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BOUNDARY CONDITIONS FOR GAS-DYNAMICAL MODELING OF EVAPORATION PROCESSES

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Summary. The features of gas-dynamic jump at the evaporation front are considered. Comparative analysis of different models of boundary conditions needed to describe the process of evaporation of condensed matter under the influence of intense flow of energy within the continuum mechanics is performed.

1 INTRODUCTION

Investigation of evaporation process began in the nineteenth century [1], [2] and continues to this day [3-26]. This happens due to practical importance of evaporation and not fully clarified features of the non-equilibrium behavior of matter when it evaporates.

Intense surface evaporation is essentially non-equilibrium process. In addition to the thermodynamic non-equilibrium, this process also has a gas-kinetic non-equilibrium in a thin (Knudsen) layer of vapor, directly adjacent to the interface. Gas-kinetic non-equilibrium is due to the flow of material through the phase boundary. The mass flow rate increases as the rate of evaporation grows and, consequently, the degree of non-equilibrium of the process increases as well. From physical considerations, the maximum velocity of the material flux at the outer side of the Knudsen layer is limited by the local speed of sound $u \leq u_{sound} = (\gamma RT_v)^{1/2}$, $M = u / u_{sound} \leq 1$, where u – is the gas-dynamic velocity, M – is the Mach number. The maximum value of non-equilibrium is determined by the maximum value of the mass flux which, as it is known, is reached at $M = 1$.

Under the conditions of phase equilibrium, when the vapor pressure p_{sat} is equal to external pressure, the flow of vaporized material is balanced by the return flow of particles, and total mass flux through the boundary is zero. The velocity distribution of vapor particles is equilibrium and can be described by the Maxwell function with zero average velocity. In cases where the vapor pressure above the surface is less than the saturated vapor pressure p_{sat} , directed movement is formed with $u > 0$ in the system of condensed medium and vapor, where non-zero material flow moves over the phase boundary. At the same time, the decreasing reverse flow results in the deviation of the particle distribution from the equilibrium. With the increase of the rate of evaporation, the flux of returning particles

decreases and the distribution function at the evaporation surface becomes increasingly different from the Maxwell one.

In general, the non-equilibrium distribution function is found by solving the Boltzmann equation in a region with a characteristic size of a few mean free paths. This region is adjacent to the evaporation surface, at which the kinetic boundary conditions are set, taking into account the interaction of individual particles with the interface. Similar problem was solved by various methods in many studies, taking into account, in particular, the difference from unity and variability of the coefficient of condensation, which determines the probability of attachment of the particle in its collision with the evaporation surface. (see, for example. [3 - 7]).

The methods of nonequilibrium thermodynamics and other approximate phenomenological approaches [8 - 13] are also used to describe the evaporation process. A more general and fundamental approach is to use the method of molecular dynamics, which was used in [14, 15] to analyze the evaporation process. A recent review on the issue of non-equilibrium boundary conditions at the liquid - vapor interface is given in [16].

In this paper we consider such forms of boundary conditions at the evaporation jump, which can be obtained based on different assumptions about the form of non-equilibrium function of surface evaporation. Additional attention is paid to the peculiarities of the behavior of the flows of mass, momentum and energy as the Mach number tends to unity, which allows to use the requirement of the extremum of the total mass flux j_m , momentum j_i and energy j_e at $M = 1$ as one of the criteria.

2 THE SIMPLEST MODEL OF KINETICS OF EVAPORATION IN VACUUM

The driving force of the phase transformations of the 1st type is determined by the difference of the Gibbs energies (or value of overheating/overcooling ΔT) for the two phases at the interface, and can be written in two forms [17]

$$\Delta G = \Delta \varepsilon + p_{eq} \Delta V - T_{eq} \Delta S \quad (1)$$

$$\Delta G = V \Delta p - S \Delta T \quad (2)$$

where $\Delta p = p - p_{eq}$, $\Delta T = T - T_{eq}$, $\Delta \varepsilon = \varepsilon_1 - \varepsilon_2$, $\Delta V = V_1 - V_2$, $\Delta S = S_1 - S_2$

From the thermodynamic relation (2) it follows, that at the constant temperature, the difference of the Gibbs energy between the two phases (one of which is ideal gas) is linearly proportional to the pressure difference:

$$\Delta G = V \Delta p = k_B T \frac{\Delta p}{p} \quad (3)$$

Based on the formula (3), one can suggest that the rate of the phase transformation at the constant temperature must be linearly proportional to the pressure difference:

$$\nu = \nu_0 \frac{\Delta p}{p}, \quad (4)$$

where ν_0 - is some typical constant.

