Thermal effect on the film of a solution with a volatile component

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Abstract. Interfacial convection is a widespread phenomenon occurring in various fields of technology, including chemical technology. Marangoni convection is of greatest interest in the case of thin liquid films. Phase transitions significantly affect the convective flow by changing the surface tension coefficient. In this work, we study the behavior of a thin film of a binary homogeneous solution when it is heated. A change in the temperature of the free surface together with the escape of the volatile component leads to two opposite effects in the direction of the surface tension gradient. The necessity of taking into account the motion of the volatile component over the solution surface is substantiated, analytical estimates and solutions are obtained.

1. Main equations
A review of works on interfacial convection is given in [1,2]. The motion of thin films is considered, as a rule, within the framework of the long-wave approximation [3,4]. Balance relations at the interface between the media with allowance for phase transitions are described in [5,6].

Let a thin layer of a homogeneous solution is located on a flat horizontal surface $z = 0$. The gas above the free surface of the film $z = h(x, y, t)$ contains vapors of volatile component, which are in thermodynamic equilibrium with the liquid. At some point of time, the substrate is heated, which leads to deformation of the film. We have the following system of equations and boundary conditions [1,3]

$$
\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} = -\nabla p/ \rho + v^2 \mathbf{v} + \mathbf{g}, \\
\frac{\partial C}{\partial t} + \mathbf{v} \cdot \nabla C = D \nabla^2 C, \\
\frac{\partial T}{\partial t} + \mathbf{v} \cdot \nabla T = \chi \nabla^2 T, \\
\nabla \cdot \mathbf{v} = 0 .
$$

$z = 0$:

$\mathbf{v} = 0, T = T_s, \partial C/\partial z = 0$;

$z = h$:

$$
-(p - p_a) + 2\mu D \cdot \mathbf{n} \cdot \mathbf{n} + 2k_g \gamma = 0, \\
2\mu D \cdot \mathbf{n} \cdot \mathbf{r} = \nabla \gamma \cdot \mathbf{r}, \\
-k \mathbf{n} \cdot \nabla T = J L_v, \\
\rho D \mathbf{n} \cdot \nabla C = -f(1 - C).
$$

Here $\mathbf{v}, p, \rho$ and $T$ are the velocity, pressure, density and temperature of the liquid, respectively; $C$ is the mass concentration of the volatile component in the solution; $D$, $k$ and $\chi$ are the coefficients of diffusion, thermal conductivity and thermal diffusivity; $\mu, v = \mu/\rho$ are the dynamic and kinematic viscosities; $\gamma$ is the surface tension coefficient; $L_v$ is the latent heat of vaporization; $p_a$ is the external heat.
atmospheric pressure; $k_g$ is the free surface curvature; $D$ is the strain velocity tensor; $n$, $\tau$ are the normal and tangential unit vectors to the free surface; $g$ is the acceleration of gravity; $J$ is the intensity of mass transfer. The kinematic condition on the free surface has the form
\[
\frac{\partial h}{\partial t} + v \cdot \nabla (-z + h) = -J/(\rho n \cdot e_z).
\]
(2)

The initial conditions correspond to a homogeneous liquid at rest $t = 0$
\[
h = h_0,
\]
\[
0 < z < h; \quad v = 0, \quad T = T_0, \quad C = C_0.
\]
(3)

The substrate temperature is assumed to be a given function of coordinates $T_s = T_s(x, y)$.

The mass transfer intensity depends on the parameters of the free surface of the liquid film, as well as on the vapor pressure above it. Due to nonuniform heating, the mobility of the lower boundary, and evaporation in the gas layer, in addition to the diffusional one, convective transfer of the volatile component also occurs. Assuming the velocities and gradients of the vapor density to be small, we leave only the diffusion process
\[
\frac{\partial \rho_v}{\partial t} = D_v \nabla^2 \rho_v.
\]
(4)

The initial and boundary conditions are the following
\[
t = 0, \quad z > 0; \quad \rho_v = \rho_v^0,
\]
\[
z = 0; \quad D_v \frac{\partial \rho_v}{\partial z} = -J,
\]
(5)

where $\rho_v$ is vapor density of the volatile component; $D_v$ is the diffusion coefficient in the gas.

