Blackbody Spectra for Sonoluminescing Hydrogen Bubbles

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The dynamical motion of sonoluminescing bubbles formed from a mixture of water and hydrogen gas indicates that these bubbles contain hydrogen. Their spectrum is well matched by an ideal 6000 K blackbody radiating from a surface with a radius less than $\frac{1}{4}$ μm. According to this model, the state of matter inside the collapsed bubble is so stressed that the photon mean free path is much smaller than 1 μm. Implications for various theories of the light-emitting mechanism and the role of chemical reactions are discussed.

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The clocklike transduction of sound into light by the highly nonlinear pulsations of a gas bubble in water [1–4] displays a number of universal properties. The spectra of bubbles formed from solutions of all noble gases in water are remarkably similar being broadband, lacking lines, and tailing off as the same function of λ, where λ is the wavelength of the emitted light [5]. The bubble radius as a function of time "$R(t)$" shows, for all systems, a slow expansion followed by a runaway collapse that is arrested as its density approaches a value determined by the van der Waals hard core of the gas in the bubble, at which moment light is emitted [6]. At a fixed concentration of noble gas in water the width of the flashes of sonoluminescence (SL) is accurately characterized by the intensity of a flash again being independent of the particular noble gas [7]. These flash widths are furthermore at most weakly dependent on λ (as suggested by measurements of helium and air bubbles in 20 °C water). The intensity of SL from all noble gases increases by a factor of 10 as the water is cooled from room temperature to 0 °C [6].

Measurements of SL from hydrogen, deuterium, and ethane bubbles in water and heavy water are reported. These systems form the only non-noble gas bubbles from which stable synchronous SL has been observed. In addition to testing the role of chemistry in SL [8], this system yields a spectrum whose ultraviolet cutoff can be measured as it is sufficiently redshifted that it is no longer masked by the extinction coefficient of water (Fig. 1). This spectrum [9] is remarkably well fit by Planck's blackbody formula for the energy emitted by a surface of radius R_e during an interval of time Δt_{SL}:

$$P(\lambda)d\lambda = 8\pi^2 hc^2 R_e^2 \Delta t_{SL} d\lambda/\lambda^5 \times [\exp(hc/\lambda k_B T_{BB}) - 1], \quad (1)$$

where h, c, and k_B are, respectively, Planck's constant, the speed of light, and Boltzmann's constant and T_{BB} is the temperature of the blackbody emitter. When supplemented with the measured SL flash width Δt_{SL} (110 ps at 20 °C and 180 ps at 0 °C) the spectrum is remarkably well fit by (1) with $T_{BB} = 6200$ K (at 20 °C) and R_e between 0.2 and 0.25 μm. The curvature of the spectrum is a sensitive measure of T_{BB} and the overall intensity determines R_e.

If one assumes that the customary conditions for a blackbody are met, then these results challenge theories of the light-emitting mechanism that invoke a transparent plasma [3,4,10–13]. An ideal equilibrium blackbody emitter possesses a density of states characteristic of an infinite radiator [14] and is opaque to light. In the case of SL the $\frac{1}{4}$ μm radius of the bubble is smaller than the vacuum wavelength of the light emitted. Furthermore, we find that except for a small variation the flash width is independent of λ (for H_2 it is about 20% longer in the ultraviolet: Fig. 2). Thus the state producing a blackbody-type spectrum in SL is not approached through an adiabatic process. It remains to be seen whether the opacities characteristic of SL have physical similarities to those which account for radiation from (i) nanoscale clusters [15] and (ii) shock generated

