Theory of the teapot—boiling kinetics of a pure fluid in a gravitational field

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(Submitted 5 January 1993)
Zh. Eksp. Teor. Fiz. **103**, 2039–2047 (June 1993)

The problem of pure liquid boiling in a gravitational field is solved. The energy conservation law in the boiling fluid is formulated. The height dependence of the distribution function of buoyant bubbles is investigated, taking into account energy conservation. It is shown that one of two scenarios is realized, depending on the extent of superheating. Bubbles collapse at a finite height when the amount of superheating is slight. Above the critical amount of superheating, a process is established in which the bulk of the energy flux is transported by bubbles. The decrease in their number, in inverse proportion to height, is balanced by the increasing energy of an isolated bubble.

1. In the present paper the boiling problem of a pure liquid is treated. Boiling is a special case of first-order phase transitions. The general theory of nucleation is discussed in Refs. 1–3. The current status of the problem is discussed, for example, in the reviews of Refs. 4 and 5.

Unlike other phase transitions, in the boiling process bubble buoyancy plays an important role. The buoyancy is accompanied by energy transport. For this reason it is required to solve simultaneously the kinetic evolution equation of the bubble distribution function and the energy conservation equation.

The given problem is similar to the coalescence problem in supersaturated solutions, treated by Lifshitz and Slezov.[1,2] The coalescence process occurs with conservation of the number of dissolved particles, causing the supersaturation of the solution to decrease with time. In our case the energy of the bubble and fluid system is conserved. The corresponding conservation law is formulated in Sec. 2, where it is shown that energy pumping from the growing supercritical bubbles in the fluid generates an increase in the extent of superheating. The self-heating can be terminated with thermal explosion. The bubble buoyancy stabilizes the process due to heat transport from the superheating site. The corresponding time-independent problem is solved in Secs. 3–6. It will be shown that the boiling process varies according to the extent of fluid superheating at the bottom of the container. Bubble buoyancy leads either to disappearance of superheating at a finite height with subsequent collapse of all bubbles, or to an asymptotic behavior similar to coalescence.

Preliminary results of this study were presented in the Riga conference.[6]

2. Consider initially the time evolution of the bubble distribution in size R, neglecting the gravity field. In this case the boiling process of a pure liquid is similar to coalescence of nuclei in solutions.[1,2]

The evolution of the distribution function $f(t,R)$ is described by the equation of continuity

$$\frac{\partial f}{\partial t}+\frac{\partial}{\partial R}(\dot{R}f)=0. \qquad (1)$$

For weak superheating bubbles have macroscopic sizes. This makes it possible to omit the term in (1) corresponding to "diffusion" in space of small sizes in the parameter $1/n_gR_c^3$, where n_g is the density of molecular vapor, and R_c is the critical radius (see below).

The rate of bubble growth in a weakly superheated pure fluid is

$$\dot{R}=c(\Delta-R_0/R). \qquad (2)$$

Here c is a quantity of the order of the speed of sound in the vapor, $R_0=2\sigma/p$, σ is the surface stress coefficient, and Δ is the extent of nonequilibrium (superheating):

$$\Delta=\delta p/p=(q/T)(\delta T/T),$$
$$\delta p=p_s-p, \quad \delta T=T-T_b, \qquad (3)$$

where q is the heat of molecular vapor formation, p_s is the saturated vapor pressure, and T_b is the boiling temperature. Taking into account thermal conductivity and viscosity, the validity limits of expression (2) are discussed in detail in Ref. 3.

If the system is thermally isolated, the extent of nonequilibrium Δ is time-dependent, and an additional condition needs to be introduced so as to solve Eq. (1). One must relate $\Delta(t)$ to the distribution function. In a supersaturated solution such a condition was obtained from the conservation law of the number of particles of the dissolved material.[1,2] For a superheated pure fluid this role is played by the energy conservation law

$$E=C\delta T+\int dR\varepsilon f(t,R). \qquad (4)$$

The first term on the right hand side is the superheating energy of the fluid itself, and C is its heat capacity. The second term is the bubble energy. The energy of a single bubble

$$\varepsilon=4\pi\sigma(R^2-\tfrac{2}{3}R^3/R_c) \qquad (5)$$

is maximum at $R=R_c$ ($R_c=R_0/\Delta$ is the critical size), and becomes negative for $R>\tfrac{3}{2}R_c$.