2. Closing relations

The density $\rho$ and viscosity $\mu$ of the solution are determined by the initial composition $C = C_0$ and temperature $T = T_0$ and further considered constant. The surface tension coefficient is approximated according to [7], writing it in linearized form
\[
\gamma = \gamma_T(T_0 - T_0) + \gamma_C(C_0 - C_0).
\]
(6)

Similarly, we represent the intensity of mass transfer. According to [1], we have
\[
J = \alpha_{com} \sqrt{M_v/(2\pi RT_0)} [p_{vs}(T, C) - p_v] .
\]

The saturated vapor pressure of an alcohol solution $p_{vs}$ is defined as
\[
p_{vs}(T, C) = x(C)p_{vs}^0 \exp[(L_v/R)(1/T_0 - 1/T)],
\]
mole fraction of the dissolved component
\[
x(C) = CM_w/(CM_w + (1 - C)M_v),
\]
the saturated vapor pressure of the pure component $p_{vs}^0$ at temperature $T = T_0$ is assumed to be known. The partial pressure of vapor above the free surface $p_v$ is expressed from the equation of state
\[
p_v = (p_{vs}/M_v)RT_0.
\]

Thus, we will consider $J$ as a function of temperature $T_1$, concentration $C_i$ and vapor density $\rho_v$ at the interface between media. Initially, the vapor above the free surface is assumed to be saturated
\[
\rho_v = p_v \rho_v^0 M_v/(RT_0) = x(C_0) p_v^0 M_v/(RT_0) = x(C_0) p_v^0 RT_0.
\]

Expanding the function $J$ in powers in a neighborhood of $(T_0, C_0, \rho_v^0)$, we obtain in the first approximation
\[
J = J_T(T_1 - T_0) + J_C(C_1 - C_0) + J_v(\rho_v - \rho_v^0); \quad J_T = \alpha_{com} \sqrt{M_v/(2\pi RT_0)} x(C_0) p_v^0 L_v/(RT_0^2) (1 - RT_0/L_v),
\]
\[
J_C = \alpha_{com} \sqrt{M_v/(2\pi RT_0)} (x(C_0)/C_0)^2 (M_v/M_w)p_v^0,
\]
\[
J_v = -\alpha_{com} \sqrt{M_v/(2\pi RT_0)} L_v R T_0 / M_w.
\]

In the above formulas $\alpha_{com}$ is the commodity coefficient; $M_v$, $M_w$ are the molar masses of the volatile and main components of the solution; $R$ is the universal gas constant. The calculations presented below will correspond to an aqueous solution of isopropanol (IPA), the parameters of which will be taken as in [8].
3. Equations of a thin layer
Let us analyze the equations of motion by introducing a small parameter in the form of the ratio of the transverse and longitudinal characteristic lengths. For this purpose, we write the equations in projections, highlighting the vertical coordinate $z$

$$
\mathbf{v} = \mathbf{v}_\perp + w \mathbf{e}_z , \quad \nabla = \nabla_\perp + \frac{\partial}{\partial z} \mathbf{e}_z ; \quad \nabla_\perp = \frac{\partial}{\partial x} \mathbf{e}_x + \frac{\partial}{\partial y} \mathbf{e}_y .
$$

Let $l$ be the longitudinal and $d$ the transverse characteristic lengths, and $l \gg d$, so that $\varepsilon = d/l$ is a small parameter of the system. The characteristic longitudinal and transverse velocities $u_0$ and $w_0$ are related to each other by the relation $w_0 = \varepsilon u_0$. The characteristic pressure is determined by the expression $p_0 = (\mu u_0 l)/d^2$. The characteristic temperature drop is denoted as $\theta$, the process time is $\tau$.

