Vapor Supersaturation in Collapsing Bubbles. Relevance to the Mechanisms of Sonochemistry and Sonoluminescence

A. J. Colussi* and M. R. Hoffmann*

W. M. Keck Laboratories, California Institute of Technology, Pasadena, California 91125

Received: August 2, 1999; In Final Form: October 18, 1999

Small amplitude oscillations of gas bubbles in sonicated liquids are quasi-reversible events, but the sudden collapse of widely expanded bubbles results in extensive vapor supersaturation. However, Hilgenfeldt et al. (*Nature* **1999**, *398*, 402) explain single-bubble sonoluminescence by assuming that collapsing bubbles revisit their equilibrium radii, R_o, filled with vapor-saturated gas ([gas]/[H_2O] $\approx$ 31 at 300 K) before becoming impermeable and adiabatic en route to uniform $\geq$25 kK temperatures. We find that the above assumption is physically untenable and seriously in error. In contrast, we calculate robust [gas]/[H_2O] $\leq$ 0.12 ratios at R_o by using realistic $\alpha_{H_2O} \leq 0.3$ values for the mass accommodation coefficient of H_2O molecules on liquid water at 300 K, and by taking into account the diffusive resistance developing within collapsing bubbles. Therefore, water vapor, rather than any particular gas, is the main component of collapsing bubbles. Its large heat capacity and atomization energies preclude reaching *uniform* peak temperatures exceeding 5 kK. We briefly analyze the consequences of this analysis and their relation to existing information.

Introduction

Liquids irradiated with high-power ultrasound undergo chemical decomposition and emit light.[1−4] These phenomena occur near the end of the collapse of bubbles expanded many times their equilibrium sizes. The nonlinear dynamics of these complex events is reasonably well described by the Rayleigh−Plesset (RP) equation—which is based on the energy balance of a simplified model bubble—except near the sonochemically relevant rebound stage.[2,3] Although extreme conditions can only originate from mass and energy transfer limitations across the bubble interface, the RP equation does not explicitly deal with changes in the gas amount or composition due to the permeability of bubble walls or to chemical reaction. However, it is often used in its original form to analyze the sonochemical and sonoluminescence effects of cavitation.

It was recently argued that the adiabatic collapse of bubbles filled with inert gas would actually lead to the extremely high, *uniform* temperatures apparently required by single bubble sonoluminescence SBSL experiments.[5] It turns out that such conditions could only be attained if liquid−vapor equilibrium were maintained within bubbles until very late in the collapse. This widespread conjecture can be traced to a continuum mechanical analysis of thermal effects in forced radial oscillations of gas bubbles.[6] The analysis focused on the variation of the effective heat capacity ratio $\gamma = C_p/C_v$ associated with finite rates of heat dissipation but, paradoxically, overlooked the fact that restrictions on the transfer of hot vapor molecules would also control the composition of the gaseous mixture and, by extension, affect γ.[7] This is a fundamental issue that deserves to be clarified.

A self-consistent discussion of this problem must take into account the thermochemical kinetics of mass and energy transfer processes, as well as of water vapor decomposition and the ensuing reactions that occur at high temperatures. We have already carried out such a program.[8] However, the intricate interplay of diverse factors suggests that a perturbative analysis may be a more transparent setting for establishing the importance of vapor supersaturation in cavitating bubbles. In this paper we improve our assessment of the extent of mass transfer in bubbles exhibiting SBSL using a molecular approach based on a recent extension of the kinetic theory of gases to the relevant transition regime.[9−11] The physical basis of the argument is that only a fraction of vapor molecule−liquid collisions actually result in condensation. In fact, $\alpha_{H_2O} \approx 1$ values are incompatible with the nonvanishing vapor pressure of water,[2,8] and with the small relative yields of O_2 in the sonolysis of water.[8,13] Direct measurements of mass accommodation coefficients of polar species on liquid water confirm and quantify this claim.[10,12]