It is assumed that the evaporation and condensation processes are adiabatic, so that the increase in the bubble entropy during its growth is fully balanced by the decrease

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in the fluid entropy. For this reason the heat of vapor formation is not included in the bubble energy (5).

Using expressions (2) and (5), we find the rate of change of the bubble energy

$$\dot{\varepsilon}=\frac{\partial\varepsilon}{\partial R}\dot{R}=-8\pi\sigma c R_0(1-R/R_c)^2. \quad (6)$$

This implies that in a superheated fluid bubbles extract energy both in dissipation ($R<R_c$) and in growth ($R>R_c$), and superheat the surrounding fluid layer. This is qualitatively distinct from the evolution of nuclei in a supersaturated solution, in which supercritical nuclei decrease the solution concentration, while subcritical ones increase it.

Differentiate Eq. (4) with respect to time:

$$0=C\dot{T}+\int dR\dot{f}\varepsilon=C\dot{T}-\int dR\varepsilon\frac{\partial(\dot{R}f)}{\partial R}$$

$$=C\dot{T}+\int dRf\dot{R}\frac{\partial\varepsilon}{\partial R}. \quad (7)$$

Using (6), one thus obtains

$$\dot{T}=-C^{-1}\int dRf\dot{\varepsilon}>0. \quad (8)$$

It is seen that a superheated fluid with bubbles under thermally insulating conditions is self-heated and, what is more, the extent of superheating Δ and the saturated vapor pressure p_s increase. We emphasize that this derivation refers to a constant volume system. The system pressure p increases with increasing temperature. The competition of pressures $p(t)$ and $p_s(t)$ determines whether thermal explosion takes place, or a weakly superheated state occurs with slowly increasing temperature and pressure.

3. In a more realistic statement of the boiling problem the heat is supplied to the bottom of the container and departs through the upper surface of the fluid. Bubbles are created at the bottom surface and depart with the velocity

$$\dot{z}=\alpha R^2, \quad (9)$$

determined by equating the Archimedes and Stokes forces.

The distribution function and the energy start depending on the height coordinate z. Their simultaneous evolution is described by the system of equations

$$\frac{\partial f}{\partial t}+\frac{\partial}{\partial z}(\dot{z}f)+\frac{\partial}{\partial R}(\dot{R}f)=0, \quad (10)$$

$$\frac{\partial E}{\partial t}+\frac{\partial Q}{\partial z}=0. \quad (11)$$

Here E is the energy density at height z [see Eq. (4)]. The quantity Q is the energy flux density

$$Q=-\varkappa\nabla(\delta T)+\int dRf\varepsilon\dot{z}, \quad (12)$$

where the first term on the right hand side is the heat flux in the fluid, and $\varkappa$ is the heat conduction coefficient. The last term in (12) is the bubble energy flux. It is assumed that superheating is slight, and that convective energy transport can be neglected.

Consider steady boiling. In this problem the continuity equation (10) acquires the form

$$\frac{\partial}{\partial z}\varphi'+\frac{\partial}{\partial R}(v\varphi')=0,\quad \varphi'=\dot{z}f,\quad v=\dot{R}/\dot{z}. \quad (13)$$

It is seen that the height plays the role of time, and the bubble flux $\dot{z}f$—that of the distribution function. For superheating independent of height Eq. (13) has a simple solution

$$\varphi'=v^{-1}F[z-Z(R/R_c)],$$

$$Z(u)=\int dRv^{-1}=z_\Delta\int du\,u^3/(u-1), \quad (14)$$

$$z_\Delta=\alpha R_0^3/(c\Delta^4).$$

The shape of the function F is given by the distribution shape at $z=0$. The solution gives the physically obvious result—bubbles having a size less than the critical radius R_c collapse at a height of order z_Δ. Larger bubbles increase as $z^{1/3}$.

