light, although electron-atom bremsstrahlung has been proposed as the dominant emission mechanism [4,5]. However, emission from molecular excited states appears to be responsible for the light in lower-temperature multibubble situations [6] and in the onset of single-bubble sonoluminescence [7] in water. Emission from excited states is thought to dominate at lower temperatures than have been assumed by the bremsstrahlung models. In this Letter we show that the dissociation hypothesis is supported by simulations, although the associated temperatures of about 7000 K seem too low again for bremsstrahlung as modeled. Moreover, the model predicts an excess of vapor trapped in the bubble at collapse. The findings suggest that emission from water vapor and its radicals may play a more important role in SBSL than was previously thought [7,8].

While it seems that many researchers have converged on a consistent qualitative understanding of SBSL, the models of the conditions in the bubble interior and the light emission remain incomplete. Recently, the central importance of water vapor in SBSL has been identified. Two recent calculations [5,9] have shown (independently and through very different methods) that the bubble can often be composed of 30%–50% water vapor at the time of collapse [10]. Furthermore, the primarily endothermic reactions of water vapor in the hot interior lower the prediction of peak temperatures from $>20\,000$ K when vapor was neglected to about 7000 K [9]. There is a commonly held view that the temperature of collapse must be >9000 K for the dissociation hypothesis to hold true [1,11], and higher still for bremsstrahlung to be the dominant light emission mechanism as proposed [4,5]. The dissocia-

tion hypothesis states that the polyatomic species in an air bubble undergo dissociation in the hot interior during violent collapses. The gases are thought to react with water vapor to form soluble products, which are taken up by the liquid water outside the bubble. The result is a net loss of the non-noble components of air (or other mixtures), resulting in a stable bubble composed of nearly pure argon. Chemical changes were predicted to follow when the gas temperature exceeds 9000 K [1], a value which is obtained by consideration of the Gibbs free energy change of oxygen and nitrogen undergoing dissociation. Here it is shown through direct simulation that such high temperatures are not necessary for the dissociation hypothesis to be valid. We find that radical attack of the diatomic gases—and other reaction pathways—lead to the manifestation of the dissociation hypothesis at considerably lower temperatures. For example, the forward dissociation reaction $N_2 + M \rightarrow 2N + M$ requires a net energy of formation of 9.76 eV, whereas the forward rearrangement reaction $N_2 + O \rightarrow NO + N$ requires 3.27 eV and $N_2 + O_2 \rightarrow 2NO$ requires only 1.90 eV [12].

In previous work, we proposed a simplified model [13] of the interspecies mass diffusion, heat transfer, and finite-rate chemical kinetics that provided good agreement when compared to a more complete direct numerical simulation [9]. This basic sonochemical model, originally developed for a noble gas bubble with water vapor, has been extended to more complex mixtures through the addition of air chemistry by a different chemical reaction mechanism [14]. In the present work, we track 19 species which undergo 70 forward and reverse finite-rate reactions. The model has been further developed to include gas exchange with the liquid. The influx of all stable dissolved gas species from the liquid (such as argon, nitrogen, hydrogen, and oxygen) is computed using the long time scale rectified diffusion growth rate; see Eq. (4.6) of [15]. The highly soluble species (such as OH, NH₃, or H₂O₂) are assumed to be removed proportional to the rate at which they

strike the bubble interface. One in ten collisions with the liquid interface is assumed to remove these species from the bubble in a simple uptake model [9]. This was done in [9,13] in order to calculate OH, but now it is implemented for all soluble radical species. At steady state, the diffusion growth rate of diatomic species must match the loss due to chemical reactions and subsequent uptake of the soluble products. The argon, on the other hand, must be in perfect balance only with respect to rectified diffusion [1]. The low concentration of argon needed for a bubble to be in rectified diffusion equilibrium happens to be similar to the amount found in air. In summary, the basic sonochemical model of [13], suitable for calculations of a single collapse, has been considerably improved for the present study. We track more species involved in more reactions, we simulate directly rectification of neutral species, and we use an uptake model for all soluble radical species.

With our improved sonochemical model, it is possible to search for the chemical composition of a stable bubble that repeats each period of the driving acoustic field of a given pressure amplitude [16]. Once such a periodic composition is found, it is shown to be locally attracting by perturbing with respect to amounts of the various gases in the bubble. The bubble must also simultaneously be considered for stability of the assumed spherical shape [17]. Because it was recently shown that the location of the stability boundary in parameter space is very sensitive to details of the radial dynamics, a complete Navier-Stokes model of the gas is used to compute the shape stability boundary [18]. Finally, we note that the only free parameters in the model are the rate of uptake of soluble radical species and the accommodation coefficient of water vapor. The results we report are not sensitive to reasonable changes in these parameters.

We considered a driving frequency of 32 800 Hz and air dissolved at 20% saturation in liquid water in order to compare to recent data [19]. The stable ambient radius of the bubble as the pressure amplitude is varied is shown in Fig. 1. The solid curve is the radius of the stable bubble in chemical-diffusive equilibrium. The dashed curve is the shape stability boundary, below which bubbles are spherically stable. The experimental points [19] are also shown. The agreement between the present model and the experiment is striking. The result confirms that the dissociation hypothesis is correct, and that the linear stability analysis for shape perturbations is accurate at strong forcing. Most importantly, the dissociation hypothesis is supported in a calculation with internal peak temperatures of only about 7000 K and large amounts of trapped vapor.