The conclusion that collapsing bubbles are largely filled with water vapor throughout implies that the mechanism by which dissolved gases affect sonochemical and sonoluminescence phenomena may be different than previously thought.[14] In this regard, notice that H_2O_2 formation rates in the sonolysis of water saturated with Ar and He differ by a factor 14 at 20.2 kHz but are identical at 39.4 kHz.[4] These observations cannot be solely accounted for by the larger thermal conductivity of He ($\kappa_{He}/\kappa_{Ar} = 8.2$), a factor that would quench the adiabatic collapse and depress H_2O_2 yields at both frequencies. Similarly, the fact that the SBSL intensity is over 1 order of magnitude larger under N_2 doped with 1% Ar than under either gas alone cannot be certainly construed as evidence of thermal conductivity or heat capacity effects on bubble collapse.[15] The fact that the various gases differ in their thermal properties as well as in their solubilities in water precludes experimental tests of the relevant variables in isolation.[4] In such cases, a valid approach is to identify the constraints imposed on elementary process by first principles and available information. Our calculations reveal that vapor condensation rates are much slower than previously assumed, that vapors become highly supersaturated during collapse, and that it is thermodynamically impossible to reach peak temperatures above 5 kK across the bubbles analyzed by Hilgenfeldt et al.[5] These results may have critical implications on our understanding of cavitational phenomena.

10.1021/jp9927202 CCC: $18.00

Results and Discussion

The evolution of a $R(0) = R_o$ bubble driven by an acoustic wave of frequency f and amplitude P_a, is given by the classical RP equation:[2,3]

$$R\ddot{R} + 1.5\dot{R}^2 = \rho^{-1}\left[\left(P_h + \frac{2\sigma}{R_o} - P_v\right)\left(\frac{R_o}{R}\right)^{3\gamma} - \frac{2\sigma}{R} - 4\eta\frac{\dot{R}}{R} - (P_h - P_a \sin 2\pi f t)\right] \quad (1)$$

The density of water at 300 K is $\rho = 1000$ kg/m^3, its vapor pressure $P_v = 3$ kPa, its surface tension $\sigma = 73$ mN/m^2, and its dynamic viscosity $\eta = 1$ g m^{-2} s^{-1}. $\gamma = C_p/C_v$ is the heat capacity ratio of the bubble contents, and $P_h = 0.1$ MPa is the hydrostatic pressure. The kinetic theory of gases provides the basis for evaluating the rate of change of the vapor number density $dn/dt = dn_{H_2O}/dt$ within variable volume bubbles at relatively low pressures:[8,16,17]

$$\frac{dn}{dt} = -\frac{S}{V}\alpha_{eff}\left[\left(\frac{c}{4} - \dot{R}\right)n - \frac{c}{4}n_o\right] - (1 - \alpha_{H_2O})\frac{n}{V}\frac{dV}{dt} = -\frac{3}{R}\left\{\alpha_{eff}\left[\left(\frac{c}{4} - \dot{R}\right)n - \frac{c}{4}n_o\right] + (1 - \alpha_{H_2O})n\dot{R}\right\} \quad (2)$$

$S/V = 3/R$ is the bubble surface-to-volume ratio, $c = (8kT/\pi M)$ is the mean thermal speed of $H_2O(g)$, M its molecular mass, n_o is the number density of saturated water vapor, and k is Boltzmann's constant. α_{H_2O} is the mass accommodation coefficient in single collisions of H_2O molecules with $H_2O(l)$ surfaces. On the other hand, α_{eff} represents the effective mass accommodation coefficient for the transfer of H_2O molecules from the bulk vapor to the liquid (see below). Notice that in this context c is actually the mean gas speed relative to the center of the bubble. Hence, the gas speed relative to the moving bubble wall is $(c/4 - \dot{R})$. The relative speed at which $H_2O(g)$ molecules evaporate from the liquid remains, of course, $c/4$. In physical terms, eq 2 means that only a fraction $\alpha_{H_2O} < 1$ of the stationary vapor swept by the bubble shell during the compression stage is directly incorporated into the advancing liquid. The rest of the molecules must overcome the resistance of the remaining gas–vapor mixture—that undergoes compression at a rate reduced by the factor $(1 - \alpha_{H_2O})$—in order to reach the bubble wall. In other words, we consider that molecular trajectories may not be strictly independent under the conditions relevant to bubble collapse. The departure from molecular flow is indicated by Knudsen numbers $Kn = \lambda_{H_2O}/R$ smaller than 1. The mean free path of water molecules λ_{H_2O} in a H_2O–Ar mixture is given by[16]

