Evaporation of a liquid, initiated by condensation of vapor on its surface

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Abstract. The paper considers mechanisms of initiation of liquid evaporation by contact with hot vapor (with temperature greater and much greater than the temperature of liquid). Two fundamentally different mechanisms of such initiation are distinguished - equilibrium and non-equilibrium. The process of non-equilibrium initiation of evaporation by hot vapor was studied using the method of molecular dynamics; the results agree with the theoretical estimate given in the work for determining the temperature of the beginning of the non-equilibrium mechanism of evaporation initiation.

1. Introduction
In the theoretical analysis of sonoluminescence (the glow observed during the oscillation of a vapor bubble under ultrasonic influence), the solution of the Rayleigh equation \cite{1}, the equation describing the bubble dynamics under the influence of the pressure difference inside and outside (in the liquid), plays an important role. The solution of this equation, assuming that the process is adiabatic, makes it possible to obtain, generally speaking, any high temperatures inside the bubble: according to the Poisson adiabatic equation we have

\[ T(t) = T_0 \left( \frac{R_0}{R(t)} \right)^{\gamma-3}, \]

where $\gamma$ is the adiabatic exponent; that is, when the radius tends to zero $R(t) \to 0$ we get $T(t) \to \infty$. Such a conclusion can justify the so-called thermal theory of sonoluminescence – the theory according to which the luminescence of a bubble is caused by its considerable heating (up to thousands of degrees and higher) \cite{2–5}. Note that the temperature increase of the liquid in this case is not considered in any way.

Figure 1 shows the dependence of the vapor bubble radius on time, as well as the temperature inside it, calculated from the model \cite{2}. As one can see, temperatures of ~3000 K are reached at the maximum collapse of the bubble. Generally speaking, several theories can be outlined, according to which, when such temperatures are reached inside the bubble, luminescence should be excited (either in the vapor phase or on the liquid surface). However, this paper is not devoted to clarifying these or other mechanisms of sonoluminescence, but to investigating a more primary question: setting the boundary conditions for the dynamics of a vapor cavity located in the field of ultrasonic influence, since the very possibility of bubble collapse to very small sizes requires, in our opinion, additional justification. The
point is that when the temperature inside a bubble rises, one can expect an additional inflow of vapor mass into the bubble due to evaporation of liquid from its surface; an increase in the amount of vapor, in turn, may lead to stopping the bubble contraction before its significant collapse.

Thus, for a more correct modeling of bubble evolution, the processes of vapor evaporation and condensation on its surface must be taken into account. In some works, the vapor mass balance inside the bubble is taken into account using the well-known Hertz-Knudsen equation [4, 5]:

\[
dM dt = 4\pi R^2 \sqrt{\frac{m}{2\pi k_B}} \left( \frac{p_s}{\sqrt{T_l}} - \frac{p_v}{\sqrt{T_v}} \right),
\]

(2)

where \( k_B \) is the Boltzmann constant, \( p_s \) is the saturated vapor pressure at liquid temperature \( T_l \), \( p_v \) and \( T_v \) are the vapor pressure and temperature, respectively. The evaporation coefficient can be added to equation (2) (multiplying it approximately by 0.8), but its essence is unchanged: the evaporation flux is determined by temperature of the liquid and pressure of its saturated vapor. Thus, equation (2) considers evaporation and condensation fluxes only separately, without analyzing the influence of one flux on the other, in particular, without considering in any way the influence of the condensation process on evaporation, and calculation at the aforementioned assumption \( T_l = \text{const} \) gives a constant evaporation flux from the surface of the vapor bubble.

Meanwhile, condensation of vapor cannot fail to initiate the process of evaporation in some way. The evaporation process itself is a flight of liquid particles possessing sufficient kinetic energy for this [6, 7]. Since when vapor molecules fall on a liquid surface, the kinetic energy of liquid molecules, which have taken on this "blow", will inevitably increase, we should expect an increase in the evaporation flow as well. Consequently, when calculating evaporation flux correctly, it is also necessary to take the interrelation of condensation and evaporation processes into account.

