ON SPINODAL MANIFESTATION DURING FAST HEATING AND EVAPORATION OF THIN LIQUID FILM

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Summary. Recent results of molecular dynamic (MD) modelling of surface evaporation and explosive boiling of thin liquid film during its fast heating are analyzed in the framework of continual approach. Approximate solution of the inverse problem shows that heat conductivity coefficient at the film temperature maximum T_0 before the explosive boiling differs significantly from its value at the surface temperature T_S which is lower than T_0 due to evaporating cooling. This difference can be probably attributed to the spinodal manifestation near the superheating limit of the considered liquid metastable state.

It is widely known that liquids can be superheated to the temperatures well above its equilibrium boiling temperatures [1]. Such nonequilibrium metastable states can exist only during finite time interval t because of spontaneous development of growing vapor bubbles. This interval t depends strongly on superheating degree and from macroscopic point of view tends practically to zero at the superheating limit.

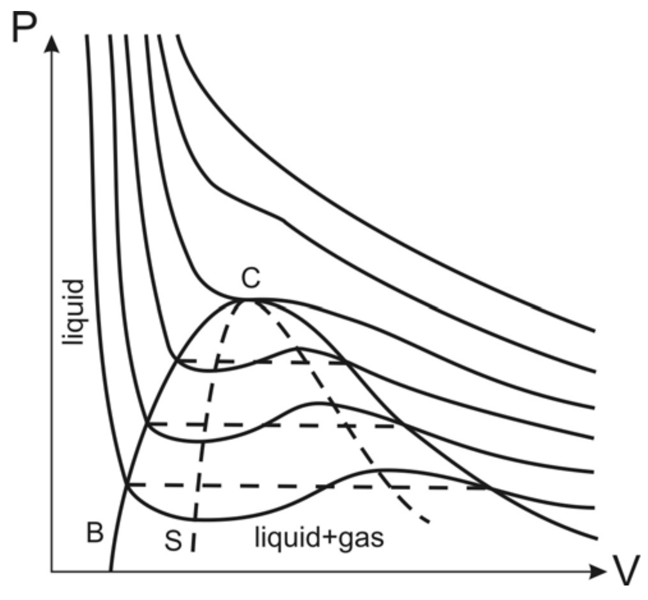

Fig.1 Equation of state in pressure (P) volume (V) plane with metastable liquid region between the curves B (binodal) and S (spinodal). C – critical point.

On the other hand, in continuous equation of states, e.g., van-der-Waals EoS, there is a definite spinodal line which divides metastable and unstable (labile) states (Fig.1) with no

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reference to any time dependence. Having the two different approaches one may ask about relation between superheating limit and spinodal lines. The question ha a rather old history (see, e.g., [2] and references therein) and it is not yet completely resolved. In particular, it is not clear at what extent spinodal singularities manifest itself near the superheating limit. In paper [3] dependence of t on superheating degree was studied in the framework of constant pressure MD simulations while the spinodal singularities problem was not considered. The problem of spinodal singularities near the superheating limit attainable during nanosecond liquid film heating is considered in the present paper on the basis of recent MD calculation results [4, 5].

We suppose that temperature distribution in the heated and evaporating film with thickness $2l$ located at $-l \le x \le l$ can be described with usual heat conduction equation:

$$\rho \cdot c_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(æ \frac{\partial T}{\partial x} \right) + W, \qquad (1)$$

where ρ - density, c_p – heat capacity , æ - heat conduction coefficient, $W=q\rho$, q – input power per unit mass, which is supposed to be constant. Due to evaporation process the film thickness is not constant. If this time dependence is neglected then in the steady state case equation (1) reduces to (2):

$$\frac{\partial}{\partial x}\left(æ \frac{\partial T}{\partial x} \right) + q\rho = 0, \qquad (2)$$

Integration of equation (2) from $x=0$ to $x<<l$ gives for the heat conduction coefficient æ in the region of temperature maximum $T_o=T(0)$:

$$æ_0 = \frac{q\rho_0 l^2}{2T_0 a_2}, \rho_0 = \rho(0),\ a_2 = \left(\frac{l^2}{2}\right) lim \left(\frac{1}{x}\frac{\partial T}{\partial x}\right), \qquad \text{at } x \to 0 \qquad (3)$$