$$\lambda_{H_2O} = \frac{1}{\pi\sigma_{H_2O,Ar}^{\;2}[1.8n + 1.2n_{Ar}]} \quad (3)$$

$\sigma_{H_2O,Ar} = {}^1/_2(\sigma_{H_2O} + \sigma_{Ar}) = 0.37$ nm is the mean molecular diameter, and n_{Ar} is the argon number density. Within the bubble at equilibrium, with $R = 5.5$ μm, $n_{Ar} = 2.4 \times 10^{25}$ molecules/m^3, and $n_o = 7.6 \times 10^{23}$ molecules/m^3 at 300 K, we get $\lambda_{H_2O} = 77$ nm and $Kn = 0.014$. Therefore, it is necessary to consider a diffusional hindrance in addition to the condensation and evaporation resistances implicit in $\alpha_{H_2O} < 1$ values.[9,17] Transport theory in the transition regime $(0.01 \le Kn \le 1)$ is a complex subject that involves a spatially dependent molecular velocity distribution function.[18] Recently, Davis et al. reviewed theoretical results on the solution of Boltzmann's equation for droplet evaporation and condensation processes over a wide range of Kn's.[19] They found that the Knudsen numbers prevailing down to the onset of collapse (see below) warrant the use of an effective accommodation coefficient α_{eff} given by[10,11]

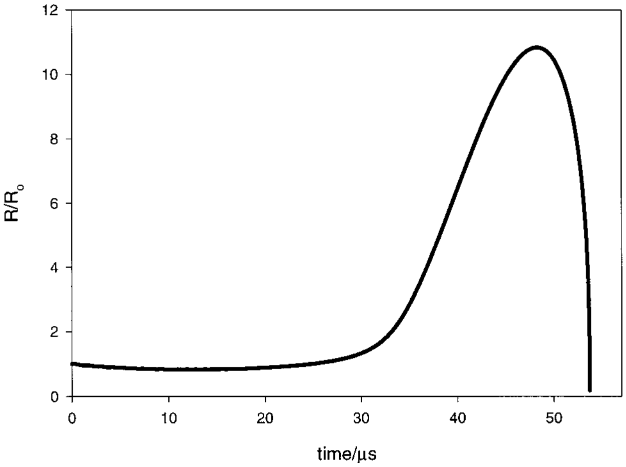

Figure 1. Ultrasonically driven expansion and collapse of a spherical bubble. Bubble radius vs time calculated using the Rayleigh–Plesset equation (eq 1) for a bubble of initial radius $R_o = 5.5$ μm, under a sound wave of amplitude P_a/MPa = 0.135 sin($2\pi f$), $f = 20$ kHz, with $\gamma = 1.34$.

$$\frac{1}{\alpha_{eff}} \approx \frac{1}{\alpha_{H_2O}} + \frac{1 + 0.3Kn}{Kn(1 + Kn)} \quad (4)$$

in eq 2. Notice that (1) if $\alpha_{H_2O} > Kn \approx 0.01$, $\alpha_{eff} \approx Kn$ and (2) α_{eff} would depend on α_{H_2O} only if $\alpha_{H_2O} < Kn$. Experimental values for the closely related parameter α_{H_2O2} extrapolated to 300 K actually suggest that $\alpha_{H_2O} \approx 0.03$.[12a] Since the purpose of this paper is to establish a hard lower limit to n_{H_2O} within collapsing bubbles we will consider that $\alpha_{H_2O} \le 0.3$.[12b]