2. The effect of condensation on evaporation

This issue was briefly discussed in [7]; here we will consider it in more details. Two limit scenarios of process development can be distinguished when liquid and hot vapor come into contact:

- hot vapor with temperature \( T_G \), condensing into the liquid with temperature \( T_l \), transfers its energy to the particles of the surface layer, the temperature of which increases locally – this increases the evaporation flow; in this case we can talk about increasing the liquid temperature, i.e., the distribution of liquid molecules by kinetic energy remains equilibrium (Maxwellian) at the new – elevated – temperature;
a hot vapor molecule with a very high temperature \( T_G \), falling on the surface of a liquid with temperature \( T \), interacts with \( M \) particles and transfers to them the energy sufficient to overcome the work function \( \Delta \); in this case, the liquid molecules immediately fly out – the resulting energy has no time to thermalize (thermalization occurs at times much longer than \( \tau \approx 10^{-12} \) s – the time of energy relaxation in a liquid); thus, the speed of these \( M \) particles does not obey the Maxwell distribution.

The first scenario can be called an equilibrium scenario, since the effect of hot vapor is reduced only to the fact that it locally increases the temperature of the liquid. The vapor with temperature \( T_G \), condensing into the liquid with temperature \( T \), transfers its energy to the particles of the surface layer, the temperature of which becomes equal to \( C \cdot T (1 \leq C < T_G/T) \). If before the interaction with vapor the fraction of particles capable of evaporating was proportional \( \Gamma(1/2, A/(k_B T)) \) \([6]\), then during the contact with hot vapor this fraction is higher and amounts to \( \Gamma(1/2, A/(k_B T \cdot C)) \).

The question of what to consider as the work function is quite interesting and is discussed in \([7]\). Without repeating the main points of this discussion, we will formulate only the main results here. In general, the energy which must be overcome by a particle on the surface of a liquid to leave this surface can be determined in different ways: by tracing the evolution of the particle which has finally left the liquid, one can observe different values of its potential energy - that is, different values of the binding energy. The very change of this energy is obviously caused by interaction of the particle of interest with other particles; together with the potential energy its total energy changes too. It seems logical, however, to observe a particle leaving only when its total energy remains constant: starting from this point in time we can talk about the actual process of the particle's departure from the surface. Note that the values of \( A \) obtained in this manner are noticeably lower than the binding energy inside the liquid \([7]\).

Using the velocity distribution function of the evaporated particles \([6]\), we can obtain an expression for the mass and energy flux density during evaporation \([8]\):

\[
J_e = n_e \sqrt{\frac{\pi \cdot m \cdot k_B T}{2}},
\]

\[
Q_e = n_e \cdot k_B T \sqrt{\frac{\pi \cdot k_B T}{0.32 \cdot m}},
\]

where \( T \) is the temperature of the liquid; \( n_e \) is the concentration of evaporating particles, which is proportional to the fraction of particles in the liquid that have sufficient velocity for evaporation in the direction normal to the surface; \( m \) is the particle mass.

The fluxes are conveniently given in a dimensionless form, using as a unit of mass flux density:

\[
J_0 = 0.8 \cdot n_s \sqrt{\frac{m \cdot k_B T}{2 \cdot \pi}},
\]

and as a unit of energy flux density:

\[
Q_0 = n_s \cdot k_B \cdot T \sqrt{\frac{2 \cdot k_B T}{\pi \cdot m}}.
\]

Then the dimensionless fluxes are defined as \( j_e = J_e/J_0, j_c = J_c/J_0, q_e = Q_e/Q_0, q_c = Q_c/Q_0 \) and in this case in the equilibrium state (with the evaporation coefficient equal to 0.8 \([8]\)):

\[
T = T_G = T_s; \quad n_G = n_s;
\]

\[
j_e = j_c = 1; \quad q_e = q_c = 1.
\]
If we apply expressions (3) and (4) for the temperature of the liquid $T\cdot C$, the dimensionless evaporation fluxes can be written as:

$$j_e = C^{1/2} \cdot \frac{A}{2} \frac{C}{k_B T} \left/ \frac{1}{2} \frac{A}{k_B T} \right.,$$

(7)

$$q_e = C^{3/2} \cdot \frac{A}{2} \frac{C}{k_B T} \left/ \frac{1}{2} \frac{A}{k_B T} \right..$$

(8)

However, this mechanism of evaporation initiation is equilibrium – the condensing vapor only superheats the liquid locally. Such an analysis is, in fact, only suitable for coefficient $C$ slightly exceeding unity: in this case, the condensing vapor only slightly increases the local temperature of the liquid.

