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Irreversible condensation conditions near the cryosurface

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Abstract—The circumstances attending irreversible condensation through the mechanism of heterophase fluctuations within the boundary layer, are discussed theoretically within the scope of approximation called 'monophase boundary-layer approximation' (MBL). Both the classical theory of nucleation and the theory of the monophase binary boundary layer are used in predicting the spontaneous phase change within the binary gas, free convective, laminar boundary layer. As opposed to what is called the 'critical supersaturation model' (CSM), in the MBL approximation the fields of temperature and condensing component concentration are not determined *a priori* but rather so as to satisfy both the system of partial differential equations of the boundary layer and the corresponding boundary conditions, on the one hand, and the additional thermodynamic condition collocated on the boundary of the fog sublayer, in accordance with the theory of heterophase fluctuations, on the other. The findings of this analysis are illustrated by the example of the binary mixture of air and water vapour in contact with the vertical isothermal surface at cryogenic temperature. Theoretical predictions are compared with experimental data.

INTRODUCTION

THEORETICAL and experimental analyses of the thermodynamic conditions at spontaneous phase change within the binary boundary layer (condensation or evaporation of one of the components—the second, dominant one being inert) have yet to provide a final answer to the uniform prediction of fog formation* in the vicinity of isothermal surfaces.

There have been several attempts at theoretically considering the phenomenon of fog formation in the boundary layer. Among investigations dealing with the kinetics of the emergence process of the new phase nuclei, in keeping with the theory of heterophase fluctuations, the following papers merit special mention. (Toor [1, 2] treats fog as the third component in the mixture 'condensable vapour, non-condensable gas and condensed vapour or fog'. This approach will not be considered in this paper.) In many of their papers, Rosner and Epstein [3–5], as well as Hayashi *et al.* [6], develop the so-called 'critical supersaturation model' (CSM), mentioned for the first time in literature by Turkdogan [7, 8]. The central point of interest in all these papers is analysing the influence of spontaneous phase change on changes in the heat and mass flux rate during evaporation or condensation from gas mixture on the isothermal surface or vice versa. The physical model in these studies is based on the view that the spontaneous phase change occurs after 'critical supersaturation'† of the metastable condensable component in the temperature field and in the field of partial pressure of the binary boundary layer. It is irrelevant, here, whether evaporation into some cooler gas medium [3, 8] (metal evaporation into the helium atmosphere), [6] (naphthalene sublimation into the air atmosphere), [5] (methyl alcohol evaporation into the air atmosphere), or condensation at the cooler isothermal surface [4] (water vapour from moist air) are in question. It is important to point out that according to the initial idea [7] and subsequent elaborations of the CSM model [3, 4, 6], the site of the local achievement of critical supersaturation was defined on the basis of *a priori* accepted fields of temperatures and partial pressures. According to Turkdogan [7], the field of temperatures and partial pressures is formed by free convection around the sphere; Rosner [3, 4] talks about linear profiles along the approximation of 'one-dimensional stagnant film' formation, while Hayashi [6] accepts the square, two-dimensional profile of temperatures and partial pressures for laminary convection along the vertical flat plate.

Finally, as a point of interest, let us mention two papers dealing with the same problem before the nucleation theory became the basis of analytical modelling. The first is Piening's paper [10] (Die Nebelbildung an Wärmeaustauschenden Körpern, Dealing with the problem of heat and mass transfer from the moist air to a moist surface) and the second is a paper by Johnstone *et al.* [11] which appeared 20 years later as a 'theoretical and experimental study of conditions under which fog will form in a cooler-condenser'.

Our research, the findings of which are summed up in this paper, proceeded from the standpoint that fields of temperature, partial pressure and velocity in the boundary layer have to *simultaneously* satisfy both the requirements of the mathematical model of the boundary layer (that is, the corresponding system of

* In the context of this analysis, the concept of 'fog' implies a quasi-static population of the condensed particles wherein the rate of formation of stable condensation nuclei per unit volume per second is higher than some present values.

† In terms of the classical theory of nucleation [9] critical supersaturation is defined as that supersaturation in the metastable component which causes the critical rate of formation of the new phase nuclei, wherein this present value defines the notion of fog (see previous footnote).

