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Numerical solution of the problem of homogeneous nucleation in the liquid phase

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The paper considers the processes taking place in the liquid phase: nucleation in liquids and liquid metals, electrical explosion of conductors and spark cavitation. It is established that all these processes are well described by the basic equation of cavitation, which is solved numerically by the Runge–Kutta method. For this purpose, a program in the Fortran programming language has been created, and a method for determining the time of appearance of cavitation nuclei by the method of numerical integration has been described. A mathematical model of homogeneous nucleation in the liquid phase was created. With the help of the created model, such parameters as the time of appearance of a cavitation bubble for various frequencies of external influence were calculated. The maximum amplitude and period of the natural oscillations of a bubble at various frequencies.

Key words and phrases: numerical solution, cavitation, mathematical model of cavitation, spark cavitation, liquid metals.

1. Fluid nucleation

The theory of thermodynamic stability was developed by Gibbs in the last century. Thermodynamic stability of a system is understood as the equilibrium of a system of relatively small changes in its thermodynamic parameters, such as volume, pressure, temperature, etc. For thermodynamic equilibrium of a system, it is necessary that its internal energy be minimal. The condition of the positivity of the value of the second derivative of the internal energy [1] follows from the requirement of a minimum of internal energy. It, in turn, leads to a number of thermodynamic inequalities, which are the conditions of thermodynamic stability.

The boundary of the thermodynamic stability of the phase is the spinodal. The position of the spinodal can be calculated from the thermal equation of state for liquids and gases, the simplest of which is the Van der Waals equation. Spinodal consists of two branches: steam and liquid. The spinodal of the vapor phase determines the vapor saturation limit. The spinodal of the liquid phase determines the boundary of the thermodynamic stability of the liquid [2], [3]. With a positive pressure - the limiting temperature of the liquid overheating, with a negative pressure (tension) - the ultimate tensile strength of the liquid.

Between the binodal (line of phase equilibrium) and the spinodal of the liquid phase lies the region of the metastable liquid, overheated or stretched. From the point of view of thermodynamics, a superheated liquid is essentially no different from a stretched one.

In the region of a metastable liquid, cavities filled with steam, gas, or their mixture (cavities) appear in the process of heating a liquid at constant pressure or in the process of decreasing pressure at a constant temperature.

The process of the formation and development of bubbles depends on the state of the liquid, including the presence of solid or gaseous impurities in it, and on the pressure in the liquid.

Thus, for nucleation in a liquid it must be stretched to a certain pressure, not exceeding in absolute value the limits of the thermodynamic stability [4] of the liquid (spinodal).

2. Nucleation in liquid metals

The theory of nucleation was proposed in the works of V.P. Skripov and students [5], [6], [7].

Later it was shown that the implementation of unstable states is also possible for liquid metals, which follows from experiments with an electric explosion of conductors [8]. In the process of such an electric explosion, an emission of X-rays and multiply charged ions was detected. This is explained by the fact that in the process of the spinodal decomposition of the unstable liquid metal phase, regions with a sharp local temperature rise appear, which leads to thermal excitation of atoms and electronic transitions that generate X-ray quantums. The presence of such local “hot centers” with an “anomalous” electrical explosion of conductors is confirmed by the release of multiply charged ions from the explosion zone [9], [10]. The output of short-wave X-ray quantums with an electric explosion of titanium and iron was detected in [11].

Overheating cannot be arbitrarily large, since there is a boundary between the thermodynamic stability of the phase and the spinodal. When approaching the spinodal, the fluctuation mechanism of nucleation or homogeneous nucleation comes into play, which ensures the rapid disintegration of the metastable phase [12]. The process of homogeneous nucleation manifests itself most vividly when the liquid phase is pulsed, which is expressed in the explosive boiling up of the liquid phase that is superheated to the vicinity of the spinodal. Such an explosion also occurs after the release of pressure from a fluid that has been preheated under pressure to a temperature close to the critical one.

3. Electrical explosion of conductors

Experiments have shown [8] that overheating of the liquid metal to the vicinity of the spinodal is possible when the metal conductors are heated by a microsecond current pulse. With this heat, the mass of metal evaporated through the surface the conductor and through the surface of vapor nuclei arising on the ready-made centers is insignificant, so the conductor remains in a liquid state up to the vicinity of the spinodal.

Overheating of a thermodynamically stable liquid above the spinodal point is impossible, since when approaching this point, an explosive boiling mechanism comes into play, caused by a high frequency of homogeneous nucleation of vapor nuclei.

