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Induction relaxation of thermodynamic parameters in nonstationary evaporation

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Abstract

Nonstationary evaporation of liquid is analyzed on the bases of the phenomenological theory—thermodynamics of irreversible processes. It is shown that relaxation of vapor generation is observed in the case of sharp change of heat flux.

1. Introduction

Evaporation and condensation processes play an important role in modern engineering, vapor-generating systems, contact heat exchangers of industrial power equipment, vacuum metallurgy, obtaining of ultra-pure materials and specimens with special properties in microelectronics and different chemical technologies, in fuel systems of internal combustion engines, cryogenic engines of rockets, and different technological processes of pharmaceutic industry. From the point of view of exploitation safety, processes of nonstationary evaporation are of special importance in engineering calculations of transient models of vapor-generating systems of powerful electric power plants.

At present, the problem of a stationary evaporation–condensation process has been studied adequately. To earlier works in this field there refer studies of Stefan, Hertz, and Knudsen [1,2] where the known Hertz–Knudsen relation for rate of evaporation under stationary conditions

$$j = \beta \frac{P_S - P_0}{\sqrt{2\pi R T_S}}, \tag{1}$$

was obtained. Here β is the empirical coefficient of evaporation which characterizes the ratio of the number of molecules reflected by the phase interface to the number of molecules incident on this surface and P_S is the pressure of saturated vapor of liquid at temperature T_S. From the viewpoint of the molecular-kinetic theory, the rate of evaporation of the condensed phase with the energy of thermal motion kT much smaller than the bond energy of atoms is determined by two processes: separation of atoms from the surface due to thermal motion and their back motion as a result of collision with atoms of the gas phase. Thus, the Hertz–Knudsen relation is the difference of two one-sided Maxwellian flows of particles. A detailed review of works on evaporation and condensation phenomena can be found in [3,4]. Further studies were conducted on the basis of the kinetic Boltzmann equation and its models at small transfer rates. In [5,6], the kinetic theory of evaporation with account for variation of the distribution function of the gas phase due to macroscopic motion of medium was developed for the first time. At small degree of nonequilibricity, to a resultant flow of substance $J = nu$ there corresponds a small, compared to mean thermal velocity of motion of molecules, velocity of vapor motion u toward the normal to the phase interface. In [7–9] a more thorough kinetic analysis of evaporation and condensation processes is given; in this analysis, use of a two-flow function in modeling allows one to take into account both macroscopic motion of the vapor phase and the discontinues character of the distribution function near the phase interface. The kinetic Boltzmann equation is solved by the method of moments in a

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Nomenclature

h	specific heat of vaporization
J	specific density of mass vapor flow
j	specific density of molecular vapor flow
k	Boltzmann constant
L_{ij}	phenomenological coefficients
l	characteristic macroscopic scale of the process
l_{ef}	characteristic scale of a thermodynamic system
m	mass of one molecule
n	concentration of molecules
P	pressure
P_Q	specific volumetric power of heat liberation
R	universal gas constant
S	surface area of evaporation
T	temperature
t	time
u	flow velocity
V	volume of the system

Greek symbols

α_i	empirical coefficient of evaporation
β	thickness of the Knudsen layer
δ	dynamic and kinematic viscosities
ρ	vapor density
τ	characteristic time of relaxation
ϕ	thermodynamic potential

Subscripts

P	pressure
S	parameters on the line of saturation
i, j, k	current indices
r	relaxation of the thermodynamic system
v	relaxation of the vaporization process
O	initial parameters of the system

stationary problem formulation. In [10], similar methods are used for analysis and numerical solution of one-dimensional stationary problems which model intense stationary processes of evaporation and condensation. As a result of solution of the equations of gas dynamics for an outer region (relative to the Knudsen layer), the authors obtained approximation of the distribution function of vapor on the outer boundary of the Knudsen layer. In [11], the process of supercondensation at a small temperature difference was studied. The distribution function was obtained as a result of approximate solution of the stationary Boltzmann equation. In zero approximation, the dependence of the distribution on the velocity of vapor motion was taken into account. In [12], the problem of vapor supercondensation was considered from the viewpoint of modern kinetic theory by solving the Boltzmann equation in a correct problem formulation. The conditions of origination of a reverse temperature profile on the phase interface are found for the mode of continuous medium motion. At present, development of the methods of solution of the kinetic Boltzmann equation allowed one to study the problem of stationary evaporation or condensation rather thoroughly. A review of the state-of-the-art of the problem can be found, e.g., in [13].