Consider now the height dependence of the extent of superheating and of R_c. We neglect heat departure through the lateral walls. The energy flux (12) is then constant, and is independent of height. Its value Q is given by the heat supplied to the bottom of the container. In the notation

$$x=R(z)/R_c(0),\quad y=\Delta(z)/\Delta(0),\quad t=z/z_0,$$

$$z_0=\alpha R_0^3/c\Delta^4(0),\quad B=Q/Q_0,$$

$$Q_0=4\pi\sigma R_c^2 J,\quad A=\Delta(0)\varkappa T^2/(qz_0Q_0), \quad (15)$$

$$\varphi=R_c(0)zf,\quad J=\int dx\varphi|_{t=0}$$

Eqs. (12), (13) acquire the form

$$\frac{\partial\varphi}{\partial t}+\frac{\partial}{\partial x}[x^{-3}(xy-1)\varphi]=0, \quad (16)$$

$$B=-Ady/dt+S(y), \quad (17)$$

$$S(y)=J^{-1}\int dx\varphi(x^2-\tfrac{2}{3}x^3y). \quad (18)$$

The physical meaning of the parameter B is the relation between the thermal fluxes in the fluid and bubbles. If the main thermal flux is transported by the fluid, then $B\gg 1$ holds. As follows from Eq. (17), the ratio $A/B\sim\Delta^5(0)/Q$ determines the "fast" cooling of the fluid.

4. To simplify the analysis of the system evolution, consider nucleation at the bottom of bubbles of identical size. In this case the distribution function is