The calculation shows that when approaching the spinodal, the frequency of homogeneous nucleation increases by 28 orders of magnitude, which ensures the explosive boiling of the superheated liquid metal. This process is the main factor determining the electrical explosion of conductors when they are heated by a microsecond current pulse.

4. Spark cavitation

This phenomenon is observed in a vacuum diode with a cathode in the form of an edge and a flat anode. When a voltage pulse is applied to the diode, electrons are ejected from the tip through a tunneling mechanism; this phenomenon is called field emission. As the voltage pulse increases, the autoelectronic current increases and, when its density reaches a certain limit value, the tip of the tip explodes, which leads to an increase in the emission current *10 - 100 times*. The process of microexplosions can be repeated many times, so as after the explosion of this tip, new microprotrusions are formed on the cathode.

The electrical explosion mechanism of the tip is similar to the electrical explosion of conductors; it is determined by the phase explosion of the superheated liquid metal [13], [14].

In the case of an explosion of the edges, the probability of reaching unstable states of the liquid phase and its spinodal decomposition is greater than with the explosion of conductors.

A shock wave arises in the liquid, and a cavity filled with metal vapor forms around the microprotrusion. The cavity expands to a maximum radius, after which it makes damped oscillations. With each compression of the cavity, the gas contained in it is heated. Such a mechanism for the development of the spark cavitation process is confirmed by experimental studies.

Thus, if the developed interpretation of the observed effect in the process of spark cavitation is fair, then with spherical cumulation of a sufficiently strong shock wave in the center of the spherical cavity in a certain short period of time, we should expect the realization of the extreme state of matter [15], [16].

5. The mathematical model of homogeneous nucleation

It can be said that all the processes described above, namely nucleation in liquids and in liquid metals, electrical conductor explosion and spark cavitation can be represented by the same model of homogeneous nucleation in the liquid phase.

We have created a mathematical model of homogeneous nucleation in the liquid phase. It applies to all the processes described here and has already been used by us in the case of spark cavitation [17].

The model is built on the basis of an equation describing the dynamics of a cavitation bubble:

$$\ddot{R}R + \frac{3}{2}\dot{R}^2 = \frac{1}{\rho}\left[\left(p_o + \frac{2\sigma}{R_0}\right)\left(\frac{R_0}{R}\right)^{3\gamma} - \frac{2\sigma}{R} - p_0 + p(t,t_1)\right], \qquad (1)$$

Here: R_0 - radius of the nucleus at $t = 0$; R -radius of the nucleus at the next time instant t; ρ -density of a liquid; σ - surface tension of the fluid; $k = 1$ - adiabatic index

for steam in the bud; p_o - hydrostatic pressure in a liquid ($p_o = p_b$); $\ddot{R}$ - acceleration of the cavity wall; $\dot{R}$ is the speed of movement of the cavity wall; $\frac{2\sigma}{R_0}$ - Laplace pressure; $\frac{R_0}{R}$ - amplitude of oscillations of the cavity, t_1- the time of appearance of the first germ of homogeneous cavitation.

Time t_1 is determined from the condition

$$B \cdot \int_0^{t_1} \exp\left(\frac{C}{t^2}\right) dt = 1. \tag{2}$$

Taking into account the geometric meaning of a definite integral (2), one can determine the point t_1, by numerical method knowing that the area of the figure bounded by the function $f(x)$ on the interval $[0, t_1]$ should be equal to 1.

Part of the program of numerical integration for finding the time t_1 is given below (see Listing 1). The program is written in a programming language *Fortran*.