NOMENCLATURE

a	thermal diffusion constant [dimensionless]
A	coefficient, equation (8a) [dimensionless]
$\mathcal{A}$	coefficient, equation (11)
B	coefficient, equation (8a) [K]
$\mathcal{B}$	coefficient, equation (9)
c	specific heat [J kg^{-1} K^{-1}]
D	diffusion coefficient [m^2 s^{-1}]
g	local acceleration due to gravity [m s^{-2}]
I	constant, equation (14) [dimensionless]
J	rate of nucleation [s^{-1} m^{-3}]
$\tilde{M}$	molecular weight of the vapour [kg mol^{-1}]
m	constant, equation (10) [dimensionless]
n	constant, equation (9) [dimensionless]
N	Avogadro's number [mol^{-1}]
p	pressure [Pa]
Pr	Prandtl number [dimensionless]
r	radius [m]
R	gas constant [J mol^{-1} K^{-1}]
S	supersaturation [dimensionless]
Sc	Schmidt number [dimensionless]
T	temperature [K]
u	velocity component in x direction [m s^{-1}]
v	specific volume [m^3 kg^{-1}]
w	water vapour mass fraction [dimensionless]
x	coordinate along the plate surface [m]
y	coordinate normal to the plate surface [m]

Greek symbols

α	thermal diffusivity [m^2 s^{-1}]
β_m	binary expansion coefficient [dimensionless]
β_T	thermal expansion coefficient [K^{-1}]
Δ	boundary-layer thickness ratio [dimensionless]
δ	boundary-layer thickness [m]
Θ	dimensionless temperature
ν	kinematic viscosity [m^2 s^{-1}]
ρ	density [kg m^{-3}]
σ	surface tension [N m^{-1}]
Φ	dimensionless vapour mass fraction.

Subscripts

c	critical
eq	equilibrium
fog	refers to fog
m	mass
mp	monophase
p	at constant pressure
w	at wall
1	refers to component 1 (water vapour)
2	refers to component 2 (air)
12	refers to 1 and 2
∞	refers to value at great distance.

Superscripts

+	fog boundary
lim	limit.

partial differential equations and corresponding boundary conditions) and the additional thermodynamic condition (which introduces the CSM model, collocating it on the 'fog sublayer boundary'). Neither the fields of temperature and partial pressure nor the thickness of the boundary layer, nor the sites where the critical supersaturation condition is locally met are known in advance. Such an approach, like those before it, invariably introduces any number of approximations, but it brings some new hypotheses as well.

THE MATHEMATICAL MODEL

Auxiliary hypotheses

A schematic presentation of the physical model is given in Fig. 1. The conditions for fog sublayer formation are created in the boundary layer (the conditions themselves will be discussed later). It is important to bear in mind that, as we said in the introduction, the content of the condensable component in the binary mixture is considerably lower than the dominant inert component content. The two-dimensional temperature field $T(x, y)$ for the constant value of the longitudinal coordinate (x) presents the monotonous function of the distance vertical to the isothermal surface (y). We ascribe significant properties to the field of partial pressures of the condensable component. Namely, the partial pressure of the condensable component (for the given value of the longitudinal coordinate) need not have a monotonous flow from the ambient to the isothermal surface. As it approaches the surface, the partial pressure decreases inside the boundary layer reaching its equilibrium value at some location within it (the value corresponding with the local temperature value at that location). The phase change may occur from this point on to the isothermal surface, but whether it does or not depends on the homogeneous level of the gas phase. If it is completely homogeneous, the phase change will not occur until the partial pressure decreases so much that the supersaturation ($S = p_1/p_{1\,\mathrm{eq}}$) attains a critical value corresponding with the phenomenon of homogeneous heterophase fluctuations. The geometrical location of the points within the boundary layer, wherein the supersaturation in the field of temperature and partial pressure of the boundary layer is equal to the critical, can be called the 'fog sublayer boundary'. If the phase change takes place, the partial pressure of

