Sonochemical yields of cavitation collapse by molecular dynamics simulation

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Introduction

Bubbles in a standing sound field can be trapped at a pressure antinode and driven to strongly nonlinear oscillations with fast collapse, whereby shock waves and also faint, short light pulses are emitted. The physical and chemical processes within the bubbles associated with these phenomena are still not completely understood and also defy spatially resolved experimental investigation. In this paper, he processes within collapsing sonoluminescing bubbles containing argon and water vapor are investigated by molecular dynamics (MD) simulations with several million particles.

The Model

The MD simulation uses a hard-sphere model with point collisions between particles[1, 2]. After a collision, particles follow straight trajectories. This allows to use an efficient, event-driven algorithm to calculate the system's time evolution. In order to keep the computational costs low, the simulation region is divided into cells. For every particle all *possible* future collisions within its own and the neighboring cells are calculated. Therefore, only particles in 27 cells have to be examined to find collisions for a given atom. Collisions between particles and other incidents (such as wall-collisions and cell-crossings) are handled as *events*, occuring at a specific simulation time. Whenever an event takes place, all future events scheduled for the particles involved become invalid and have to be deleted.

The bubble wall is simulated as a spherical boundary whose motion is calculated by the Rayleigh-Plesset-Equation (RPE) that includes a term describing the sound radiation into the liquid:

$$RR\ddot{} + \frac{3}{2}\dot{R}^2 = \frac{1}{\rho_W}\ (P_L - P_\infty) + \frac{R}{\rho_W c_W}\ (\dot{p}(R,t) - \dot{P}_\infty),\ \ (1)$$

where R is the bubble radius, ρ_W the density of water ($996, 6\,\text{kg/m}^3$), P_L the liquid pressure at the bubble wall, P_∞ the pressure far away from the bubble, c_W the speed of sound in water ($1481\,\text{m/s}$) and $p(R,t)$ the gas pressure at the bubble wall. This pressure is determined from wall collisions of particles given by the MD simulation. A thermal boundary layer in the liquid is implemented to model heat transfer between gas and liquid. Wall temperature evolution is calculated by the thermal energy imparted to the wall by colliding particles, assuming heat conduction with a quadratic temperature profile in the liquid's boundary layer. The MD simulation starts at maximum bubble radius and stops shortly before rebound. Beforehand, the bubble is expanded from a given equilibrium radius R_0 using the RPE with a polytropic model for the bubble interior.

During its growth, water molecules evaporate into the bubble. Via the ideal gas law the initial number of water molecules in the bubble, N_v, can be calculated by

$$N_v = \frac{P_{sat}(T_\infty)(4/3)\pi R_{max}^3}{k_B T_\infty},\ \ (2)$$

where $P_{sat}(T_\infty)$ is the saturation vapor pressure at ambient temperature and R_{max} the maximum radius. In the collapse phase water condensation at the bubble wall is taken into account: for every wall collision, a sticking probability is calculated, which is a function of the temperature of the colliding particle, the wall temperature and the current water vapor pressure.

Near the end of the collapse temperatures are sufficiently high to dissociate the water molecules trapped in the bubble. The generated products are chemically active, so that reactions between Ar, H_2O, O, O_2, O_3, H, H_2, OH, HO_2 and H_2O_2 have to be taken into account (Ar acting as a catalyst). Bimolecular and catalytic reaction mechanisms are implemented for calculating the bubble chemistry. While bimolecular reactions simply need a certain amount of collision energy, catalytic reactions consist of two steps: (i) the formation of an excited complex of educts, that (ii) either decays again after a certain lifetime or reacts by collision with the catalyst.

For a more accurate description of the particle interaction, a Variable Soft Sphere (VSS) model [[3]] is used: the diameter of the hard spheres depends on the relative kinetic energy of the collision partners. Thus the fact that two particles with similar velocity vectors affect each other by long-range interaction is incorporated.

In order to determine the conditions in the bubble, hydrodynamic and thermodynamic quantities are calculated by averaging the corresponding particle properties (number, mass, energy etc.) over small volumes. To this end, the bubble is divided into 2000 spherical shells of equal volume. in the following, the calculated physical fields (temperature, concentration, etc.) are plotted as a color-coded function of time and radius to demonstrate their spatio-temporal evolution.

Results

Calculations with 10^6 particles were performed for several bubbles in water (T=300 K) with equilibrium radii R_0 of $1.125\,\mu$m to $4.5\,\mu$m, driven by an ultrasonic wave of acoustic pressure ranging from 1.2 bar to 1.7 bar at frequencies of 26.5 kHz to 106 kHz. These parameters have been chosen to investigate the changes of interior dynamics and sonochemical reactions, when bubble size is decreased and the excitation pressure is adjusted achieve similar compression ratios (R_{max}/R_{min}). In all cases
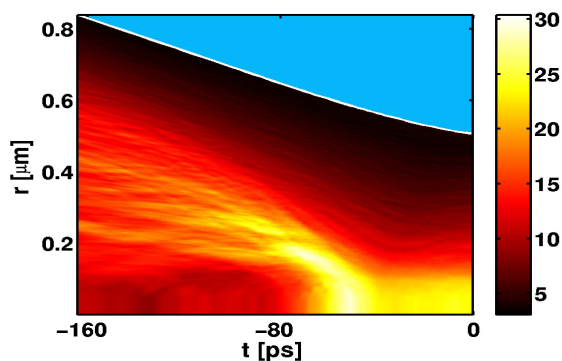
Figure 1: Fraction of H_2O molecules (in %) in a bubble without chemical reactions. $R_0 = 4.5\,\mu m$, driving frequency $= 26.5\,kHz$, driving pressure $= 1.3\,bar$