At present, the processes of nonstationary evaporation or condensation, where a value of molecular flow of evaporating substance is the function of time, have been studied relatively unadequately. In this case, according to the Le Chatelier–Brown principle, a sharp change in a value of evaporating-substance flow must cause such changes in the system, which could lead to compensation of this change [14,15].

The effect of the dynamics of variation of a value of evaporating-substance flow on evaporation rate can also be obtained in hydrodynamic approximation. As is seen from the Hertz–Knudsen formula, a value of pressure above the surface of the Knudsen layer is not constant but depends on the hydrodynamic conditions of vapor flow and must be found from the Navier–Stokes equations

$$\frac{\partial u}{\partial t}+u\frac{\partial u}{\partial x}=-\frac{1}{\rho}\frac{\partial P}{\partial x}+v\frac{\partial^2 u}{\partial x^2}. \tag{2}$$

Having integrated Eq. (2) for x and having used the theorem of the mean, we obtain the expression for pressure above the surface of the Knudsen layer

$$P(t)=P_0-\rho l_{\text{ef}}\frac{\partial u}{\partial t}-\frac{\rho}{2}u^2+\mu\frac{\partial u}{\partial x}. \tag{3}$$

Having substituted expression (3) to the Hertz–Knudsen formula, we finally obtain

$$J(t)=\frac{P_S-P_\infty-\rho l_{\text{ef}}\frac{\partial u}{\partial t}-\frac{\rho}{2}u^2+\mu\frac{\partial u}{\partial x}}{\sqrt{2\pi mkT}}. \tag{4}$$

It should be noted that the term of the form $\rho l_{\text{ef}}(\partial u/\partial t)$ in expression (4) determines inertial properties of vapor flow, $(\rho/2)u^2$ is the dependence of the rate of vaporization on the kinetic energy of flow, and $\mu(\partial u/\partial x)$ is the effect of viscous friction, which, in turn, depends on the specific configuration of the system of vapor removal, the presence of contradictions or expansions in the channel, curvilinear portions, steps, etc.

The problem of nonstationary evaporation of condensed substance to vacuum is solved numerically in [16] on the basis of the uniform model Boltzmann equation. The authors have analyzed the process of transition from a free-molecular mode of vapor expansion at the initial stage of evaporation to the model of continuous medium motion. As a result of numerical solution of the kinetic equation, time dependences for temperature, density of flow of evaporating substance and vapor density were obtained. It is interesting to note a wave-like character of temperature variation that is caused by relaxation phenomena in setting of a badward molecular flow. Collisions of atoms in the gas phase bad to appearance of the backward molecular flow and decrease of "pure" evaporation rate. As is shown in [16], time, during which backward flow is stabilized, is of about 20 times of free motion and this time can conventionally be taken the time of establishment of a hydrodynamic mode of vapor motion, although in act this mode cannot be reached within the Knudsen layer. The authors also showed that in pulse heating the conditions, at which the hydrodynamic mode cannot be reached at all, can be implemented.

Thus, detailed investigation of the dependence of evaporation rate on thermodynamic parameters of the system in the case of a nonstationary process is of great scientific interest. The present paper is aimed at theoretical and experimental study of the process of nonstationary evaporation in the system liquid-saturated vapor in the case of sharp changes of one or several thermodynamic parameters of the system.