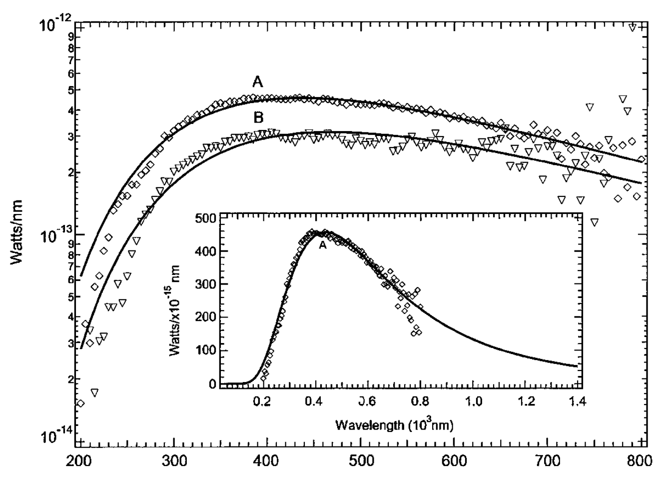

FIG. 1. Spectrum of a sonoluminescing bubble formed from a mixture of hydrogen and water at 0 °C (A) and 20 °C (B). The solid lines are fits to Planck's formula for 6644 and 6200 K. The radius of the surface of emission is also fit to 0.25 μm at 20 °C and 0.2 μm at 0 °C. The uncertainty in T_{BB} of 200 K is dominated by scatter in the spectral data. The uncertainty in R_e of 0.02 μm is dominated by imprecise determination of the solid angle subtended by the photodetector. The inset displays a linear scale.

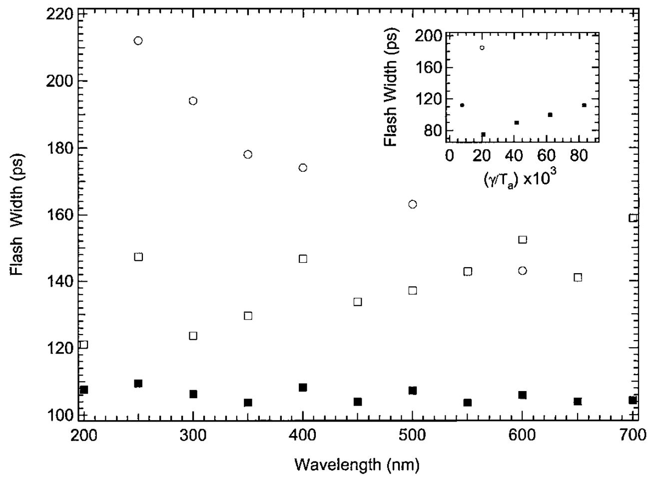

FIG. 2. Flash width (taken at fixed intensity) as a function of wavelength of the emitted light for a hydrogen bubble at 0 °C (open circles) and a helium bubble at 20 °C (filled squares) and 0 °C (open squares). The inset shows the flash width as a function of photons per cycle "γ/T_a" (the filled circle is room temperature hydrogen).

plasmas, which have been modeled as a strongly coupled plasma [16–18].

Measurement of SL from hydrogen bubbles poses various experimental challenges. The intensity is weak: about $\frac{1}{10}$ to $\frac{1}{20}$ of air bubbles at room temperature so that the signal is particularly sensitive to impurities and aberrations. These include (A) small leaks which can dramatically affect the spectrum [6], especially since the solubility of hydrogen in water is so low, (B) small chemical impurities [19], and (C) thermal drift.

Also seeding a bubble into a sealed acoustic resonator is difficult, again in view of the low solubility. We succeeded in seeding H_2 bubbles by testing a number of different nichrome boiler wires at various locations relative to the velocity node of the standing wave sound field, and with a variety of currents until satisfactory results were achieved for each individual resonator cavity. Experiments are run at 3 Torr (1 atm = 760 Torr) partial pressure of gas dissolved into water [20]. The gas bubble forms out of this solution and is maintained in a steady state by the sound field whose amplitude is P_a. We have found that the best way to diagnose the absence of artifacts is to observe the "redder" spectrum shown in Fig. 1. This same spectral density characterizes hydrogen, deuterium, or ethane [21] bubbles in either light or heavy water (Fig. 3). Key parameters that describe the bubble dynamics are P_a and the ambient radius R_0, which is the value of R just before the decreasing external drive passes through zero. At R_0 the ambient pressure (here 1 atm) is the total pressure acting on the bubble. These bubble parameters were measured with Mie scattering [6]. Flash widths were measured with time correlated single photon counting [7]. Experiments were carried out with a spherical resonator (40 kHz) and a double walled cylindrical resonator (33 kHz) [22].