The second of the scenarios described above, when bombardment with hot vapor leads to instantaneous flight of liquid molecules from its surface, is more interesting. In this case it is possible to expect quite an interesting effect: at very high kinetic energy of the flying molecule it can cause evaporation of several liquid particles at once. Thus, at condensation of very hot vapor we may assume that the evaporation flux (mass flux of evaporated particles) will exceed the condensation flux; in this case the liquid temperature will not increase too much, because most of the energy input from vapor to the liquid surface is spent on evaporation.

3. Non-equilibrium initiation of evaporation

In order to determine the conditions under which the initiated evaporation flux surpasses the condensation flux, let us write down the energy conservation equation for the particles involved in the process. A molecule, possessing kinetic energy $E^*$ in the vapor, falls on the liquid, thus acquiring additional energy $A$ (the bonding energy of one particle on the surface of the liquid). This energy is transferred to $M$ molecules on the surface of the liquid, each of which previously had kinetic energy $E$. If the energy per degree of freedom of each of the $M$ particles exceeds the bonding energy, the particles will leave the liquid, that is, a necessary condition for such a process.

$$\frac{E^* + A + ME}{3M} > A$$

(9)

From this expression it is possible to determine the energy of a vapor particle required for one evaporated particle to fly out in response to one condensed particle, i.e., to put the number of $M = 1$ particles in (9). Then the threshold energy

$$E^* = 2A - E,$$

(10)

or, if you express the temperature of the vapor:

$$T^* = 2(2A - E) / 3k_B$$

(11)

For example, for argon, the work function $A/k_B \approx 10^3$ K, and for a liquid temperature of 100 K, we obtain an estimate of the critical vapor temperature for the process under discussion $\approx 1200$ K.

The analytical estimates we obtained, however, cannot describe the full picture of the phenomenon in question. For a clearer picture of the process under discussion, it is desirable to provide a detailed picture of the phenomenon. It is very difficult to investigate such a problem experimentally, but there is another way: numerical simulation.
4. Numerical simulation results

Numerical modeling by molecular dynamics is almost a direct numerical experiment, with reservations about the usually modeled or approximated form of the potential. Our work uses the Lennard-Jones potential

\[
\varphi = 4\varepsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right)
\]

where \(\varepsilon\) is the potential well depth; \(\sigma\) is the distance at which the interaction energy is zero; \(r\) is the distance between the particles.

The substance under study is argon located on a copper base. To describe the interaction of copper atoms with argon atoms, a potential with constants calculated using the Lorentz-Berthelot rule is used [9, 10]:

\[
\sigma_{Ar-Cu} = \frac{\sigma_{Ar} + \sigma_{Cu}}{2}
\]

\[
\varepsilon_{Ar-Cu} = \sqrt{\varepsilon_{Ar} \cdot \varepsilon_{Cu}}
\]

The interaction parameters were taken to be \(\sigma_{Ar} = 3.345\,\text{Å}, \varepsilon_{Ar}/k_B = 125.7\,\text{K}\) for argon [11] and \(\sigma_{Cu} = 2.33\,\text{Å}, \varepsilon_{Cu}/k_B = 3168.8\,\text{K}\) for copper [12].

The computational region (Figure 2) contains 3 350 atoms of argon, which rest on a substrate of copper atoms (150 atoms). The size of the computational region 36\(\times\)2\(\times\)2 nm\(^3\) was chosen with the consideration that a small number of computational particles would simulate a liquid layer of sufficient thickness and at the same time leave a sufficient surface area for accommodation of incoming energy from hot vapor. To simulate an unbounded liquid surface, periodic boundary conditions are set on the side faces (with longer edge length – 36 nm, see Figure 2). On the face, on which the substrate is located, the reflection boundary conditions are set. And on the last face (lying opposite to liquid surface) more complicated boundary conditions are set:

1) a particle that has reached the boundary drops out of the calculation (is considered to be vaporized and no longer interacts with other particles);
2) at a given interval, atoms with velocities obeying the Maxwell distribution at temperature \(T_G\) are launched toward the liquid – thus a hot vapor with a given temperature and density is simulated.
3) As a result of the numerical experiment the mass flux densities and energies of evaporated (dropped out) and condensed (launched) particles \(J_e, Q_e\) and \(J_c, Q_c\) respectively are determined.