2. Phenomenological description of substance evaporation in the thermodynamics of irreversible processes

In the thermodynamics of irreversible processes it is adopted to use linear phenomenological laws [14,15] which close to equilibrium can be written as

$$J_i = \sum_j L_{ij} \frac{\partial \phi}{\partial \alpha_j}, \tag{5}$$

where $J_i = \partial\alpha_i/\partial t$ is the generalized velocity and $\partial\phi/\partial\alpha_j = X_j$ is the generalized force. In the case of two phases characterized by the parameters α_1 and α_2 which are related by

$$\alpha = \frac{\alpha_1}{\alpha_1+\alpha_2}, \quad 1-\alpha = \frac{\alpha_2}{\alpha_1+\alpha_2}, \quad \alpha_1+\alpha_2 = 1,$$

the thermodynamic potential of the system can be written in the form

$$\phi = \phi_1\alpha + \phi_2(1-\alpha). \tag{6}$$

It follows from Eqs. (5) and (6)

$$J = L(\phi_1 - \phi_2). \tag{7}$$

In the case of the evaporation process, expression (4) is the Hertz–Knudsen formula for the evaporation rate. Assuming L to be equal to $\beta v/4$, we obtain

$$J = \beta\frac{v}{4}(n_S - n), \tag{8}$$

where $v = \sqrt{8kT/\pi m}$.

Expression (5) is the expansion into series of the functional dependence of flow on the generalized thermodynamic force, where only the first order is taken into account. In [17] it is shown that for the case of highly intense transition processes in the expression for generalized flow a great number of expansion terms must be taken into account

$$J_i = L_i^\tau \frac{\partial J_i}{\partial t} + \sum_k \left(L_{ik}X_k + L_{ik}^\tau \frac{\partial X_k}{\partial t} \right). \tag{9}$$

Expression (9) can also be obtained on the basis of the Le Chatelier–Brawn principles. According to the given principle, in the case of sharp variation of a value of flow, an induction gradient of the corresponding thermodynamic parameter impeding this variation must originate in the system

$$\frac{\mathrm{d}J_i}{\mathrm{d}t} = -\sum_j L_{ij}^{**}\left(\frac{\partial\phi}{\partial\alpha_j}\right)_{\text{ind}}. \tag{10}$$

Combining (5) and (10), we obtain (7).

Thus, for a two-phase system in the case of highly intense processes expression (7) takes on the form

$$J = L_J\frac{\mathrm{d}J}{\mathrm{d}t} + L(\phi_1-\phi_2) + L_\phi\frac{\mathrm{d}}{\mathrm{d}t}(\phi_1-\phi_2). \tag{11}$$

For nonstationary evaporation, expression (8) with account for (9) and (11) can be

$$J = \tau_v\frac{\partial J}{\partial t} + \beta\frac{V}{4}(n_S-n) + \tau_P\beta\frac{V}{4}\frac{\partial(n_S-n)}{\partial t}, \tag{12}$$

where

$$\tau_v = \frac{\beta l_{\text{ef}}}{v};$$

or assuming that vapor obeys the law of state of an ideal gas and using an explicit expression for a logarithmic-mean velocity of motion of molecules, we obtain

$$J = \tau_v\frac{\partial J}{\partial t} + \frac{\beta}{\sqrt{2\pi mkT}}(P_S-P) + \tau_P\frac{\beta}{\sqrt{2\pi mkT}}\frac{\partial(P_S-P)}{\partial t}. \tag{13}$$

The first and third terms in formulas (12) and (13) reflect inertial properties of a molecular flow of evaporating substance which impede, according to the Le Chatelier–Brown principle, instantaneous change of flow with variation of thermodynamic parameters of the system. It should be noted that a similar expression for vaporization rate under nonstationary conditions can be obtained from hydrodynamic considerations, having substituted to expression (4) the relation $J(t) = nu$ which relates vaporization rate $J(t)$ and hydrodynamic velocity of vapor motion u

$$J(t) = \frac{P_S - P_\infty - \frac{\rho l_{\text{ef}}}{n}\frac{\partial J}{\partial t} - \frac{\rho}{2n}J^2 + \frac{\mu}{n}\frac{\partial J}{\partial x}}{\sqrt{2\pi mkT}}. \tag{14}$$