In equations (1)-(7) we pass to the dimensionless variables

$$
\nabla^* = \varepsilon \nabla , \quad x^* = \frac{x}{l} , \quad y^* = \frac{y}{l} , \quad z^* = \frac{z}{d} , \quad t^* = \frac{t}{\tau} , \quad v^*_\perp = \frac{v_\perp}{u_0} , \quad w^* = \frac{w}{w_0} , \quad p^* = \frac{p}{p_0} , \quad T^*_z = \frac{T - T_0}{\theta} , \quad h^*_z = \frac{h}{d} , \quad \rho^*_v = \frac{\rho_v}{\rho_v^0} .
$$

4. Evolution of the fields of temperature, concentration and velocity
Let us analyze the effect of evaporation of the volatile component on the heating of the liquid film and the formation of the velocity field. Setting $\tau = Pr(d^2/\nu) = d^2/\chi$, for the principal terms of the expansion in powers of the small parameter we will have

$$
\frac{\partial v^*_\perp}{\partial t^*} = \frac{\partial}{\partial z^*} p^*_v + \frac{\partial^2 v^*_\perp}{\partial z^*^2} , \quad \frac{\partial p^*_v}{\partial z^*} + \frac{Ga}{Re} \frac{\partial C}{\partial z^*} = 0 , \quad (8)
$$

Boundary conditions

$$
z^* = 0 : v^*_\perp = 0 , \quad w^* = 0 , \quad T^*_z = T^*_z ;
$$

$$
z^* = h^*_z : \quad p^*_v = p^*_v , \quad RePr \frac{\partial v^*_\perp}{\partial z^*} = \varepsilon Ma \left( \nabla^*_z T^*_z + \frac{\gamma c}{\gamma r \theta} \nabla^*_z C \right) ,
$$

$$
\frac{\partial T^*_z}{\partial z^*} = - \frac{j_T L_v d}{k} \left[ T^*_z + \eta(C - C_0) + \eta_v(\rho_v^* - x(C_0)) \right] ,
$$

$$
\frac{\partial C}{\partial z^*} = - \frac{j_T \theta(1 - C_0) d}{\rho D} \left[ T^*_z + \eta(C - C_0) + \eta_v(\rho_v^* - x(C_0)) \right] ,
$$

$$
\frac{\partial h^*_z}{\partial t^*} = 0 \quad \left( \ll \frac{u_0 \tau}{l} = \varepsilon^2 Re \ll 1 \right) .
$$

Initial conditions

$$
t^*_z = 0 : h^*_z = 1 ,
$$

$$
0 < z^* < h^*_z : \quad v^*_\perp = 0 , \quad w^* = 0 , \quad T^*_z = 0 , \quad C = C_0 .
$$

For the gas phase we will have

$$
\frac{\partial \rho_v^*}{\partial t^*} = \frac{D_v \partial^2 \rho_v^*}{\partial z^*^2} , \quad t^*_z = 0 , \quad z^* > 0 : \quad \rho_v^* = x(C_0) ;
$$

$$
\frac{\partial \rho_v^*}{\partial z^*} = - \frac{j_T \theta d}{D_v \rho_v^0} \left[ T^*_z + \eta(C - C_0) + \eta_v(\rho_v^0 - x(C_0)) \right] .
$$

The following notation is used here for dimensionless complexes: $Re = u_0 l/\nu , \quad Pr = \nu/\chi , \quad Ga = g d^3/\nu^2 , \quad Le = D/\chi , \quad Ma = \gamma r \theta l/(\mu x)$, and values: $T^*_z = (T_z - T_0)/\theta , \quad p^*_v = p_v/p_0 , \quad T^*_i = (T_i - T_0)/\theta , \quad \rho_v^* = \rho_v/\rho_v^{0 \ast} , \quad \eta = j_c/(j_r \theta) , \quad \eta_v = j_v \rho_v^{0 \ast}/(j_r \theta)$.
To analyze the film heating rate, two auxiliary problems with equations (8)-(10) are considered. In the first, the mass transfer rate is reduced to zero, and in the second, it is increased by a corresponding change in the boundary conditions (9). As a result, estimates were found for the surface temperature
\[ \frac{c_1}{c_1 + 1} T_i^* (J = 0) < T_i^* (J = 0) ; \] (11)
and concentration
\[ -\frac{c_2}{c_1} T_i^* (J = 0) < c_i - c_0 < -\frac{c_2}{c_1 + 1} T_i^* (J = 0) . \] (12)