\[\text{Figure 2. Computational region}\]

A series of numerical experiments simulating the contact of a cold liquid (95 K in temperature) with vapor of 1 000, 5 000 and 10 000 K. First of all, in this problem the dimensionless results are interesting and the correlation of the Lennard-Jones liquid with argon is necessary only for checking the approximate estimate (11), which determines the temperature of the vapor at which, on average, one particle per falling vapor particle will fly back from the liquid surface. Parameters for nondimensionalization at chosen temperature of liquid: \(J_0 = 513\,\text{kg}\cdot\text{m}^{-2}\cdot\text{s}\) and \(Q_0 = 25.4\,\text{MW}\cdot\text{m}^{-2}\).

The process of interaction of a vapor particle with a hot liquid is shown in Figure 3. Here a vapor particle with high energy (at time 0 ns) flies into the liquid, the energy of which locally increases (at
time 0.006 ns one can observe a liquid layer with energy of 125 K) – this is due to the fact that the vapor particle has transferred some of its energy to several liquid particles located in this layer. The liquid particles, having received additional energy, evaporate.

![Figure 3. Frame-by-frame view of a hot vapor particle flying into a liquid](image)

The process described above is observed for modes with vapor temperatures of 5 000 and 10 000 K. For the mode with the temperature of 1 000 K the usual process of evaporation and condensation is observed, which does not contradict the estimation (11). Hot vapor (with temperature of 5 000 – 10 000 K) is able to initiate a significant increase in evaporation flux (mass flux density increases by ~ 3-4 times, energy flux density ~ about 10-30 times; see Table 1), although the temperature of the main liquid mass does not change.

**Table 1. Parameters and results of the numerical experiment**

| $T_G$, K | $j_c$ | $j_e$ | $q_c$ | $q_e$ |
|---------|-------|-------|-------|-------|
| 1 000   | 0.73  | 0.82  | 3.77  | 0.93  |
| 5 000   | 0.915 | 3.43  | 29.4  | 9.94  |
| 10 000  | 1.19  | 4.08  | 56.1  | 27.3  |

Thus, numerical simulation shows that, indeed, the vapor temperature at which the condensation flux causes a countercurrent equal evaporation flux corresponds to a temperature of ~10^3 K in order of magnitude. These are quite achievable temperatures that are predicted by the simplest adiabatic models of bubble collapse. Thus, a correct model that takes into account the change in vapor mass in the bubble should consider the effects described in this paper.
Conclusion
Two processes of initiation of liquid vaporization due to contact with hot vapor are considered depending on whether the energy of an incoming particle in the liquid has time to thermalize. In the first case (if the energy has time to thermalize), accounting for the increase in evaporation flux is possible by using expressions for fluxes with increased temperature $T_C$, where $C$ lies in the range from 1 to $T_c/T$.

A different non-equilibrium initiation mechanism has been studied using the molecular dynamics method. Despite the fact that liquid temperature does not change in any noticeable way, there is a significant increase in evaporation flux: condensing particles transfer their energy to liquid molecules, which, possessing total positive energy, leave the surface. In this case the energy of the particle that has flown in simply does not have time to thermalize, and the local velocity distribution of liquid molecules is not described by the Maxwell function with increased temperature, since the energy transferred to the liquid is immediately spent on evaporation of the particles. In such a process, the effect of hot vapor on the liquid surface can cause an evaporation flux that exceeds the condensation flux.

The results of numerical experiments demonstrating the possibility of such a process are presented; according to theoretical estimates and simulations performed, the critical temperature of vapor, required for the evaporation flux to exceed the condensation flux that caused it, is approximately $10^3$ K. Thus, when vapor reaches a temperature of several thousand degrees, the evaporation flux from the surface of even a cold liquid will exceed the condensation flux, which will cause an increase in the vapor mass.

As applied to the problem of a collapsing bubble, this mechanism leads to a significant difficulty in reducing the bubble to very small sizes. This circumstance should be taken into account when discussing the so-called "thermal" hypothesis of sonoluminescence, according to which a bubble can collapse to such a small size that the heated vapor inside it begins to emit light.

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