In Figure 1 we show the expansion and ulterior collapse of a $R_o = 5.5$ μm bubble filled with 1 atm Ar (1 atm = 0.1 MPa) saturated with water vapor, driven by a $f = 20$ kHz, $P_a = 0.135$ MPa acoustic wave.[5] Calculations were performed by integrating eqs 1 and 2, with $\alpha_{H_2O} = 0.1$ or 0.3, c(m/s) $= 592(R_o/R)^{3(\gamma-1)/2}$, and $\gamma \approx \gamma_{H_2O} \approx 1.34$ The latter choice does not significantly affect the bubble's trajectory except in the vicinity of the rebound, which is approached more slowly, providing for increased damping and, hence, for more efficient vapor condensation. Therefore, our calculations are expected to yield the lowest possible n_{H_2O} values. Following a series of small-amplitude high-frequency oscillations, the bubble expands to $R_{max}/R_o = 10.83$ after 48.30 μs, i.e., close to the period of the applied ultrasound. Sudden collapse ensues under an average external pressure $\langle P_{ext}\rangle \approx P_h + P_a \sin(2\pi f \times 53\ \mu s) = 0.187$ MPa (Figure 2). The effective mass accommodation coefficient $\alpha_{eff} \approx Kn$ remains at or above 0.01 until the final phase of the collapse (Figure 3). Observe that the calculated ratio [Ar]/[H_2O] increases from its initial 31.6 value to about 55.5 at 14.2 μs, before dropping to 0.0451 at 50.9 μs, right after the protracted expansion preceding cavitational collapse (Figure 4). At 53.72 μs, $R = R_o = 5.5$ μm and $\dot{R} = -349$ m/s—i.e., at the point where Hilgenfeldt et al. assume that the collapse becomes adiabatic[5]—the bubble actually contains $N_{H_2O} = 1.9 \times 10^{11}$ water molecules corresponding to a [Ar]/[H_2O] = 0.1025 ratio. This "onset of adiabaticity" must be obviously interpreted as a nominal threshold that implicitly acknowledges the ongoing competition between the increasingly faster compression and the finite rates of heat and mass loss through the bubble wall.[5] In this connection, notice that [Ar]/[H_2O] only increases 2.3

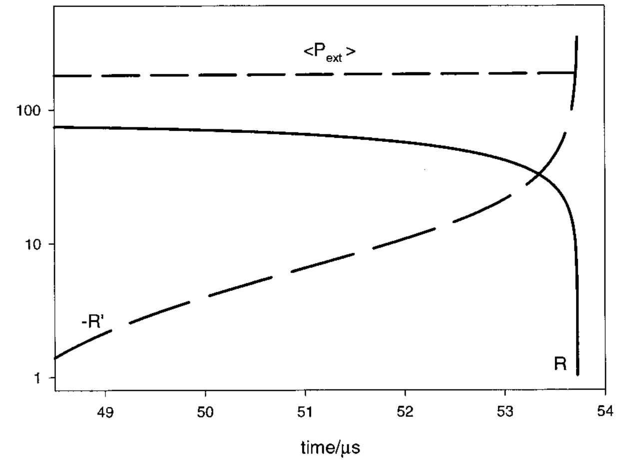

Figure 2. Final stage of the bubble collapse in Figure 1. *R* is the bubble radius in μm, $-R'$ is its speed in m/s, and $\langle P_{ext}\rangle$ is the average external pressure acting on the bubble in kPa.

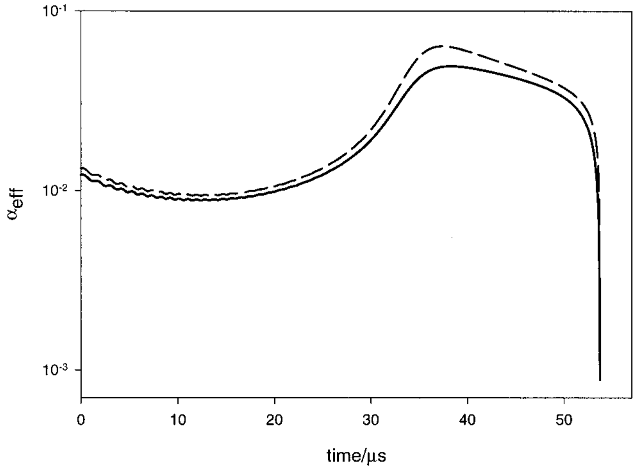

Figure 3. Effective accommodation coefficient α_{eff} for water vapor transfer across the bubble interface calculated with eq 4 and $\alpha_{H_2O} = 0.1$ (solid line) or $\alpha_{H_2O} = 0.3$ (dashed line) under the conditions of Figure 1.