$$\Phi(t,x)=J\delta[x-x(t)] \quad (19)$$

and Eqs. (16) and (17) reduce to the ordinary differential equations

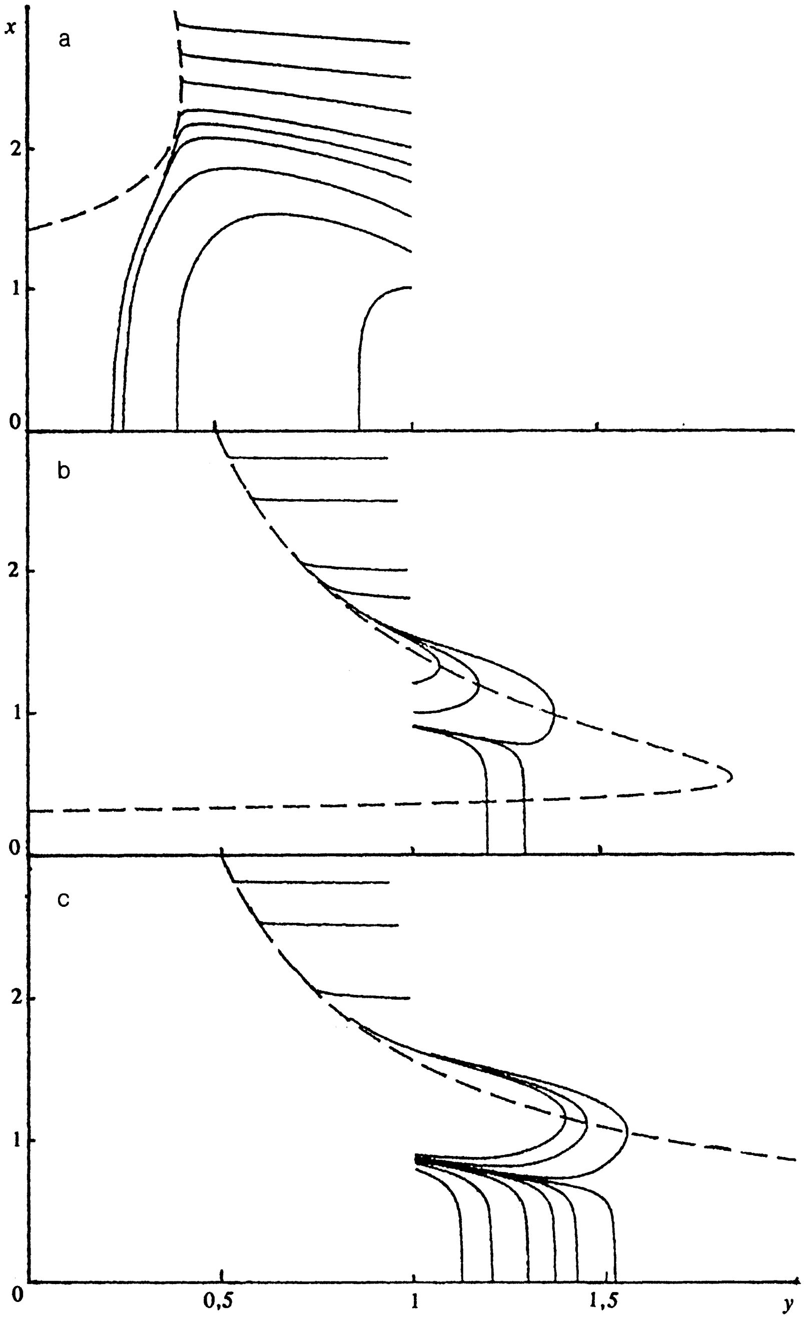

FIG. 1. Evolution trajectories of a system of bubbles of identical size, solid lines. The critical curve (23) is shown by the dashed line. Explanation in text.

$$\frac{dx}{dt}=\frac{xy-1}{x^3}, \tag{20}$$

$$\frac{dy}{dt}=\frac{-B+x^2(1-\frac{2}{3}xy)}{A} \tag{21}$$

with initial conditions

$$y(0)=1, \quad x(0)=x_0. \tag{22}$$

It follows from Eq. (22) that the nature of the trajectory $x(y)$ differs to the right and the left of the critical curve $x^*(y)$, on which $\dot{y}=0$. The critical curve equation is (see Fig. 1):

$$B=x^*(y)^2-\tfrac{2}{3}x^*(y)^3y. \tag{23}$$

To the left of this curve we have $dy/dt>0$, and the extent of superheating increases with "time," namely height. To the right of this curve the extent of superheating drops.

The nature of the trajectory is determined by the ratio A/B. For $A \ll B$ and $B \gg 1$, almost everywhere in the (x,y) plane one has the obvious solution

$$dy/dt \approx -B/A, \quad x(t) \approx \text{const}. \tag{24}$$

If the initial bubble size is sufficiently large, $x_0 > \sqrt{B}$, then the trajectory passes horizontally to the critical curve, and for $y \to 0$ it approaches asymptotically either its upper branch $x^* \approx 3/2y$, or its lower, tending to the point $\sqrt{B}$. In the first case one has the asymptotic law

$$x=(2t)^{1/4}, \quad y=\tfrac{3}{2}(2t)^{-1/4}. \tag{25}$$

For $x_0 < \sqrt{B}$ the trajectory is horizontal up to $y=0$, except for the region $x_0 < A/B$, when the trajectory emerges from the abscissa at a finite value of y.

Thus, when the bottom of the container is preheated and the energy flux is large, the fluid cooling is basically determined by the thermal conductivity, and the bubble size hardly changes until the whole energy flux is transported to the bubbles. Subsequently, either the asymptotic regime (25) is reached, or the fluid cools off to the boiling temperature following a finite time. In the latter case bubbles collapse either for a finite superheat value, or later, when $y<0$.

The region in which the curve (23) affects the trajectory is extended for decreasing energy flux as the ratio A/B increases. At the same time the beam of trajectories lost to the point $\sqrt{B}$ is narrowed down.

As seen from Eq. (21), for $A \gg B$ and $B > \sqrt{1/3}$ the extent of superheating varies slowly in comparison with the rate of bubble growth. If the initial size is $x_0 < 1$, bubbles collapse at a height of the order of z_Δ. For $x_0 > 1$ the bubbles initially grow. At the same time the critical size $1/y$ increases due to cooling. The asymptotic regime starts when the critical size is comparable with the bubble radius. Figure 1 provides the results of numerical solution of the system (20), (21) for the ratio $A/B=10$ and $B=2$.