The simplest model for the vapor phase mass flux was developed by Hertz [2] and Knudsen [3] about 100 years ago. Its formulation is qualitatively the same as the thermodynamic model (3), (4)

$$j_m = j_m^+ - j_m^- = \frac{1}{\sqrt{2\pi m k_B}} \left(\frac{p_{sat}}{\sqrt{T_{sur}}} - \frac{p}{\sqrt{T}} \right) = \frac{\Delta p}{\sqrt{2\pi m k_B T}} \quad (5)$$

where $\Delta p = \sqrt{\frac{T}{T_{sur}}} p_{sat} - p$ j_m^- - is the non-equilibrium flux of atoms at the evaporation surface;

j_m^- - is the flux of atoms under the assumption that they collide with the surface with mass accommodation coefficient of 1. One may try to determine this flux using the relation connecting the vapor pressure in equilibrium with the particle flux directed to the condensed surface: $p = \sqrt{2\pi m \nu} j_m^-$, where ν - is the mean velocity in one direction, $\nu = \sqrt{\frac{2k_B T}{m}}$, so that

we obtain $j_m^- = \frac{p}{\sqrt{2\pi m k_B T}}$. Since the nature of the flux $j_m^{(-)}$ remains undefined and the value of T and correspondingly p unknown, then, when formulating the boundary conditions in the problem of evaporation into vacuum, it is suggested [20, p.281] to determine the velocity of evaporation using the single-term form of the Hertz- Knudsen formula:

$$j_m \approx j_m^+ = \frac{p_{sat}}{\sqrt{2\pi m k_B T_{sur}}}, \quad (6)$$

where p_{sat} depends on the surface temperature T_{sur} . This expression follows from integration of equilibrium distribution function over the velocity of particles flying off the surface.

However, the representation of the process of surface evaporation in the form of the simplest model, which does not take into account the reverse flow of evaporated atoms, does not remove the internal contradictions inherent in the model of Hertz - Knudsen. If the corresponding expressions for the flux of momentum $j_i^{(+)}$ and energy $j_e^{(+)}$ of the particles, moving away from the evaporation surface are used together with (6), and expressions for equilibrium fluxes containing supposed vapor velocity, temperature and density form three equations for equilibrium vapor flow parameters, where $p_v = \rho_v R T_v$, ρ_v , T_v , u - are the pressure, density, temperature and gas-dynamic velocity of gas, R - is the gas constant,

$$\rho_{sat} \langle V_z^2 \rangle = j_i^{(+)} = \frac{p_{sat}}{2} = \frac{1}{2} (\rho_{sat} R T_{sat}) = \rho_v R T_v + \rho_v u^2$$

$$\rho_{sat} \langle V^2 V_z \rangle = j_e^{(+)} = 2 p_{sat} \left(\frac{R T_{sur}}{2\pi m} \right)^{1/2} = 2 \rho_{sat} R T_{sur} \left(\frac{R T_{sur}}{2\pi m} \right)^{1/2} = \rho_v u \left(\frac{u^2}{2} + C_p T_v \right),$$

then one can see that the system of equations has two distinct complex solutions, which have no physical meaning. In other words it means that these three fluxes have no equilibrium counterparts.

Two solutions with real values of the thermodynamic parameters are associated with the possibility of discontinuous solutions of the type of shock wave, while complexity of the solution in this case is caused by thermodynamic non-equilibrium of the Hertz-Knudsen evaporation flow, which can not be described in terms of thermodynamic concepts. When taking into account the collisions in the non-equilibrium layer, the evaporative flux is thermalized, but the temperature on the outer side of this layer no longer coincides with the surface temperature.

3 APPROXIMATION OF THE KNUDSEN LAYER

For the equations of continuum mechanics, thin Knudsen layer is a gas-dynamic discontinuity (jump). Knowledge of the relations at this jump, connecting the parameters of the condensed medium and the evaporated material, is needed to deal with the full gas-hydrodynamic problem that arises, for example, during the description of laser ablation, taking into account the variability of the Mach number because of the spatial - temporal instability of a plane evaporation front [18] or in case of modulations of laser intensity [26]. The features of the behavior of the flow of vaporized material at values of M close to unity are important in such cases.

3.1 The basic models

The use of kinetic approaches which explicitly consider the structure of the Knudsen layer in such cases is difficult because of the emerging problem of significant difference of space-time scales. The solution of these problems is associated with the additional computational difficulties and is not always possible. Therefore, another common approach is used that allows to determine the boundary conditions with certain assumptions about the form of the non-equilibrium distribution function inside the jump [19] - [22] without solving the kinetic problem. The approximation of the distribution function in the Knudsen layer was carried out by different models. But to obtain physically reasonable boundary conditions, it is necessary to formulate the criteria which these conditions must meet. As one of the criteria, you can use the requirement of extremum of the full flows of mass j_m , momentum j_i and energy j_e at $M = 1$.