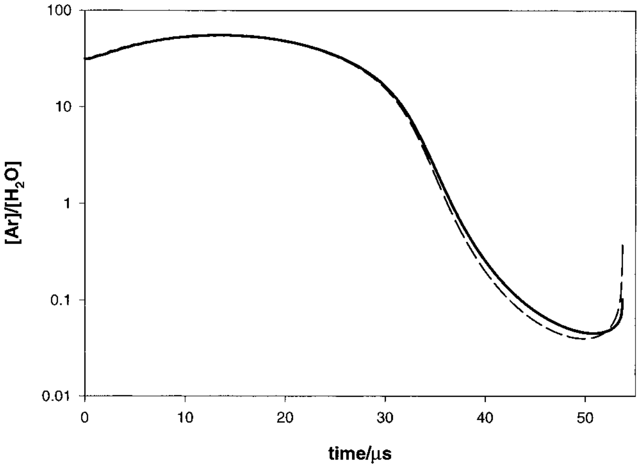

Figure 4. Instantaneous composition of the bubble contents as it evolves as in Figure 1 for $\alpha_{H_2O} = 0.1$ (solid line) or $\alpha_{H_2O} = 0.3$ (dashed line).

times while the bubble shrinks from $R_{max}/R_o = 10.83$ to 1.0 (Figure 4, far right), revealing the inefficiency of gas−liquid equilibration and undermining the notion of a late onset.

We can now calculate the maximum temperatures attainable in a real bubble from the energy available for heating the vapor in the adiabatic stage. The latter comprises the kinetic energy of the bubble liquid shell at R_o, plus the external work to be performed on the vapor while compressing it from R_o down to $\{R_f \ll R_o, \dot{R} = 0\}$:

$$2\pi\rho\dot{R}^2{R_o}^3 + \frac{4\pi}{3}\langle P_{ext}\rangle({R_o}^3 - {R_f}^3) = N_{H_2O}\int_{300}^{T_{max}} C_{v,H_2O}(T)\,dT \tag{5}$$

where $C_{v,H_2O}(T)$ is the heat capacity of $H_2O(g)$ as a function of temperature.[20] In this manner, we calculate 127 nJ of available kinetic energy (the first term of the left-hand side), negligible compression work (0.13 nJ), and $T_{max} = 4240$ K. This temperature is in line with those obtained in ref 8. Any further heating would involve, in addition to the trivial thermal excitation just considered, the dissociation of water vapor: $H_2O \Leftrightarrow O + 2H$, with $\Delta H \approx 1.5 \times 10^{-18}$ J/molecule.[21] Therefore, more than $\Delta E = N_{H_2O}\Delta H \approx 8.0 \times 10^{11} \times 1.5 \times 10^{-18} = 1200$ nJ would be actually needed to uniformly heat the bubble to temperatures above 20 kK, where H_2O is expected to be fully atomized. The inevitable conclusion is that the high temperatures demanded by SBSL experiments must be confined to a small core for the simple reason that the acoustic field does not provide enough energy to heat up the entire bubble.[22]

In summary, the commonly held view that bubbles are filled with saturated gas is inconsistent with a realistic estimate of condensation rates. Extensive solvent vapor supersaturation in bubbles uniformly heated to a few kK, depending on the conditions, is in accord with sonochemical rates and products.[8,13] The much higher temperatures required by SBSL observations can only be attained in a small core region.[22]

References and Notes

(1) Suslick, K. S.; Crum, L. A. In *Sonochemistry and Sonoluminescence, Handbook of Acoustics*; Crocker, M. J., Ed.; Wiley: New York, 1998; Chapter 23.