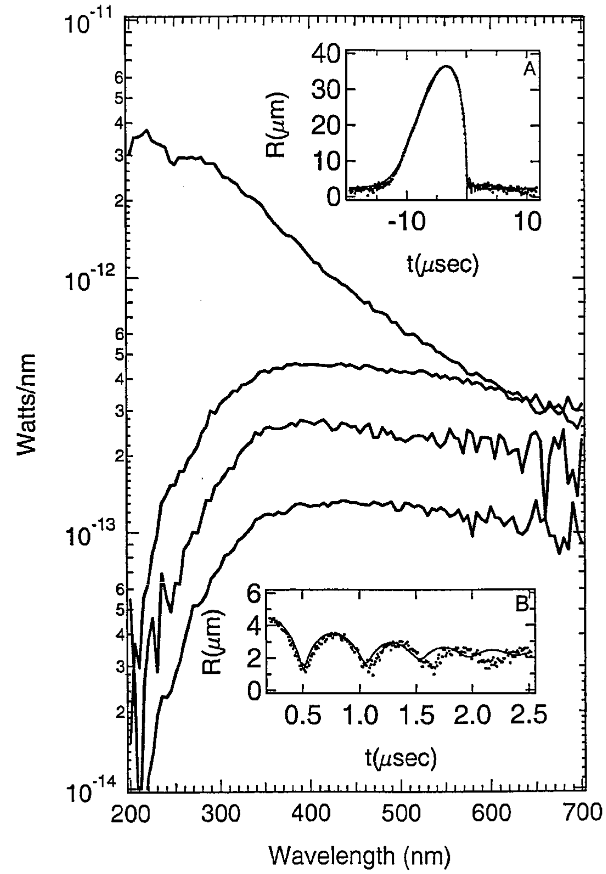

FIG. 3. From top down, spectra of He at 20 °C, H_2 in H_2O at 0 °C, C_2H_6 at 0 °C, and D_2 in D_2O at 4 °C. Insets: (A) radius versus time for one acoustic cycle for a hydrogen bubble at room temperature; (B) bubble pulsations shortly after light emission. Solid lines are fits to the RP equation with $R_0 \sim 3$ μm.

Figure 3 (insets) display $R(t)$ for an H_2 bubble for one acoustic cycle. These measurements repeated at various P_a determine the range of ambient radii "R_0" and P_a at which bubbles can be stable. Results for room temperature water are displayed in Fig. 4. As the observed P_a and R_0 lie near values which follow from equilibrium with respect to mass diffusion [6,19,23] we conclude that the bubble indeed contains hydrogen. This is the first nonmonatomic gas for which this statement can be made.

The observation of SL from an H_2 bubble provides another perspective from which the role of chemical reactions in SL can be studied. In order to see stable SL from other mixtures of water and diatomic molecules such as O_2 or N_2 requires doping with a noble gas [5]. An interpretation of this effect is that the process which generates SL drives N_2 out of the bubble rectifying the Ar. An appealing explanation of the mechanism invokes chemical reactions which form highly soluble compounds from dissociated N_2, or O_2 and the water [8] (e.g., NH_3, NO, H_2O_2), which then flow into the surrounding water faster than N_2 or O_2 diffuse back into the bubble. Application of this criterion to bubbles formed from a water-hydrogen mixture is not direct [24]. On the one hand there is no neutral reaction