3. Molecular-kinetic description of the process of nonstationary evaporation of the condensed phase

We consider the density of the flow of vapor molecules directly at the liquid surface as a difference of two molecular flows: descended by the liquid and absorbed by the phase interface from the surrounding vapor

$$j(t) = \int_{-\infty}^{+\infty} \mathrm{d}\xi_y \int_{-\infty}^{+\infty} \mathrm{d}\xi_z \int_0^{+\infty} \xi_x f(r_S, \vec{\xi}, t)\, \mathrm{d}\xi_x - \int_{-\infty}^{+\infty} \mathrm{d}\xi_y \int_{-\infty}^{+\infty} \mathrm{d}\xi_z \int_{-\infty}^{0} \xi_x f(\delta, \vec{\xi}, t)\, \mathrm{d}\xi_x. \tag{15}$$

We assume that vapor above the liquid surface is ideal and that molecules emitted by the liquid have the Maxwellian distribution with a temperature T_S and pressure P_S. In this case, the density of the molecular flow emitted by the phase interface is determined by the expression

$$j_S = P_S/\sqrt{2\pi mkT_S}, \tag{16}$$

which is obtained as a result of integration of the first term of Eq. (15) with the Maxwellian distribution function. In the case of evaporation to vacuum, it coincides with the Hertz–Knudsen formula. To calculate the second term of Eq. (15), which characterizes the density of flow of molecules reflected back to the phase interface, it is necessary, in a general case, to solve the kinetic equation in order to determine the nonequilibrium distribution function. If for determination of the distribution function on the outer boundary of the Knudsen layer we restrict ourselves to consideration of only binary collisions of molecules in vapor, we can use the kinetic Boltzmann equation in the absence of external forces

$$\frac{\partial f}{\partial t} + \vec{\xi}\frac{\partial f}{\partial \vec{x}} = \frac{1}{m}J_c. \tag{17}$$

We use an approximate solution of Eq. (17) obtained in [21]. We expand the distribution function into a series in terms of the Hermit polynomials

$$f = f^{(0)} \sum_{n=0}^{\infty} \frac{1}{n!} a_i^{(n)} H_i^{(n)}, \tag{18}$$

where $f^{(0)}$ is the function of the Maxwell distribution. As a result of substitution of (18) into Eq. (17) we obtain an infinite system of differential equations. Restricting ourselves to first three terms of (18) and assuming all the rest coefficients $a_i^{(n)}$ to be zero, we come to the distribution function in the so-called 13-moment approximation [21]

$$f = f^{(0)} \sum_{i,j} \left\{ 1 + \frac{p_{ij}}{2pRT} C_i C_j - \frac{q_i}{RT} C_i \left(1 - \frac{C^2}{\xi RT} \right) \right\}, \tag{19}$$

where $C_i = \xi_i - u_i$, $q_i = m \int C_i C^2 f\, \mathrm{d}u_i$.

Thus, the state of the system is described by the ρ, T, u_i, p_{ij}, and q_i which obey the system of differential equation of conservation of mass, momentum, pulse, and energy and also the equations for the tensor of viscous stresses and heat flux. As a result of substitution (19) to the second term of (15) we obtain

$$j = 2\left(\frac{P_S}{\sqrt{2\pi mkT_S}} - \frac{P(\delta, t) + m\delta \frac{\partial j}{\partial t}}{\sqrt{2\pi mkTt(\delta, t)}} \right). \tag{20}$$

In the kinetic theory, the equation of dynamic balance of molecular flows on phase, interface can be obtained from the Enskog general equation [20], which, with account for disappears of collision integrals for total invariants, can be written as

$$\frac{\partial n_i}{\partial t} + \left(\frac{\partial}{\partial \vec{r}_i} \cdot n_i \vec{v}_i \right) = 0. \tag{21}$$

where r_i, v_i, and n_i are the radius vector, velocity, and density of the number of the ith-kind molecules.