" β^n " - model. In the " β^n " - model [23, 24], one-dimensional non-equilibrium particle flow at the inner side of the flat Knudsen layer is described using the composite distribution function $f = f^{(+)} + f^{(-)}$, where the distribution $f^{(+)}$ for particles flying out from the surface is given by a Maxwell function $f^{(+)} = f(\rho_{sat}, T_{sur}, 0)$ with the density of saturated vapor ρ_{sat} at the surface temperature T_{sur} . The distribution $f^{(-)}$ characterizes the flow of particles returning to the surface and is supposed to be proportional to the "shifted" Maxwell function $f^{(-)} = f(\rho_v, T_v, u)$ with density ρ_v , temperature T_v and mean velocity u of the steady state flow of vapor at the outer side of the Knudsen layer:

$$f^{(+)} = f(\rho_{sat}, T_{sur}, 0), \quad V_z > 0$$

$$f^{(-)} = f(\rho_v, T_v, u) = \beta \left(\frac{m}{2\pi k_B T_v} \right)^{3/2} \exp \left(- \frac{V_x^2 + V_y^2 + (V_z - u)^2}{2k_B T_v} \right) \quad V_z < 0$$

The calculated flows of mass, momentum and energy $j_k = j_k^{(+)} + j_k^{(-)}$; $k = m, i, e$, using $f^{(+)}, f^{(-)}$ must be equal to their gas-dynamic values j_k , determined by the function f :

$$\begin{aligned} \rho \langle V_z \rangle &= j_m^{(+)} + j_m^{(-)} = j_m = \rho_v u \\ \rho \langle V_z^2 \rangle &= j_i^{(+)} + j_i^{(-)} = j_i = \rho_v R T_v + \rho_v u^2 \\ \rho \langle V^2 V_z \rangle &= j_e^{(+)} + j_e^{(-)} = j_e = \rho_v u \left(\frac{u^2}{2} + C_p T_v \right), \end{aligned} \quad (7)$$

where $C_p = \frac{\gamma}{\gamma+1} k_B$ - is the heat capacity of the gas at constant pressure per particle, for single-atom gas $\gamma = \frac{5}{3}$. From the solution of the equations (7) one can obtain the gas-dynamic conditions at the break that allow to determine the values of ρ_v, T_v and β , via ρ_{sat}, T_{sur} and M . The calculations showed, that full fluxes j_m, j_i, j_e have extremum depending on M at $M = 0.88, 1.18$ and 1.22 accordingly.

Thus, the requirement of extremum of all fluxes in the selected point $M = 1$ in the model [23, 24] is not met, that can serve as evidence of an unfortunate choice of the distribution function $f^{(-)}$.

" $\varepsilon - \delta$ " - **model**. Limitations of the " β " - model can be eliminated by selection of more general form of the distribution function for the reverse flux of particles $f^{(-)}$ [25]:

$$f^{(-)} = \beta f + \alpha f_1 \quad \alpha + \beta = 1$$

All 3 fluxes j_k can have extremum at $M = 1$, if the function f_1 is set equal to $f_1 = f(\rho_1, T_1, u_1)$, where the values of ρ_1, T_1, u_1 by means of additional adjustable parameters ε and δ are written in terms of $\rho_{sat}, T_{sur}, \rho_v, T_v$ and

$$\begin{aligned} \rho_1, T_1^{1/2} &= \varepsilon \rho_{sat} T_{sur}^{1/2} + (1 - \varepsilon) \rho_v T_v^{1/2}, \\ \rho_1, T_1^{1/2} &= \varepsilon T_{sur}^{1/2} + (1 - \varepsilon) T_v^{1/2}, \\ u_1 &= \delta M (\gamma R T_1)^{1/2} = \delta (T_1 / T_v)^{1/2} u. \end{aligned}$$

For example, for $\varepsilon = 0.70$ and $\delta = 0.32$ all three fluxes j_k can have extremum at $M = 1$ with values $j_m = 0.853, j_i = 0.557, j_e = 0.892$. This option in the choice of fitting coefficients, of course, is not the only one.