Here \( T_i^* (J = 0) \) corresponds to the heating of the liquid film without taking into account the heat consumption for evaporation [8]
\[ T_i^* (J = 0) = \left(1 - 2 \sum_{n=0}^{+\infty} (-1)^n \frac{e^{-\eta_n^2 t_i}}{\eta_n^2}\right) T_s^* , \quad \eta_n = \left(n + \frac{1}{2}\right) \pi ; \]
the constants \( c_1, c_2 \) are defined by the equalities
\[ c_1 = \left(\frac{J_c - J_0}{J_T} \sqrt{\frac{D}{D_v}} \frac{\rho}{1 - C_0} \right) c_2 , \quad c_2 = \frac{\sqrt{Le} (1 - C_0) k}{\rho D L_v} . \]

Since the changes in the concentration of the solution begin on the free surface, we can confidently assert that at the initial stage the actual temperature \( T_i^* \) is close precisely to \( T_c (z_c = 1) \).

The relative difference of the bounding functions for \( T_i^* \) is
\[ \delta = \frac{T_i^* - T_0}{T_i^* + 1} < 1 - \frac{c_1}{c_1 + 1} = \frac{1}{c_1 + 1} < \frac{1}{c_1} . \]

Taking into account expressions (7), as well as the definition \( \chi = k / (\rho c_p) \) in the number \( Le, c_p \) is the heat capacity at constant pressure of the solution, it can be seen that the process constant \( c_2 \) is proportional to \( \sqrt{c_p / k} \) and in fact \( (1 / L_v)^2 \), but does not depend on the amount of heating and the initial film thickness. Figure 1 shows the dependences of the coefficient \( c_1 / (c_1 + 1) \) and the deviation \( \delta - c_1^{-1} \) on the mass content \( C_0 \).

Next, we establish the dynamics of the velocity field development
\[ \begin{align*}
&\nu_1^* = -\frac{4c_1 \nabla_1 T_s^*}{c_1 + 1} \sum_{n=0}^{+\infty} \sum_{k=0, \text{ even}}^{+\infty} (-1)^{n+k} \eta_k \left( -\eta_n^2 + -\eta_k^2 \right) \frac{e^{-\eta_n^2 t_i} - e^{-\eta_k^2 t_i}}{\eta_n^2 - \eta_k^2} \sin(\eta_n z) + \\
&+ \frac{c_1 \nabla_1 T_s^*}{c_1 + 1} \left\{ 4 \sum_{n=0}^{+\infty} \frac{\eta_n}{\eta_n^2} e^{-\eta_n^2 t_i} \sin(\eta_n z) + \left(2 \sum_{n=0}^{+\infty} (-1)^n \eta_n e^{-\eta_n^2 t_i} - 1 \right) z \right\} .
\end{align*} \]
5. Conclusions
As a result of the study, the importance of taking into account the movement of the volatile component over the free surface is indicated. The limiting functions are found that determine the dynamics of heating and changes in the concentration of the solution. The beginning of the process is described analytically. The change in the concentration of the volatile component in the liquid and gaseous states is inversely proportional to the ratio of the corresponding diffusion coefficients raised to power 1/2. The surface temperature of the solution film decreases monotonically nonlinearly with an increase in the initial mass content of the volatile component. The magnitude of this deviation is proportional to the square of the heat of vaporization, as well as the coefficient of thermal conductivity and heat capacity in powers (−1/2), but does not exceed 1.5%.

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