In the case of an isotropic space, the quantity

$$\sum_i n_i \vec{v}_i = 0$$

and Eq. (21) is reduced to the discontinuity equation of the gas mixture. However, in the presence of the phase interface integration of Eq. (21) with respect to the coordinate normal to the evaporation surface, allows obtaining of the equation of the dynamic balance of molecular flows. In the stationary case, integration bads to the Hertz–Knudsen relation and in a nonstationary case we obtain a more complex expression which allows for induction properties of evaporating-substance flow

$$J(t) = \beta u(n_S - n) + \beta \frac{\partial n}{\partial t} l.$$

Taking the expression relating the rate of vapor generation $J(t)$ and the hydrodynamic velocity of vapor motion u into account, we obtain

$$J(t) = \beta u(n_S - n) + \frac{\partial J}{\partial t}\frac{\beta l}{u}.$$

The dynamics of pressure change in the closed volume under nonstationary evaporation. The character of pressure changes in evaporation in the closed volume in the case when the value of this pressure is smaller than the pressure of saturated vapor at the set temperature has been studied, probably, for the first time in [18,19]. The relation between an increase of pressure and the rate of evaporation can be obtained assuming that vapor pressure in the volume levels out instantly (i.e., pressure is the same over the whole volume). The concentration of vapor molecules in the volume in evaporation is the function of time and can be presented in the form

$$n(t) = n_0 + S\int j\,\mathrm{d}t, \tag{22}$$

where S is the surface of the evaporation surface. Taking the system to be thermostated and differentiating the equation of state of the ideal gas by time, we obtain

$$\frac{\mathrm{d}p}{\mathrm{d}t} = \frac{\beta S}{V}(P_S - P)\left(\frac{kT}{2\pi m}\right)^{1/2}. \tag{23}$$

The authors of [18] used the integral presentation of (23)

$$\ln(P_S - P) = -\frac{\beta S}{V}\left(\frac{kT}{2\pi m}\right)^{1/2} t + \text{const}. \tag{24}$$

Relations (23) and (24) were checked experimentally and hold with sufficient accuracy in the case of slow processes, when the density of evaporating-substance flow j changes smoothly and monotonously

$$\left|\tau_v \frac{\partial j}{\partial t}\right| \ll 1. \tag{25}$$

When the rate of the change of the evaporating-substance density is rather high, the inertial term is (13) must be allowed for in the system of thermodynamic equations describing the process.

We consider the process of liquid evaporation caused by constant heat supply to the system. The amount of vapor formed per time unit from the unit surface can be calculated in this case from the equation of energy conservation

$$Jm = \frac{P_Q V}{hS}. \tag{26}$$

In this case, expression (14) for estimation of the degree of the effect of inertial properties of the system on the process of nonstationary evaporation can be written as

$$\left(\frac{P_Q k T \tau_v}{hm(P_S - P)}\right)^{1/2} < 1. \tag{27}$$

The last term in Eq. (13) described the change in rate of evaporation caused by relaxation of local pressure, this can be neglected since this process occurs at the velocity close to the velocity of sound. Assuming that vapor obeys the equation of state for an ideal gas and using (13) we can obtain equation describing the dynamics of change of pressure in the system in nonstationary evaporation

$$\frac{\tau_v V}{SkT}\frac{\mathrm{d}^2 P}{\mathrm{d}t^2} + \frac{V}{SkT}\frac{\mathrm{d}P}{\mathrm{d}t} + \frac{\beta}{\sqrt{2\pi mkT}}(P_S - P) = 0. \tag{28}$$

Solution of Eq. (28) can be obtained in the form

$$P_S - P = P_{\max}\exp\left(-\frac{t}{2\tau_v}\right)\cos\left(\left[\frac{\beta SkT}{V\tau_v\sqrt{2\pi mkT}}\right]^{1/2} t\right), \tag{29}$$

where a maximum amplitude of pressure $P_{\max}$ can be found from (26)

$$P_{\max} = \frac{P_Q V\sqrt{2\pi mkT}}{\beta hSm}.$$

Expression (29) describes the change of pressure in the case of sudden interruption of heat supply in the system. A typical curve of $P_S - P$ dependence on time is shown in Fig. 1.