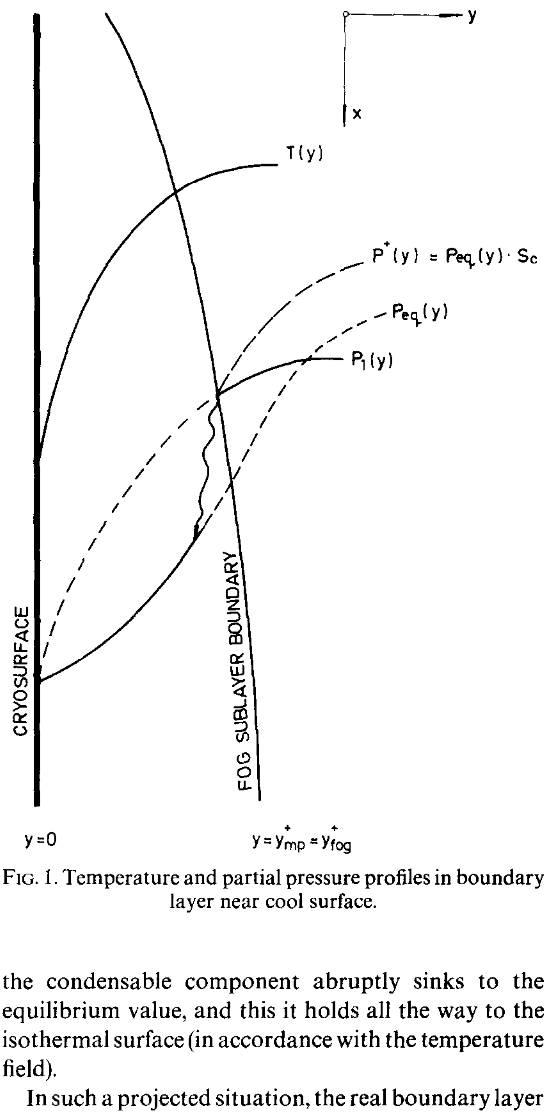

FIG. 1. Temperature and partial pressure profiles in boundary layer near cool surface.

the condensable component abruptly sinks to the equilibrium value, and this it holds all the way to the isothermal surface (in accordance with the temperature field).

In such a projected situation, the real boundary layer consists of two parts: the monophase part outside the fog sublayer boundary and the multiphase part inside the fog sublayer boundary. As can be seen, the phenomenon for which the model has been formed is extremely complex. First of all, it is not a monophase but a multiphase boundary layer (certainly a three phase one for the temperatures of the isothermal surface to be low enough). The phenomenon of heterophase fluctuations brings into consideration the kinetics of spontaneous phase change. In addition to all this, simultaneous heat and mass transfer from the ambient to the isothermal surface, along with condensate deposition, takes place within the boundary layer. So, it is obvious that hypotheses and approximations are necessary for facilitating analytical treatment, but they must be introduced carefully and verified *a posteriori* both indirectly and directly.

Let us introduce the following hypotheses:

Hypothesis 1. The boundary $y^+_{mp}(x, y)$ at which the conditions for critical supersaturation within the quasi-steady monophase boundary layer are realized, is preserved (i.e. exists in the same place, even in the new situation) within the real multiphase boundary layer, after the advanced process of heterophase fluctuations, as the fog sublayer boundary $y^+_{fog}(x, y)$.

Hypothesis 2. The boundary defined under Hypothesis 1 is self-similar.

These hypotheses allow one, in the mathematical model, to determine the field of physical values (such as temperature, partial pressure and flow velocity) on the basis of the binary monophase boundary-layer theory, and enable the collocation of the additional thermodynamic condition on the fog sublayer boundary. In Hypothesis 1, the analytical procedure is transposed from the theory of the multiphase to the theory of the monophase boundary layer. It also defines the existence of a clear boundary between the binary gas mixture region, where there are no condensed particles, and the region in which they exist in the form of fog. Finally, this hypothesis provides an opportunity to identify the fog formation mechanism in the boundary layer. Furthermore, it avoids the difficulties posed by consistently treating the boundary layer as a multiphase system. (A similar stand is present in the CSM model as seen in the following approximation: 'condensing vapour is dilute in a noncondensable gas in the sense that the vapour mass fraction far from the surface (at ∞) is small compared to unity' [4].)

Hypothesis 2 allows relatively simple estimation of the geometrical location of the points considered to present the fog sublayer boundary and, at the same time, has a considerable bearing on the analytical methodology of solving the mathematical model.