" α " - **model**. You can propose another phenomenological model [25], in which a strict localization of the extrema $j_k(M = 1)$ is achieved without the use of adjustable coefficients for these distribution functions $f^{(-)}$, that do not depend on the gas-dynamic values. An example of such function is the function

$$f^{(-)} = \alpha^7 f_0(\rho_{sat}, \alpha^2 T_{sur}),$$

which takes into account the decrease of temperature $T_\alpha = \alpha^2 T_{sur}$ of the reverse particle flux relative to the surface temperature T_{sur} . Due to this change of T_α , the relation of the normalized fluxes j_e/j_m ceases to be constant and takes the form $(1-\alpha^8)(1-\alpha^{10})$, which gives correct limiting value of 1.25 in the equilibrium case for $\alpha=1$. The equation for α , that is obtained from the equity of fluxes (7), has relatively simple form:

$$\frac{(1-\alpha^8)(1-\alpha^{10})}{(1-\alpha^9)^2} = \frac{\pi \gamma^2 M^2 [(\gamma-1)M^2 + 2]}{8 (\gamma-1)(1+\gamma M^2)^2} \quad (8)$$

The right-hand side of equation (8) has maximum at $M=1$, that determines localization of extrema of α and j_k . The values of $j_k(M=1)$ are equal correspondingly to $j_m = 0.85, j_i = 0.56, j_e = 0.90$.

Modified model of Crout. The property of localization of the fluxes $j_k(M=1)$ also belongs to the model that was suggested by D. Crout [19]. It uses non-equilibrium function of particle distribution, written in analytical form with temperature that is anisotropic by direction T_L and T_T .

$$f(\rho, T_L, T_T, u, v, w) = \left\{ \rho \left[\frac{\pi^3}{h_T m^3} (2k_B T_L) \cdot (2k_B T_T) \right]^{1/2} \cdot \exp \left[-m \left(\frac{(u-u_0)^2}{2k_B T_L} + \frac{v^2}{2k_B T_T} + \frac{w^2}{2k_B T_T} \right) \right] \right\}$$

where T_L - is the lateral temperature along x axis, T_T - transverse temperature along the y axis, z; u, v, w - are components of the velocity vector along corresponding axes x, y, z , u_0 - is the drift velocity.

M	"β"-model (Knight)		"ε-δ"-model		"α"-model		Crout model	
	T	N	T	n	T	n	T	N
0.0	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
0.1	0.960	0.861	0.958	0.864	0.960	0.869	0.953	0.861
0.2	0.922	0.748	0.916	0.753	0.920	0.758	0.910	0.749
0.3	0.866	0.654	0.876	0.662	0.881	0.666	0.870	0.658
0.4	0.851	0.576	0.837	0.587	0.844	0.588	0.833	0.582
0.5	0.817	0.511	0.799	0.525	0.808	0.524	0.798	0.519
0.6	0.785	0.457	0.763	0.472	0.773	0.470	0.763	0.466
0.7	0.754	0.410	0.727	0.428	0.740	0.424	0.730	0.421
0.8	0.724	0.371	0.693	0.391	0.705	0.386	0.697	0.384
0.9	0.696	0.337	0.660	0.360	0.672	0.355	0.665	0.352
1.0	0.669	0.308	0.628	0.333	0.640	0.328	0.633	0.326

Table 1.

The modification of the Crout model consists of explicit introduction of the Mach number into the main relations and allows to obtain:

$$T_v = \alpha_T(M) T_{sur}, \quad \rho_v = \alpha_\rho(M) \rho_{sat}, \quad (9)$$

$$\alpha_T(M) = \frac{2\gamma M^2 (m^2 + 0.5)^2}{(1 + \gamma M^2)^2 m^2 t^2},$$

$$\alpha_{\rho}(M) = \frac{1}{\exp(-m^2) + \pi^{1/2} m (1 + \operatorname{erf}(m))} \cdot \frac{(1 + \gamma M^2) m^2}{\gamma M^2 (m^2 + 0.5)^2}$$

The value of m is determined from the non-linear relation

$$\text{where } F(M) = 1 + \frac{F(M)(m^2 + 0.5)^2 - m^2(m^2 + a + 1.5)}{(\gamma M^2 - 1)^2}, \quad a = 2t^2 - 0.5\pi^{1/2} m t - 1, \quad (10)$$

$$t = \frac{2m}{\pi^{1/2}} + \frac{1 + \operatorname{erf}(m)}{\exp(-m^2) + \pi^{1/2} m (1 + \operatorname{erf}(m))}, \quad \operatorname{erf}(m) = \frac{2}{\sqrt{\pi}} \int_0^m e^{-y^2} dy.$$

$$\text{At } M=1: \quad T_v = 0,633 T_{sur}, \quad \rho_v = 0,328 \rho_{sat}, \quad p_v = 0,208 p_{sat},$$

$$M=0: \quad T_v = T_{sur}, \quad \rho_v = \rho_{sat}, \quad p_v = p_{sat}$$

Numerical solution of the equation (10) can be achieved by the Newton iterative procedure. All fluxes j_m, j_i, j_e have extremum at the point of $M=1$. Calculations using an anisotropic non-equilibrium particle distribution function give the corresponding extreme values of the fluxes: $j_m = 0.84, j_i = 0.55, j_e = 0.88$.