Listing 1: Program for the numerical determination of the stretching time t_1

```
    print *, ''
    print *, 'The program is designed to calculate:'
    print *, '=============================='
    print *, '1) amplitude of acoustic pressure P1 at the
       ↪ point of appearance of one germ cavitation based on
       ↪ the theory of V.P. Skripov; '
    print *, '2) the duration of the exercise of t1 until the
       ↪ appearance of a single cavitation nucleus (at point
       ↪ P1);'
    print *, '3) Radius of the critical embryo.'
    print *, ''
    print *, 'the program will not work without the data file
       ↪ for the test. substances - water1.dat, as well as
       ↪ without the supporting file amplit.txt. '
    print *, ''
    print *, 'The results of the calculations will be
       ↪ displayed on the screen.'
    open (1, file = 'amplit.txt')
    read (1, *) aniu, amu, dt
    print *, ''
    print *, 'The following parameters are used in the program:'
    print *, ''
    print *, '1) External field frequency =', aniu, 'Hz;'
    print *, '2) Molar mass of substance mu =', amu, 'kg / mol.'
    print *, '3) Integration step dt =', dt, 's;'
    print *, ''
    print *, 'If you are NOT satisfied with these parameters,
       ↪ press "1", then 'Enter', '
    print *, 'if satisfied, press "2", then "Enter".'
    print *, 'To interrupt a program, press "Ctrl + c".'
    read (*, *) n
    if (n-1) 11,11,9
11  continue
    print *, 'Enter parameters:'
```

```
    print *, '1) The frequency of the external field (Hz);'
    print *, '2) Molar mass of substance mu (kg / mol);'
    print *, '3) Integration step dt (s).'
    read (*, *) aniu, amu, dt
    close (1)
    open (2, file = 'amplit.txt')
    write (2, *) aniu, amu, dt
9 continue
    open (3, file = 't1-res.dat')
    open (4, file = 'water-1.dat')
    print *, ''
    write (*, *) 'T A B L I C A'
    print *, ''
    write (*, *) 'External field frequency =', aniu, 'Hz'
    write (*, *) 'temperature-time stress-pressure-crit. radius'
    write (*, *) 'T, grade. C-t1, mks-P1, MPa-Ro, nm'
    ak=1.3806581212e-23
    ana=6.02213673636e23
    pi=3.141592654
    w=2*pi*aniu
    expo=2.7182818284590459
1   continue
    read(4,*)tt,sig,rol,rov,pb,pa
    if(tt)13,13,12
12  b=(rol/rov)*sqrt(2*sig*ana/(amu*pi))
    an=ana*rol/amu
    akk=an*1.0e-06*b
    al=16*pi*(sig**3)/(3*ak*tt*(1-rov/rol)**2)
    tau=pi/(2*w)
    t0=1.0e-15
    t2=tau*5
    ai=0
    aint=0
    alev1=1/akk
    do 2 t=t0,t2,dt
    ptt=pa*sin(w*t)
    pok=(-1*al)/(ptt*ptt)
    pr=expo**pok
    aint=aint+pr*dt
    r=aint-alev1
    k=k+1
    if(r)7,7,8
7   continue
2   continue
8   continue
    p1=pb-ptt
    TEM=tt-273.15
    t1=t*1.0e6
    p11=p1/1.0e6
    aro=(2*sig)/ptt
    aro1=aro/(1.-rov/rol)
```

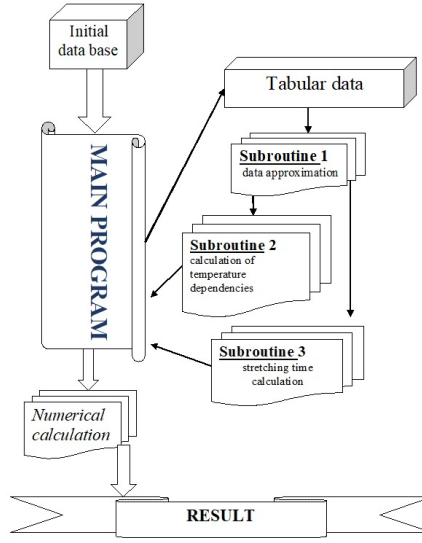

Figure 1. Block diagram

```
    aro2=aro1*1.0e9
    write(*,10)tem,t1,p11,aro2
10  format('␣|␣␣␣',f6.1,'␣␣|␣␣␣␣',f7.4,'␣␣␣␣␣|␣',f8.5,'␣|␣
     ↪  ',f7.3,'␣␣␣|')
    goto 1
    end
```

6. The program for the numerical solution of the equation (1)

We have created a program for the numerical solution of the cavitation equation in the *Fortran* programming language. It work is based on the Runge-Kutta method. The block diagram of the program is shown in the figure 1.

Initially, the main program asks for the values of external parameters, such as fluid temperature, oscillation frequency, and others. Then the main program refers to an array of tabular data for the values of surface tension, fluid viscosity, fluid pressure, vapor pressure at a given temperature. These tabular data are discrete values and do not always correspond to a given temperature. Therefore, the main program refers to auxiliary subroutine 1, which approximates or extrapolates the table data to a given point.

To calculate parameters such as the initial radius of the cavity, the pressure at which the first cavitation nucleus appears, the initial phase of external oscillations, the main program refers to subroutine 2, which calculates these values based on the data already calculated by subroutine 1.

Subroutine 3 then receives from subprogram 2 a task to calculate the time t_1 during which the first cavitation nucleus appears in the fluid. The required tabular data is

requested from subroutine 1. The result of the calculation is reported to the main program.

Having collected all the necessary data, the main program calculates the basic cavitation equation for the maximum amplitude of oscillations of the cavity.