Inspiration for both hypotheses can be found in the empirical experience of analysing the fog sublayer under experimental conditions. A detail of the boundary layer in which the fog sublayer formation is clearly present can be seen in Fig. 2.

It can be concluded that the fog sublayer boundary is clearly discernible (the boundary introduced in the model by Hypothesis 1). The existence of such a sub-layer, the thickness of which undergoes monotonous growth from zero at the beginning of the boundary layer and along its length, suggests that the introduction of Hypothesis 2 is possible. The deeper physical sense of hypotheses will not be discussed here.

The analytic equations for these hypotheses are as follows:

$$y^+_{mp}(x, y) = y^+_{fog}(x, y) \tag{1}$$

$$\left(\frac{\partial p_1(x, y)/\partial y}{\partial T(x, y)/\partial y}\right)_{y=y^+_{mp}} \neq f(y). \tag{2}$$

Approximations

It can be assumed that the introduction of Hypotheses 1 and 2 will appreciably facilitate consideration of the mathematical model. But, in order to arrive at quantitative indicators, an entire range of approximations still need to be introduced. First of all, there are standard approximations that follow an

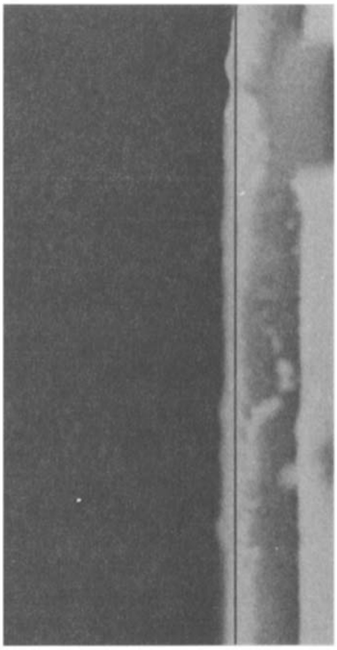

FIG. 2. Photograph of fog formation.

analysis of simultaneous heat and mass transfer within the free-convective laminary binary boundary layer. The most important approximations would be as follows:

1. The boundary layer is monophase.
2. The boundary layer is two-dimensional.
3. The flow is laminar.
4. The analytical model implies quasi-steadiness.
5. The total pressure is constant.
6. In differential equations all the properties of the binary mixture are constant except density in the buoyancy term of the momentum equation.
7. Viscous dissipation effects in the energy equation are negligible.
8. Both components of the binary mixture are considered as perfect gases.
9. The partial pressure of the condensable component at the isothermal surface is negligible in relation to the total pressure, but is equal to the equilibrium pressure at the given temperature.
10. The heat released during the process of heterophase fluctuations negligibly influences the temperature field.
11. Heat transfer of the radiation mechanism is negligible.

Approximation 1 is in accordance with Hypothesis 1, while Approximation 2 is the customary approximation when considering the boundary layer on a flat surface and it requires no extra comment.

Rosner and Epstein [4] discussed this problem in their paper, applying the CSM model for the first time, and they considered the boundary layer as one-dimensional. Such an approach excluded an analysis of the fog sublayers geometry, whereas the MBL approximation does not.

Approximations 3–7 are standard in analyses of the monophase binary boundary layer, and are not discussed.

Viewing binary mixture components in the first approximation as perfect gas (Approximation 8) is particularly important given the applied theory of heterophase fluctuations. Dufour and Defay [12] argue effectively in favour of using this approximation in the nucleation theory.

(If we accept the correction coefficient $(pv)/(RT)$ as an evaluation of gas perfection, it may veer by less than 1% from the value 1 in the ranges of temperatures and pressures which are relevant to our discussion. 'In the case of humid air, it is useful to make sure that interactions between the water molecules and the molecules of gases of the dry air do not appreciably alter this situation' [12].)

Low isothermal surface temperatures facilitate the satisfaction of all the requirements of Approximation 9 with great exactness. The low condensable component content in the binary mixture within the boundary layer makes the partial pressure on the isothermal surface negligibly high in relation to the total pressure.

(For instance, for moist air in contact with a cold isothermal temperature surface of 250 K, moist air: $T_\infty = 300\,\mathrm{K}$, $w_{1\infty} = 0.01$, $p = 10^5$ Pa, the equilibrium partial water vapour pressure at the surface is lower than the partial ambient vapour pressure by a factor of 20, and lower than the total pressure by a factor of 1300.)