In Fig. 2 is a depiction of the chemical composition of the bubble as the pressure amplitude is varied. The mole fraction of the dominant species (argon and nitrogen) at the beginning of each acoustic cycle is shown, as obtained using the simulation. The transition from a primarily nitrogen (i.e., air) to an almost pure argon bubble is clearly captured as the driving pressure increases. In the center

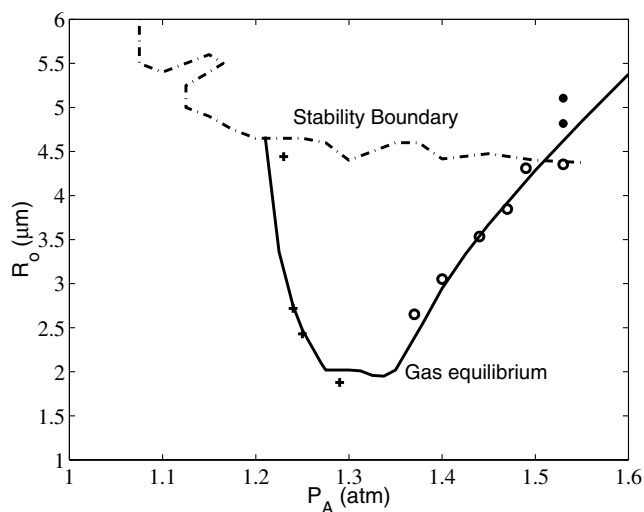


FIG. 1. A diagram of parameter space, showing the chemical-diffusive equilibrium (solid curve) and shape stability boundary (dashed curve). The points are experimental measurements [19]: open circles denote stable glowing bubbles, crosshairs are stable nonglowing bubbles, and filled-in circles are unstable glowing bubbles.

figure the mole fractions are shown at the time of collapse. Note that more water is trapped at higher driving by the mechanism we have previously described [9]. It should be emphasized that the number of moles of argon in the bubble is constant over a cycle, but that the number of moles of vapor and reaction products varies; hence the mole fraction of argon is variable. The number of moles of vapor and reaction products is roughly constant over the time scale of light emission [9]. Finally, the peak temperatures are shown in the bottom figure. Note from

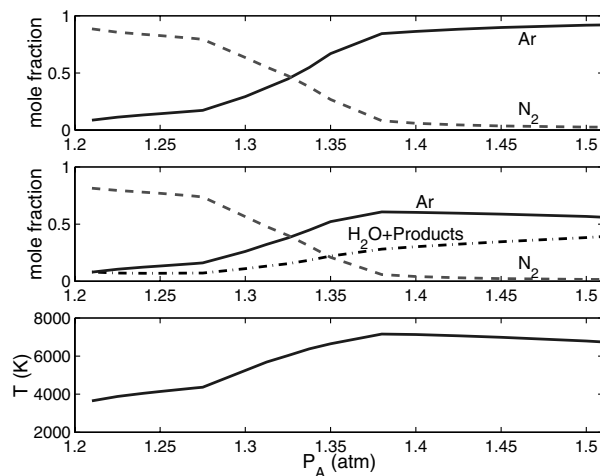


FIG. 2. Bubble composition and temperature as the pressure amplitude is varied, for bubbles on the solid curve of Fig. 1. In the top figure is the repeating mole fraction at the start of each cycle. In the center figure are the mole fractions of argon, nitrogen, and water plus all its dissociated products at collapse. In the bottom figure is the peak temperature at collapse.

Fig. 1 that the light emission in the experiments commences as the driving pressure exceeds about 1.35 atm in the experiments.

The dissociation hypothesis is supported by the sonochemical model with remarkable agreement in the observable ambient radius with experiments. However, the present model predicts temperatures that are much lower than those thought to be required for bremsstrahlung from a weakly ionized gas, which has been proposed as the dominant light emission mechanism [4,5]. That theory has been successful in developing spectra that agree well with experiments with (nominally) argon and xenon bubbles, neglecting the presence of vapor or reaction products. But with helium bubbles the emission predicted by the theory [8,20] was 3 orders of magnitude too small. It has been suggested that vapor may play a role in solving this discrepancy [4,8]. Bremsstrahlung in a weakly ionized gas model has not yet been computed with emission by electrons produced in ionization of H₂O or the radicals (OH, H, O). This may hold the key to the resolution of the underprediction of emission from helium and neon bubbles by the weakly ionized gas model.

The findings in the present work lend support to the idea that emission from water and its reaction products should receive consideration in emission models, whether from molecular excited states or electron-atom bremsstrahlung [6–8]. Water is present in considerable quantities at the collapse, and the temperatures seem consistently lower than that assumed by bremsstrahlung models that neglect vapor or chemical reactions. The temperatures that can be inferred from the validity of the dissociation hypothesis need not be so high as was thought necessary.

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