An amount of vapor formed in the system from the instant of termination of heat supply can be calculated by the formula

$$\Delta G(t) = \frac{P_Q V}{hSm}\exp\left(-\frac{t}{2\tau_v}\right)\cos\left(\left[\frac{\beta SkT}{V\tau_v\sqrt{2\pi mkT}}\right]^{1/2} t\right). \tag{30}$$

Making use of the quantity

$$\tau_r = \frac{V}{\beta S v},$$

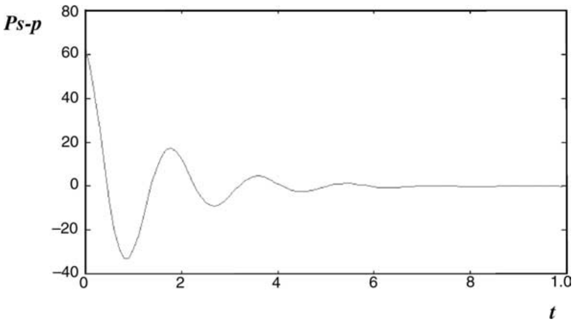

Fig. 1. Typical graph of the dependence of pressure variation on time for the case of sudden termination of heat supply to the system.

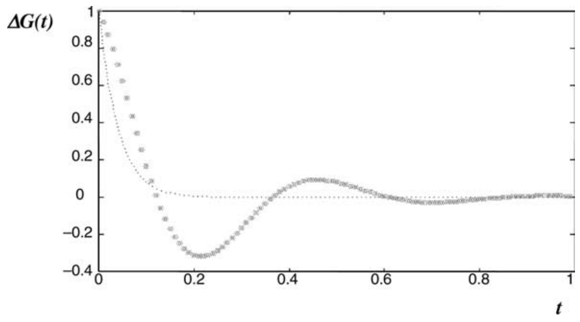

Fig. 2. Dependence of dimensionless value of additional vaporization on time in the case of sudden termination of heat supply to the system.

as a characteristic scale of time measurement and the quantity

$$\Delta G_r = \frac{P_Q V}{hSm}\tau_r,$$

as the scale of measurement of vapor amount, we can write Eq. (30) in a dimensions form

$$\Delta G(t) = \frac{1}{\tau_r}\exp\left(-\frac{t}{2\tau_v}\right)\cos\left(\left[\frac{1}{4\tau_v\tau_r}\right]^{1/2}t\right). \tag{31}$$

The time-dependence of the dimensionless value of additional vaporization caused by sudden termination of heat supply to the system is given in Fig. 2 (for comparison, the graph of the dimensionless value of additional vaporization, calculated by the Hertz–Knudsen formula, is shown by the dashed line [18]).

4. Experimental techniques and equipment

The object studied in this experiment is the hermetically closed cuvette with optical windows, a branch tube for vapor evacuation, and a heating element. vapor pressure in the cuvette was measured by a piesoceramic gauge connected to the charge-sensitive amplifier and the oscillograph. Several copper-constantan thermocouples for measuring liquid temperature near the phase interface and vapor temperature were mounted in the cuvette. The liquid in the cuvette can be heated either by a heater or due to volumetric liberation of Joule heat in electrolysis. Two types of experiments were conducted on the experimental setup: (1) study of relaxation of thermodynamic parameters of vapor in the cuvette with a sharp decrease of vapor pressure above the phase interface and (2) relaxation of thermodynamic parameters of vapor with a sharp change of liquid temperature due to pulsed heating. The experiments were conducted mainly with degassed distilled water.