The small condensable component content, especially at low temperatures, reinforce our conviction that temperature fluctuations (due to heterophase fluctuations) do not really disturb the monotony of the temperature field in the laminar boundary layer. On the other hand, the metastability of the condensed component in the monophase boundary layer, within the field of possible heterophase fluctuations, exists only if the released heat from the phase change is lower than the energy necessary to disturb the metastable state (Approximations 10 and 11).

In view of the formulated hypotheses and the aforementioned approximations (Hypotheses 1 and 2 and Approximations 1–11) it is possible to note a system of equations and boundary conditions (implying boundary conditions of the first kind), the solution of which will provide the quantitative material for making a comparison with the experience data.

Governing equations

The basic system of equations, apart from those resulting from the analytical record of Hypotheses 1 and 2, consists of continuity, momentum, energy and mass transfer equations for the free convection, binary boundary layer. Corresponding boundary conditions are collocated on the isothermal surface and the thermal sublayer boundary, as well as on the boundary of the partial pressure sublayer of the condensable component. (Analogous to the mathematical model of simultaneous heat and mass transfer during frost deposition on the cryosurface [13].)

The starting system consists of two algebraic equations (derived from Hypotheses 1 and 2) and of three integral differential boundary-layer equations:

$$p_1(x,y)_{y=y^+_{\text{mp}}} = \{p_{\text{eq}}[T(x,y)]\cdot S[J_c, T(x,y)]\}_{y=y^+_{\text{mp}}} \quad (3)$$

$$\frac{\partial}{\partial y}\left(\frac{\partial p_1(x,y)/\partial y}{\partial T(x,y)/\partial y}\right)_{y=y^+_{\text{mp}}} = 0 \quad (4)$$

$$\frac{\mathrm{d}}{\mathrm{d}x}\left[\int_0^{\delta_T} u^2\,\mathrm{d}y\right] = -\nu\left(\frac{\partial u}{\partial y}\right)_{y=0} - \int_0^{\delta_T} g\beta_T(T-T_\infty)\,\mathrm{d}y - \int_0^{\delta_m} g\beta_m(w_1-w_{1\infty})\,\mathrm{d}y \quad (5)$$

$$\frac{\mathrm{d}}{\mathrm{d}x}\left[\int_0^{\delta_T} u(T-T_\infty)\,\mathrm{d}y\right] = -\alpha\left(\frac{\partial T}{\partial y}\right)_{y=0} - D_{12}\left[\left(\frac{\partial w_1}{\partial y}\right)_{y=0} + \frac{a w_{1\text{w}}(1-w_{1\text{w}})}{T_\text{w}}\left(\frac{\partial T}{\partial y}\right)_{y=0}\right] \times\left[\frac{a}{c_p}RT_\text{w}\frac{\tilde{M}^2}{\tilde{M}_1\tilde{M}_2} + \frac{1}{1-w_{1\text{w}}}(T_\text{w}-T_\infty)\right] \quad (6)$$

$$\frac{\mathrm{d}}{\mathrm{d}x}\left[\int_0^{\delta_m} u(w_1-w_{1\infty})\,\mathrm{d}y\right] = -D_{12}\left[\left(\frac{\partial w_1}{\partial y}\right)_{y=0} + \frac{a w_{1\text{w}}(1-w_{1\text{w}})}{T_\text{w}}\left(\frac{\partial T}{\partial y}\right)_{y=0}\right]\left[1-\frac{w_{1\infty}-w_{1\text{w}}}{1-w_{1\text{w}}}\right]. \quad (7)$$

An explicit record of equations (3) and (4) and the reduction of equations (5)–(7) to algebraic form is made possible by accepting the forms of the temperature, condensable component content (partial pressure) and the flow velocity profile in the boundary layer (Karman–Pohlhausen integral method).