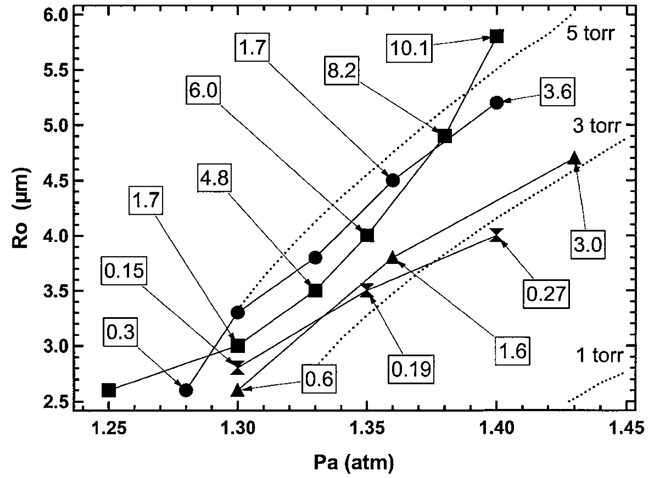

FIG. 4. Parameter space for sonoluminescing bubbles formed from room temperature water mixed with xenon, argon, helium, and deuterium driven at 40 kHz (xenon data are denoted by squares, argon by circles, helium by triangles, and deuterium by hour glasses). All systems were mixed at a partial pressure of 3 Torr. The dashed lines show the relationship between R_0 and P_a that would apply if the bubble were in diffusive equilibrium with respect to mass flow. The relative SL intensities are indicated. The minimum or collapse radius of the bubble occurs when the contents have been compressed to the van der Waals hard core "a," where $R_0/a = 9.8$ for H_2. Taking $R_0 = 3.5$ μm yields $a = 0.35$ μm, which we note is bigger than the emission radius used to match Planck's spectrum. At 0 °C a stable H_2 bubble can be observed with $P_a = 1.6$ atm, $R_0 = 1.75$ μm so that $R_m/R_0 \approx 20$ (at 33 kHz). This bubble is not in diffusive equilibrium with respect to mass flow.

which generates a net loss of H_2 due to production of a more soluble compound; on the other hand there are charge releasing reactions such as $H_2 + 4H_2O \leftrightarrow 3H_3O^+ + OH^- + 2e$, which do yield soluble products. Perhaps this reaction is ruled out by the high energy required for ionization, as well as the time scales for solution and recombination. If a high barrier suppresses a reaction, then one would expect to observe a hydrogenlike spectrum for pure N_2 [25] (3 Torr). Storey and Szeri [26] find, however, that forward rearrangement reactions (e.g., $N_2 + O_2 \rightarrow 2NO$) involve barriers lower than that for full dissociation. It remains to be seen whether such processes play a role in the H_2/H_2O system. Another related observation regarding N_2 bubbles is that it is not possible to seed a N_2 (or O_2 or SF_6 [27]) bubble in water with a 3 Torr solution of these gases. If chemical reactions sucked the N_2 out of the bubble, it would preclude steady state SL but not transient light emission from a short lived bubble. Perhaps a theory of these transient time scales could lead to further checks of the role of chemical reaction in SL.

For the bubble formed from H_2 (plus water vapor) the quantitative fit to a blackbody spectrum, shown in Fig. 1, is so good that one is tempted to conclude that SL, at least for H_2, is due to blackbody radiation. Before developing the consequences of this interpretation we summarize opposing perspectives. First there is the possibility that SL is a blackbody imposter. This could happen because the observation of a spectrum which accurately matches a blackbody does not absolutely require that the conditions generating the blackbody be the same as those invoked in the traditional derivation of an equilibrium blackbody source. In this case insight into the light-emitting mechanism cannot be obtained without additional information. On the other hand, if the blackbody spectrum is actually produced by conditions that match the traditional conditions (matter-light equilibrium, and a high density of states), then the observation of an SL blackbody spectrum leads to interesting consequences regarding the bubble's interior.