4 RESULTS OF CALCULATIONS

As calculations showed, the choice of a particular model has relatively little effect on the magnitude of the momentum flux j_2 , but it significantly affects the flux of mass j_m and energy j_e . Fig.1 shows the curves of the dependency of the normalized fluxes $\bar{j}_3 / \bar{j}_1 = j_3 j_1^{(+)} / j_1 j_3^{(+)}$ on M for all considered models. From the comparison of the extrema of the fluxes $j_k(M=1)$ and behavior of the curves $j_m(M), j_e(M)$ it follows, that " β " - model was the least acceptable to describe the kinetics of evaporation because of bad selection of the function $f^{(-)}$.

Table 1 for all models shows numerical values of ρ_v and T_v , normalized by ρ_{sat} and T_{sat} correspondingly, depending on the Mach number that changes from zero to unity. Comparative analysis of tabular data, as well as the behavior of the curves j_m, j_e , show a marked contrast of the values of ρ_v и T_v , obtained using " β " model from the values, obtained using other models. The values of ρ_v turned out to be underestimated and T_v - overestimated relative to their true values at the outer side of the Knudsen layer.

The modified Crout model, " $\varepsilon - \delta$ " - model, " α " - model fulfill the requirement of extremum of the fluxes j_k in the point $M=1$. The differences between the results obtained using these models do not exceed 1.5%. Any of these models can be used to describe the kinetics of non-equilibrium surface evaporation.

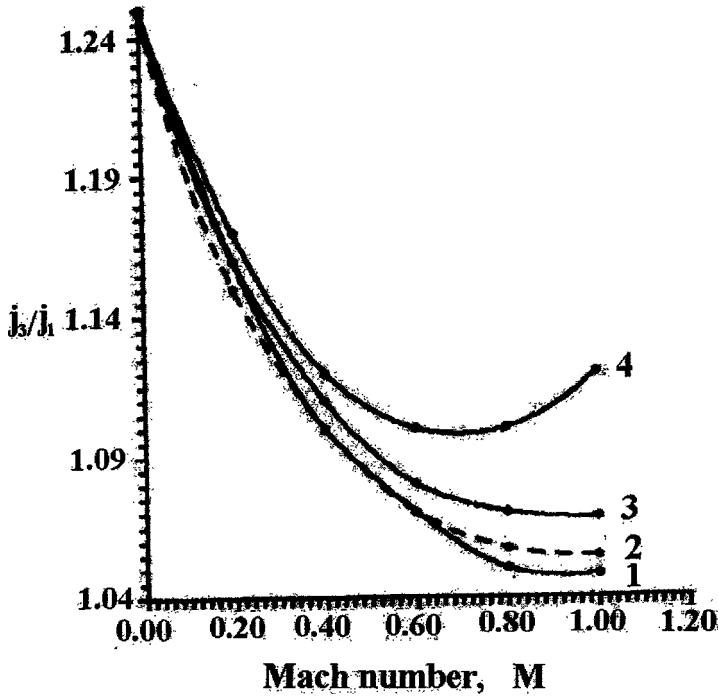


Fig. 1. The dependency of the normalized relation of the energy flux to the mass flux j_3/j_1 versus Mach number for different models: 1 – “ ε - δ ”-model, 2 – model of Crout, 3 – “ α ”-model, 4 – “ β ”-model (Knight).

5 CONCLUSIONS

A comparative analysis of different models of the boundary conditions needed to describe the evaporation process of a condensed medium under the action of intense energy flow within the continuum mechanics was carried out. The results of this analysis show that different models of evaporative boundary conditions, besides for small quantitative differences, have also different patterns of behavior of the flow depending on the Mach number M when M tends to unity. In some models [19, 25] the fluxes have extremum at $M=1$, while other models [23, 24] do not have this property. This difference may play a significant role in describing the behavior of the evaporation front perturbations in the case of the transition from subsonic ($M < 1$) to sonic ($M=1$) mode of evaporation.

The modified Crout model [19], “ ε - δ ” and “ α ” – models that meet the requirement of the extremum of the flux j_k at the point $M=1$, give the results with difference between each other lower than 1.5%. Any of these models can be used as a boundary condition for the description of kinetics of the process of non-equilibrium surface evaporation.

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