For $0 < B < \sqrt{1/3}$ the critical curve (23) intersects the line of initial values $y=1$. A region of x_0 values appears on the left of the critical curve, where the bubble energy flux exceeds the total energy flux B, while the thermal flux in the fluid becomes negative (is directed downward). As a result the extent of superheating near the bottom is enhanced in proportion to the bubble buoyancy. In the case $A \ll B$ the bubble size changes little initially: $x(y) \approx \text{const}$. The trajectory approaches the critical curve later on, and for $x_0 > \sqrt{3B}$ it turns upwards and intersects it. As a result the trajectory appears in the cooling region of the fluid ($dy/dt<0$), tending to the ordinate asymptotically close to the upper branch $x^*(y)$. If the intersection point of $x(y)$ and $x^*(y)$ is located below $x = \sqrt{3B}$, the trajectory further tends to the abscissa. If the initial bubble size x_0 is above or below the critical curve, fluid cooling starts from the very same origin, and the problem reduces to the preceding one. The nature of the trajectory does not change for $A>B$. The system evolution for the case $B=0.1$ and $A/B=10$ is presented in Fig. 1b.

It is now assumed that $B<0$ holds. This implies that the heat source is located on top. In this case the critical curve (21) is a monotonically decreasing function. Again, for simplicity we assume $A \ll |B|$. If the initial value x_0 is located above the critical curve, $dy/dt<0$ [see Eqs. (21), (23)], the heat flux in the fluid turns upwards, the extent of superheating drops with increasing height, and the preblem reduces to the preceding one. For $x_0 < x^*(1)$ the temperature gradient is initially positive. An increase in the extent of superheating leads to redistribution of the total energy flux, directed downwards, in the bubbles. The temperature gradient vanishes (the intersection of the trajectory and of the critical curve at the point $y^*>1$). Subsequently, fluid cooling starts again with increasing height, and the process acquires the former asymptotic character. It is only for $x_0 \ll 1$ that the trajectory departs from the abscissa. The bubbles have disappeared. The extent of superheating increases with further height increase, but bubbles are not newly generated, since the probability of fluctuating nucleation of bubbles in a pure fluid is very low. For increasing ratio $A/|B|$ the trajectories in the (x,y) plane become more vertical, and the transition boundaries from one regime to another are shifted, but the qualitative pattern does not change (see Fig. 1c).

5. Consider now the system evolution when the initial size distribution of bubbles is continuous. Two paths of system evolution are also possible in this case: either the fluid cools so fast that the extent of superheating Δ vanishes at a finite height and boiling stops, or Δ approaches zero asymptotically and the energy flux in the bubbles is conserved.

As in the case of single-size bubbles, the solution of system (16)–(18) is easily analyzed in two limiting cases: $A \ll |B|$ and $A \gg |B|$. Let $A \ll |B|$. The shape of the distribution function then varies substantially more slowly than the superheating. Therefore, the energy flux of bubbles $S(y)$ depends linearly on the quantity y, increasing from $S(1)$ to $S(0)$. If $S(0)<B$ holds, the system superheating is lost after a finite time [at height $z \approx (A/B) z_0$] and boiling ceases. If $S(1)<B<S(0)$ holds, the process initially occurs as in the preceding case. Almost the whole energy flux then transfers to the bubbles, initiating the asymptotic phase considered in the next section. According to (17), $S(1)>B$ implies $dy/dt>0$ and superheating increases with height at the first phase. This derivative then changes sign, initiating cooling and either transition to the asymptotic regime, or bubble collapse.

In the opposite limit $A \gg |B|$ the superheating initially changes slowly in comparison with the evolution of the bubble distribution function. At the first phase all subcritical nuclei collapse, while the supercritical ones increase rapidly and create an energy flux directed downwards. As a result superheating starts dropping rapidly, and the asymptotic regime is started. It is seen that when the ratio $A/|B|$ is large the asymptotic phase is initiated following substantial rearrangement of the initial distribution function. Therefore, this boiling phase depends weakly on both the initial distribution and on the value of the total energy flux B.