The supersaturation S which introduces equation (3) into the calculation, at $y = y^+_{\text{mp}}$ reaches its critical value. According to the standard approach in nucleation theory (see footnote on p. 1205), the critical conditions correspond to the rate of formation of stable condensed nuclei per unit volume per second: $J_c = 10^6$ nuclei $\text{m}^{-3}\,\text{s}^{-1}$. On the basis of this defined value of the critical rate of formation of condensed nuclei it is possible to arrive at an implicit connection between S and the temperature (T) in equation (3) by using the connection between the S and the rate of new phase nuclei formation (J) (from the nucleation theory for homogeneous heterophase fluctuations [9, 14]):

$$J = \left(\frac{2N^3}{\pi}\right)^{1/2}\left(\frac{p_{\text{eq}}}{RT}\right)^2 S^2\frac{(\sigma\tilde{M}_1)^{1/2}}{\rho} \times\exp\left[-\frac{16\pi N}{3R^3}\left(\frac{\tilde{M}_1}{\rho}\right)^2\left(\frac{\sigma}{T}\right)^3(\ln S)^{-2}\right]. \quad (8)$$

Extreme nonlinearities in equation (8) suggest that it will be necessary to apply numerical methods in solving the system of equations (3)–(7).

(The nonlinear implicit relation $J = J_c = J(S,T)$ may be approximated with sufficient exactitude to the explicit relation of the type:

$$S = \exp(-A+B/T). \quad (8a)$$

According to [5], the coefficients, for H_2O, are $A = 2.59$ and $B = 1100$ for the $230 < T < 300$ K range of temperature. The average deviation of supersaturation calculated in this way and supersaturation calculated according to the exact relation (8) within this range of temperatures, is less than 2%. The newly created nucleus is understood to be in a liquid state.)

This system of equations can, in principle, be solved in various ways. Adoption of the approximative integral Karman–Pohlhausen method can be disputed for at least two reasons. First of all, a persistent numerical approach to solving the system of differential equations leads to an exact solution as opposed to the integral approach which is approximative. Secondly, and not unrelated is the fact that the choice of adopted profile forms is not sufficiently subject to any objective criterion and appreciably influences the result. Nonetheless, this approach has been adopted because a comparative analytical solution of the problem of simultaneous heat and mass transfer onto the cryosurface along with the deposition of condensate but without taking into account the fog phenomenon [13], is obtained in the same way. Furthermore, this procedure is simple and straightforward.

The profile fields of temperature, partial pressure (condensing component concentration) and flow velocity in the boundary layer have been adopted in the following form:

$$\Theta = (1-\mathscr{B}^{-1}x^{-1/4}y)^n \quad (9)$$

$$\Phi = (1-\mathscr{B}^{-1}\Delta x^{-1/4}y)^m \quad (10)$$

$$u = \mathscr{A}x^{1/2}(\mathscr{B}^{-1}x^{-1/4}y)(1-\mathscr{B}^{-1}x^{-1/4}y)^2. \quad (11)$$

It should be noted that exponents n and m as well as Δ and $\mathscr{B}$ are, like constant $\mathscr{A}$, still unknown values. Also unknown is the place where the boundary fog sublayer $y = y^+_{\text{mp}}$ collocates. The six given unknown values can be determined by the system of equations (3)–(7) if one unknown is determined *a priori* or if an additional condition is introduced. The additional condition could be the so-called 'tangency condition' [3], as in the CSM model. However, analysis showed that it is very difficult to fulfil this condition and, at the same time to arrive at a satisfactory convergence in simultaneously solving the equations of the mathematical model. On the other hand, the physical sense of this condition (conservation of the continuity of the diffusion mass flux on the fog sublayer boundary) runs counter to experience (there is a discontinuity on the boundary of the field of partial pressures along with a change in the mass transfer mechanism, and this should cause a change in the values of the pressure gradient on the fog sublayer boundary). Because of all these difficulties and because of the dubiousness of its physical meaning, the 'tangency condition' has not been used here. Therefore, exponent m has been determined parametrically and then checked *a posteriori* in the course of experimental verification of the numerical results.