5. Measurement results and discussion

Fig. 3 gives a typical graph of pressure relaxation in the cuvette with a sharp decrease of vapor pressure over the liquid surface due to fast evacuation of the cuvette. As is seen from the graph, the process has a self-oscillatory character.

With a certain error, the experimental curve in Fig. 3 can be approximated by dependence (29). Although the observed pressure fluctuations are obviously anharmonic, from this graph we can also find

$$\left[\frac{\beta SkT}{V\tau_v\sqrt{2\pi mkT}}\right]^{1/2} = 2\pi; \quad \frac{1}{2\tau_v} = 5; \tag{32}$$

hence $\tau_v \sim 0.1$ and $\tau_r \sim 0.01$. The anharmonic character of pressure fluctuations is caused by different mechanisms of heat transfer in the system: (1) with an increase of vaporization flow, heat absorption in phase transition occurs due to liquid cooling; (2) with a decrease of vaporization flow, there take place partial condensation of vapor, liberation of hear in condensate microparticles, and subsequent transfer of it to the gas phase. At the same time, the quantity τ_v for water in the case of surface evaporation can be estimated from the molecular-kinetic theory. If we consider density of the flow of vapor molecules directly at the liquid surface as a difference of two molecular flows (emitted by the liquid and absorbed by the phase interface from the surrounding vapor) and use a nonstationary distribution function, which was obtained in 13-moment approximation of the solution of the kinetic Boltzmann equa-

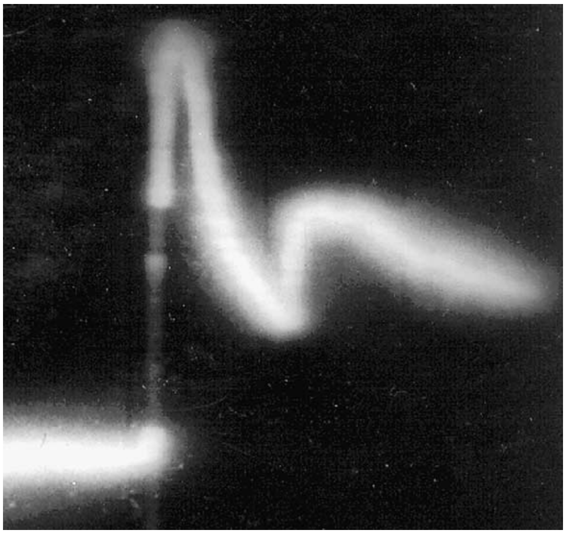

Fig. 3. Oscillogram of pressure relaxation in a thermostated volume with a sharp decrease of vapor pressure above the liquid surface due to fast evacuation of the cuvette.

tion, for calculation of density of a molecule flow, we can obtain

$$\tau_v = \frac{2\beta m\delta}{(2-\beta)\sqrt{2\pi mkT}}, \quad \tau_r = \frac{V}{\beta S}\sqrt{\frac{\pi m}{8kT}},$$

where δ is the thickness of the Knudsen layer above the phase interface. From the physical point of view, the presence of inertial properties of vaporization is associated with additional energy consumption in accelerated passage of molecules through the Knudsen layer.

Evaluation for distilled water under normal conditions gives $\tau_v \sim 0.005$ and $\tau_r \sim 0.01$. An excess of the experimental value in comparison with the theoretical estimation indicates that substantial contribution to the inertial parameter τ_v is associated with a change in the liquid evaporation of surface in boiling-up and, consequently, with the kinetics of formation and growth of vapor bubbles, and also with motion of liquid masses caused by the growth of these bubbles.

6. Conclusions

Use of the method of the thermodynamics of irreversible processes in the phenomenological analysis of nonstationary evaporation and the results of experimental study of pressure relaxation in thermostated volume with a sharp change in the vaporization flow indicate considerable effect of inertial properties of the thermodynamic system in the dynamics of development of a nonstationary process. In calculation of nonstationary modes of operation of fuel-power equipment one should allow such phenomena as additional vaporization and inductive pressure drop with a sharp change in the vaporization flow.

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