Below is a part of the main program (see Listing 2) for the numerical solution of this system of equations, written in the programming language *Fortran*:

Listing 2: Program for the numerical solution of the equation (1)

```
C       ======program cavitation==========
        external          equ, out
        dimension pt(5), u(2), du(2), au(8,2)
        common /a/ a, b,c,d,e,g
        common /b/ dt, j,ipdos
        open(unit=1, file='im.dat', status='old')
        open(unit=2, file='im.out')
 1      format(8x,e11.3)
 2      format(8x,f10.3)
 3      format(8x,i8)
        read(1,1) rnol, pnol, sigma, pmax, tau
        read(1,2) gamma, rho, vnol
        read(1,3) ichast, ipdos
        write(*,*) rnol, pnol, sigma, pmax, tau
        write(*,*) gamma, rho, vnol
        write(*,*) ichast, ipdos
        read *
C       ==========normalization============
        pi=3.14159
        tenso=2*sigma/rnol
        denso=rho*rnol*rnol
        omega=1/tau
        pa=pmax*exp(1.0)
        deno=denso*omega*omega
        a=(pnol+tenso)/deno
        b=tenso/deno
        c=pnol/deno
        d=pa/pnol
        g=3*gamma+1
        dt=1./ichast
C       ==========period step============
        t=0.
        write(*,*) 'normalization:',a,b,c,d,g,tau,dt,t
        i=1
        j=1
C       ========parameters RKGS==========
        pt(1)=0.
        pt(2)=ipdos
        pt(3)=dt
        pt(4)=1.0e-4
        pt(5)=0.
        u(1)=1.
        u(2)=vnol
```

```
      du(1)=0.5
      du(2)=0.5
      write(2,4)
 4    format('␣t/tau␣␣p(t)␣␣R/Ro␣␣dR/dt␣␣j')
      j=1
      call rkgs(pt, u, du, 2, imsg, equ, out, au)
      write(2,*) imsg
      write(*,*) imsg
      stop
      end
C     ========subroutine equ=========
      subroutine equ(t, u, du)
      dimension u(2), du(2)
      common /a/ a, b, c, e ,g
      common /c/ pe
      pe=(t**2)*(exp(-1*t))
      p=d*pe
      au=a/(u(1)**g)
      bu=-1*b/(u(1)**2)
      cu=-1*c*(1-p)/u(1)
      uu=1.5*u(2)*u(2)/u(1)
      du(2)=au+bu+cu+uu
      du(1)=u(2)
      return
      end
C     ========subroutine out=========
      subroutine out(t, u, du, imsg, numd, pt)
      dimension u(2), du(2), pt(5)
      common /b/ dt, j, ipdos
      common /c/ pe
      if(t-dt*j)1,2,2
 2    continue
      pimp=50*pe/exp(1.0)
      write(2,*) t, pimp, u(1), u(2), j
      write(*,*) t, pimp, u(1), u(2), j
      j=j+1
 1    continue
      if(j-ipdos)4,4,5
 5    continue
      write(*,*) j, ipdos
      pt(5)=1.
 4    continue
      return
      end
```

7. Conclusions

Thus, in this paper we consider the processes taking place in the liquid phase, such as nucleation in liquids, nucleation in liquid metals, electrical explosion of conductors and spark cavitation.

Table 1

Stretching time t_1, mks

Temperature, t^0C	$\nu = 100$kHz	$\nu = 250$kHz	$\nu = 600$kHz
250	0.84	0.47	0.133
300	0.81	0.46	0.129
350	0.76	0.45	0.120
373	0.54	0.22	0.092

Table 2

The maximum amplitude of R/R_0 and the oscillation period of T_1/T of a bubble at different frequencies

ν, MHz	500	100	50	10	5	0.5	0.25
$\left(\frac{R}{R_0}\right)_{max}$	1	10	120	$8 \cdot 10^3$	$3 \cdot 10^4$	$7.3 \cdot 10^5$	$2 \cdot 10^6$
$\frac{T_1}{T}$	0.25	0.5	0.6	2.5	5.0	12.5	15.0

It is established that all the mentioned processes are well described by the basic equation of cavitation.

The indicated equation is solved numerically by the Runge-Kutta method. For this purpose, a program in the Fortran programming language has been created, a scheme of its work has been presented, and a method has been described for determining the time of appearance of cavitation nuclei using the numerical integration method.

The stretching time t_1 for different frequencies of external influence ν is presented in Table 1, the maximum amplitude and period of natural oscillations of a bubble at different frequencies are given in Table 2.

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