the effect of water vapor is significant. It is observed for the typical SBSL bubble ($R_0 = 4.5\,\mu m$), as well as for the smaller bubbles, that the light water molecules are trapped at the bubble center and weaken the shock, compared to a bubble without vapor. Furthermore, water molecules have rotational degrees of freedom, which absorb energy. The effect of water trapping is illustrated in Fig. 1, showing the ratio of water molecules to argon atoms for the largest bubble considered (chemical reactions switched off).

High temperatures near the end of the collapse lead to dissociation of water molecules. The chemical reactions of the fragments are mostly endothermic and reduce temperatures significantly. The bubble of Fig. 1 with water vapor but without chemistry reaches temperatures of about 85.000 K - when also chemical reactions are simulated only up to 50.000 K are obtained. Fig. 2 shows the evolution of density in such a bubble. An incoming compression wave is focused at the bubble center, is reflected and returns to the bubble wall. Fig. 3 shows the corresponding distribution of temperature. Formation of OH-radicals, important for sonochemistry, is significant. In Fig. 4 the evolution of density for OH radicals is plotted to demonstrate the inhomogeneous distribution of this sonochemical product. As vapor is concentrated toward the bubble center, so is the formation of OH. While the relative number of OH ions, $N(OH)/N(H_2O)$ depends on temperature through the reactive equilibrium and is high in the center and outgoing shock, the absolute concentra-
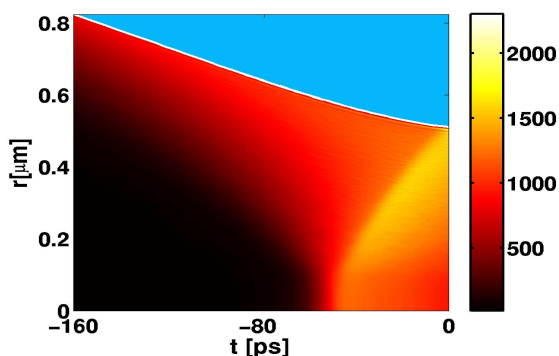

Figure 2: Density [kg/m^3] evolution in a bubble with chemical reactions. Parameters as given in Fig. 1
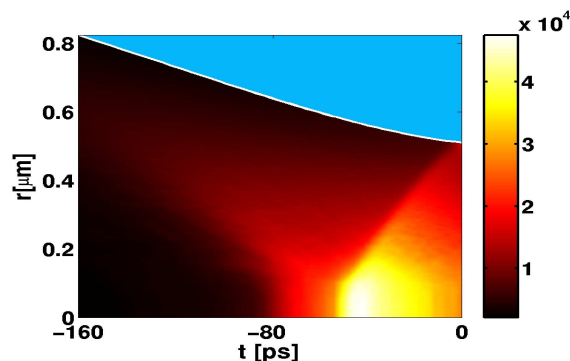

Figure 3: Temperature [K] evolution for the bubble Fig. 2.

tion of OH ions decreases significantly toward the bubble wall. Though uptake of OH particles by the bubble wall is not yet included in our model, this finding suggests that the mass flow of OH out of the bubble should be small with spherical bubbles.

When turning to smaller bubbles (and to higher acoustic pressures and frequencies in order to produce a sonoluminescent bubble), conditions in the bubble get more extreme. For bubbles with $R_0 = 2.25\,\mu m$ (driving pressure: 1.5 bar, frequency: 53 kHz) temperatures up to 55.000 K were obtained. A bubble with $R_0 = 1.125\,\mu m$ (driving pressure: 1.7 bar, frequency: 106 kHz) reached temperatures up to 61.000 K. The maximum pressure climbs from 2200 kg/m^3 to 3000 kg/m^3. This suggests that energy concentration is more efficient in smaller bubbles.
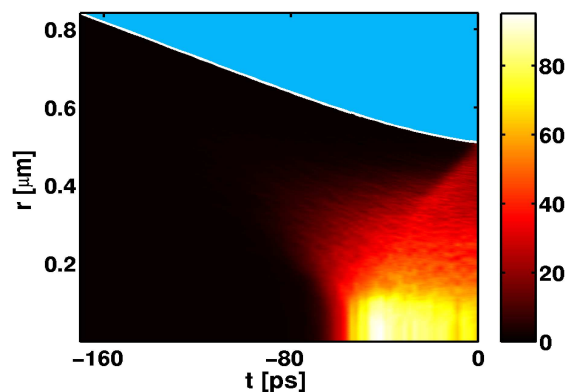

Figure 4: OH-Formation: mass density of OH-radicals [kg/m^3] for the bubble of Fig. 2.

References

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