Our observation that all spectra for stable SL can be parametrized within experimental error by the blackbody formula by use of appropriate values of T_{BB} and R_e suggests that the blackbody picture has validity, so we now consider the consequences. Regarding the density of states, we note that the Planck spectrum is reached in the limit where the number of modes in range dk (where k is the wave number of light in the cavity of volume V) is proportional to Vk^2dk/h^3. This formula applies only in the limit where the cavity is large compared to λ. Such a high density of states can be achieved if the index of refraction in the bubble's interior is large, say $\sim$10–100. Regarding matter-light equilibrium, we note that the photon matter mean free path l_γ for a dielectric heated to 6000 °C is huge [28], about $10^8 R_e$. In various theories of SL [10,11,13] calculation of l_γ uses standard formulas of plasma physics [28]. Typically Saha's equation is used to calculate the degree of ionization and bremsstrahlung formulas and their inverse are used to calculate the spectrum and the mean free path of light. These equations are derived in the dilute gas limit or under the assumption of binary collisions. As SL occurs at the van der Waal's hard core density [2,6] these theories are applied outside their realm of validity. Reconciliation to experiment could possibly result from the theory of l_γ for a plasma in a dense environment [16–18]. Another possible explanation might appeal to an interior temperature that is much higher than the blackbody temperature of the measured spectrum. For exploding (Sedov-Taylor) shock waves preheating due to thermal radiation transport can yield an arbitrarily high internal temperature with a relatively cool Planck spectrum of about 2 eV [28]. If shock waves play a role in SL, then they are of the Guderley type [11,29] where preheating is also generated by the implosion which precedes the explosion. The theory of SL based upon a uniform bubble and weak ionization [10] is also inconsistent with the integrated SL intensities shown in Fig. 4 [30,31].

The observation that the flash width for H_2 is longer in the UV suggests that the state of matter from which the spectrum originates is not following an adiabatic process. Such processes would yield a longer emission in the red portion of the spectrum. Such an effect is seen for helium in 0 °C water, but even here the effect is still only 10% [32].

Bubbles formed from solutions of hydrogenic gases in water represent the first stable non-noble gas systems, which display SL. Dynamical measurements of the bubble motion combined with diffusion calculations suggest that there is indeed hydrogen within these bubbles. The observed light is remarkably well parametrized by Planck's spectrum. Combining Eq. (1) with values for R_e, T_{BB}, and Δt_{SL} yields the SL spectrum of all measured stable cavitating bubbles within experimental accuracy. Furthermore, noble gases driven near their maximum sustainable intensity follow the scaling laws: $\chi/k_B T_{\mathrm{BB}} \approx 15$ and $4\pi\sigma R_e^2 T_{\mathrm{BB}}^4 \approx 5 \times 10^{-4}$ W, where σ is the Stefan-Boltzmann constant (for radon these laws predict $T_{\mathrm{BB}} = 8300$ K). To make a connection with the formal theoretical framework in the field of dense plasmas we note that for these systems the dimensionless parameter which compares Coulomb energy with kinetic energy of particles is $n_e(\nu_{\mathrm{th}}/\omega_p)^3 \approx 0.05 \ll 1$ (n_e, ν_{th}, and ω_p are, respectively, the electron density, thermal velocity, and plasma frequency). This limit for this parameter is taken to indicate that the plasma is strongly correlated and dilute gas formulas are invalid [33]. In the event that the SL spectrum from H_2 bubbles that is well fit by a blackbody spectrum is indeed a blackbody, then there are 8 orders of magnitude discrepancy with the standard calculation of the mean free path of light when these blackbody parameters are applied to its interior. If SL indeed originates on the surface of a blackbody, then its opacity masks the degree to which energy is focused by the collapsing bubble. While the radius of emission of the blackbody is consistent with the radius of the collapsed bubble, it remains unmeasured. The Hanbury-Brown and Twiss correlations should provide a route to this parameter [34].

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