For an arbitrary ratio of A to B the system (16)–(18) was solved numerically. The initial distribution function was selected in the form $x^* \exp(-x/x_0)$. It was found that when $B>10$ the boundary between the two evolution paths is located on the line $A \approx 45B$ and is independent of the x_0 value. When $B<10$ holds, the boundary value A for $x_0<1$ is located below this line, and for $x_0>1$ above it.

6. The asymptotic regime of boiling recalls the coalescence process in supersaturated solutions,[1,2] and can be described within the Lifshitz–Slezov theory. In this superheating phase $y=\Delta/\Delta(0)$ is a monotonically decreasing function of height. Following Refs. 1, 2, it is convenient to introduce the new variables

$$\tau=\ln[\Delta(0)/\Delta(z)]=\ln(1/y),\quad u=R/R_c(z)=xy,$$
$$\psi=R_c\dot{z}f=\varphi/y. \tag{26}$$

In these variables Eqs. (16)–(18) acquire the form:

$$\frac{\partial}{\partial\tau}\psi-\frac{\partial}{\partial u}(w\psi)=0, \tag{27}$$

$$w=u-\gamma u^{-3}(u-1), \tag{28}$$

$$\gamma^{-1}=\frac{d}{du}\frac{1}{4y^4}=\frac{-\dot{y}}{y^5}, \tag{29}$$

$$B=A\gamma^{-1}e^{-5\tau}+J^{-1}e^{2\tau}\int du\psi(u^2-\tfrac{2}{3}u^3). \tag{30}$$

Following Refs. 1, 2, for long "times" τ the parameter (29) is close to its asymptotic limit γ_0. Neglecting the dependence of γ on τ, the solution of Eq. (27) is obtained in the form

$$\psi=w^{-1}F(\tau+s),\quad s=\int du/w. \tag{31}$$

To satisfy condition (30), the function F must have the form

$$F(\tau+s)\propto\exp[-2(\tau+s)], \tag{32}$$

with

$$0<\int du(u^2-\tfrac{2}{3}u^3)e^{-2s}<\infty. \tag{33}$$

For large u the integral s in (31) increase as $\ln(u)$, so in the general case the integral (33) diverges at the upper limit. An exception is the value

$$\gamma_0=4u_0^3,\quad u_0=4/3 \tag{34}$$

when the "velocity" w in the direction of the origin of coordinates is positive for all u, and is tangent to the abscissa at the point u_0. In this case the integral s becomes infinite when $u>u_0$, the distribution function (31) becomes localized in the interval $(0,u_0)$, and condition (33) is satisfied.

Thus, if the system enters the asymptotic path of evolution, at large heights the parameter is $\gamma\approx256/27$, the critical size increases as $z^{1/4}$ [see (29)], and the number of nuclei drops as z^{-1}, i.e.,

$$N=\int dRf=\int du\frac{\psi}{\dot{z}}\sim e^{-4\tau}. \tag{35}$$

In this case the distribution function has the universal shape (31), (32), and is localized in the interval $(0,\tfrac{4}{3}R_c)$. Though the energy flux is constant, the bubble energy drops as $z^{-1/2}$. This is related to the fact that most bubbles are on the order of the critical size, and for this size the buoyancy rate (9) is proportional to $z^{-1/2}$. In this connection it must be noted that the assumption adopted concerning fluid immobility is violated not only for substantial superheating, when the fluid is entrained by a large number of buoyant bubbles, but also if the superheating is less than $\Delta_c\approx10^{-4}$, when the velocity $\dot{z}(R_c)$ is comparable with the speed of sound.

7. In conclusion we provide the characteristic parameter values, introduced above, for boiling water if $\Delta=10^{-2}$, $N=10^{18}\ \text{cm}^{-3}$, $Q=10^7\ \text{erg/cm}^2\ \text{sec}$:

$$n_g\approx10^{19}\ \text{cm}^{-3},\quad R_c\approx10^{-2}\ \text{cm},\quad z_\Delta\approx10^{-4}\ \text{cm},$$
$$A\approx1,\quad B\approx1.$$

The authors are grateful to the Dutch Organization of Scientific Studies (NWO) for support.

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Translated by Nathan Jacobi