(2) Leighton, T. G. *The Acoustic Bubble*; Academic Press: London, 1994; Chapter 4.

(3) Brennen, C. E. *Cavitation and Bubble Dynamics*, Oxford University Press: 1995; Chapters 1−4.

(4) Hua, I.; Hoffmann, M. R. *Environ. Sci. Technol.* **1997**, *31*, 2237.

(5) Hilgenfeldt, S.; Grossmann, S.; Lohse, D. *Nature* **1999**, *398*, 402.

(6) Prosperetti, A. *J. Acoust. Soc. Am.* **1977**, *61*, 17.

(7) Fujikawa, S.; Akamatsu, T. *J. Fluid Mech.* **1980**, *97*, 481. (b) Matsumoto, Y.; Takemura, F. *JSME Int. J., Ser. B* **1994**, *37*, 288.

(8) Colussi, A. J.; Weavers, L. K.; Hoffmann, M. R. *J. Phys. Chem. A* **1998**, *102*, 6927.

(9) Widmann, J. F.; Davis, E. J. *J. Aerosol Sci.* **1997**, *28*, 87 and references therein.

(10) Shi, Q.; Li, Y. Q.; Davidovits, P.; Jayne, J. T.; Worsnop, D. R.; Mozurkewich, M.; Kolb, C. E. *J. Phys. Chem. B* **1999**, *103*, 2417.

(11) Hanson, D. R.; Ravishankara, A. R.; Lovejoy, E. R. *J. Geophys. Res.* **1996**, *101*, 9063.

(12) Nathanson, G. M.; Davidovits, P.; Worsnop, D. R.; Kolb, C. E. *J. Phys. Chem.* **1996**, *100*, 13007. (b) Vapor−liquid equilibrium is maintained by the balance of evaporation and condensation rates: $A_{vap}\exp(-Q_{H_2O}/RT) = (^1/_4)c\alpha_{H2O}n_o\Omega_{H_2O}$ (see text for values and definitions). With a latent heat of vaporization $Q_{H_2O} = 40.7$ kJ/mol, and assuming a frequency factor $A_{vap} \approx 10^{13}$ s^{-1} for evaporating a water molecule from an area $\Omega_{H_2O} = \pi(3.0 \times 10^{-10}\ \mathrm{m})^2 = 2.8 \times 10^{-19}$ m^2, we get $\alpha_{H_2O} = 0.024$. While evaporation is an activated process, condensation is controlled by the dissipation of Q_{H_2O} upon collision, which is not instantaneous. The mass accommodation coefficient gives a measure of the competition between energy dissipation and re-evaporation and is expected to depend inversely on the energy content (i.e., the temperature) of the impinging molecules.

(13) Hart, E. J.; Henglein, A. *J. Phys. Chem.* **1985**, *89*, 4342.

(14) Mason, T. J.; Lorimer, J. P. *Sonochemistry. Theory, Applications and Uses of Ultrasound in Chemistry*; Wiley: New York, 1988; Chapter 2.

(15) Hiller, R.; Weninger, K.; Putterman, S. J.; Barber, B. P. *Science* **1994**, *266*, 248.

(16) Jeans, J. H. *The Dynamical Theory of Gases*, 4th ed.; Dover: New York, 1954.

(17) Frank-Kamenetskii, D. A. *Diffusion and Heat Transfer in Chemical Kinetics*; Plenum Press: New York, 1960.

(18) Chapman, S.; Cowling, T. G. *The Mathematical Theory of Non-Uniform Gases*; Cambridge University Press: Cambridge, U.K., 1970.

(19) Li, W.; Davis, E. J. *Aerosol Sci. Technol.* **1996**, *25*, 11.

(20) NIST Standard Reference Database 69, November 1998 Release: *NIST Chemistry WebBook.*

(21) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

(22) Wu, C. C.; Roberts, P. H. *Phys. Rev. Lett.* **1993**, *70*, 3424.