In eq.(3) it is supposed that $\partial T/\partial x \sim x$ at small x and $æ_o \cdot \partial T/\partial x|_{x=0} = 0$ at $x = 0$. Making use polynomial approximation for $T(x)$

$$T = T_0\left(1 - \sum_{i=2}^{2k} a_i \left(\frac{x}{l}\right)^i\right), i = 2,4,..2k \qquad (4)$$

we obtain for the heat conduction value at the film surface $æ_S$ where $T=T_S$ and for the ratio $æ_0/æ_S$

$$æ_S = -\frac{q\int_0^l \rho dx}{T_S^{'}}, T_S^{'} = \left.\frac{\partial T}{dx}\right|_{x=l} \qquad (5)$$

$$\frac{æ_0}{æ_S} = -\frac{\rho_0 l^2 T_s{'}}{2T_0 a_2 \int_0^l \rho dx} = \frac{l\rho_0}{2a_2 \int_0^l \rho dx} \sum i a_i \qquad (6)$$

In the considered approach eq. (5) coincides with the steady state energy balance relation: all absorbed power is dissipated due to surface evaporative cooling effect. The simplest case

$i = 2$ corresponds to constant values approximation for æ and ρ which gives also the relation $2\Delta T + lT_S' = 0$.

If the sum in eq. (4) contains two terms (x^2 and x^4) then one has

$$a_2 = -\frac{4\Delta T + lT_S'}{2T_0},\ a_4 = -\frac{2\Delta T + lT_S'}{2T_0}, \Delta T = T_0 - T_S, \quad (7)$$

$$\frac{æ_0}{æ_S} = -\frac{\rho_0 l^2 T_S'}{(4\Delta T + lT_S')\int_0^l \rho dx}, T_S' = \left.\frac{\partial T}{\partial x}\right|_{x=l} < 0 \quad (8)$$

From eq. (8) one can see that relation $æ_0/æ_S$ depends on temperature curve mainly through its gradients T_S' which is negative at $x=l$ and $\Delta T=T_0 - T_S$. In this description compensation of the two terms $4\Delta T$ and lT_S' leads to singular behavior of $æ_0$ while the difference between $\int \rho dx$ and $l\rho_0$ is not so important.

Using eq. (8) and results [4,5] for temperature distributions which determine values of lT_S', ΔT at power deposition rates 2 K/ps at the moment 280 ps and 4 K/ps at the moment 240 ps gives, respectively:

$$lT_S' = -46830K,\ 4\Delta T = 8847K,\ T_0 = 6630K,\ æ_0/æ_S = -1{,}76 \quad (9)$$

$$lT_S' = -53155K,\ 4\Delta T = 11600K,\ T_0 = 7063K,\ æ_0/æ_S = -1{,}83 \quad (10)$$

Negative values of the heat conduction ratio mean formally that the system states are in unstable region divided from metastable region with the spinodal line where the system thermophysical parameters are singular according to continuous equation of states. However the approximation (8) is too crude to describe the temperature distributions details properly.

If the temperature curve approximation contains three terms (x2, x4 and x6) in the sum (4) then instead of (9) and (10) at the same conditions one obtains:

$$T_0 = 6640K,\ a_2 = 0{,}169523,\ a_4 = -0{,}3103258,\ a_6 = 0{,}318249308,\ æ_0/æ_S = 4{,}94 \quad (11)$$

$$T_0 = 6925K,\ a_2 = 0{,}174011,\ a_4 = -0{,}2966999,\ a_6 = 0{,}420521493,\ æ_0/æ_S = 7{,}42 \quad (12)$$

Greater than unity values of the ratio $æ_0/æ_S$ in (11) and (12) imply that the system state is metastable and relatively close to the spinodal.

It should be noted that the heat conduction coefficient value $æ_0$ fluctuates strongly (much stronger, e.g., than the considered temperature value [6]) and this is also manifestation of its singular behavior. In the case of four terms (x^2,x^4, x^6 and x^8) sum in eq. (4) one obtains that in time interval 270-274 ps with 1 ps step the averaged ratio $æ_0/æ_S$ = 42 with maximum value 164 while during following 275-280 ps all values of the ratio are negative and its mean value is about - 2,7.

It is clear that such behavior of the ratio $æ_0/æ_S$ is mainly due to the coefficient $æ_0 = æ(T_0)$ when the temperature maximum T_0 is in the spinodal line vicinity. The obtained results suggest that in the considered heating conditions of the thin liquid film the superheating limit temperature is sufficiently close to the spinodal line to manifest its singularities before the explosive boiling process begins to develop. More investigation is necessary to clarify further details of liquid systems behavior in its strongly nonequilibrium phase state. Information of the kind is needed, e.g., to describe properly metastable region of EoS and such phase transitions as explosive boiling using continual description of the processes.

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