It is not difficult to show (although it requires hard calculation) that the system of equations (3)–(7) can be reduced to the system of two nonlinear algebraic equations with two unknowns. The solution of this system opens the door to further analysis. The following ensues from (4), (9) and (10):

$$y^+_{\mathrm{mp}} = \frac{1}{\Delta}\frac{(n-1)-\Delta(m-1)}{n-m}\mathscr{B}x^{1/4}. \quad (12)$$

Using (9)–(11) on the basis of (5)–(7) one obtains:

$$\frac{1}{I(\Delta,m)}\left(\frac{1-w_{1\infty}}{1-w_{1\mathrm{w}}}\right)\frac{Pr}{Sc}\times\left[m\Delta - aw_{1\mathrm{w}}(1-w_{1\mathrm{w}})\frac{T_\mathrm{w}-T_\infty}{T_\mathrm{w}}\frac{n}{w_{1\infty}-w_{1\mathrm{w}}}\right]$$
$$= n(n+3)(n+4)\left\{1+\frac{Pr}{Sc}\left[\frac{aR}{c_\mathrm{p}}\frac{\tilde{M}^2}{\tilde{M}_1\tilde{M}_2}\frac{T_\mathrm{w}}{T_\mathrm{w}-T_\infty}+\frac{1}{1-w_{1\mathrm{w}}}\right]\cdot\left[(w_{1\mathrm{w}}-w_{1\infty})\frac{m}{n}\Delta + aw_{1\mathrm{w}}(1-w_{1\mathrm{w}})\frac{T_\mathrm{w}-T_\infty}{T_\mathrm{w}}\right]\right\} \quad (13)$$

wherein the following expression is marked by $I(\Delta, m)$:

$$I(\Delta,m) = \frac{1-(1-\Delta)^{m-1}}{(m+1)(m+2)\Delta^2}\left\{1-\frac{2}{\Delta(m+3)}\times\left[2-\frac{3}{\Delta(m+4)}\right]\right\}-\frac{(1-\Delta)^{m+1}}{\Delta(m+2)(m+3)(m+4)}\times\left[2\left(1+\frac{3}{\Delta^2}\right)-\frac{m+10}{\Delta}\right]. \quad (14)$$

In relations (13) and (14), the general case is $m \neq n \neq 2$. (In the case of $m = n = 2$, the profiles (9) and (10) become square and equation (13) assumes standard form most often found in literature about simultaneous heat and mass transfer during frost deposition by free convection near the vertical surface [13]. In this case, $I(\Delta, m) = 1/12-(1/15)\Delta+(1/60)\Delta^2$.)

The system of nonlinear algebraic equations (3) and (13) cannot be solved analytically according to unknowns (n and Δ). In equation (3), the partial pressure of condensable component (condensing component concentration) follows profile (10), the temperature is given in (9) while the fog sublayer boundary follows dependence (12). Solutions have been sought numerically by applying Powell's (SSQMIN) algorithm [15].

Results

The system of equations (3) and (13) is solved in this way for a large scale of parameters (ambient temperature T_∞, condensable component content in the ambient $w_{1\infty}$, and the temperature of the isothermal surface T_w). After determining n and Δ, the distance between the fog sublayer boundary and the isothermal surface is determined by means of (12).

Table 1. A cut from the results listing

T_w	(K)			160	
T_∞	(K)	295	295	300	300
$w_{1\infty}$	—	0.0075	0.0083	0.0097	0.0117
Δ^+	—	1.796	1.746	1.785	1.694
T^+	(K)	251.5	253.1	255.2	258.4
S^+	—	6.097	5.925	5.715	5.421

The values of the parameters are chosen to correspond with the experimental conditions (see Fig. 6).

The auxiliary fields of temperature, partial pressure (condensing component concentration) and the flow velocity in the boundary layer are determined by means of (9)–(11). Finally the supersaturation on the fog sublayer boundary is determined via (8). Thanks to Hypothesis 1, these results can be compared to experimentally obtained data. Numerical results for some characteristic values of the parameters, when the binary mixture is moist air and the isothermal surface is a vertical plate, are presented in Table 1.

The impact of the cross-effects is ignored in this calculation [$a = 0$ in equation (13)].

The temperature values and the supersaturation on the fog sublayer boundary are of particular interest for this analysis. Figure 3 allows us to follow the dependence of these values on the temperatures of the isothermal surface. The distinguishing trait of these dependencies is reflected in the presence of the boundary temperature values of the isothermal surface below which the fog phenomenon can occur within the boundary layer (for other defined parameters). Above this temperature limit ($T^{\mathrm{lim}}_\mathrm{w}$) the fog phenomenon (under conditions of a homogeneous binary mixture and, by extension in circumstances of homogeneous heterophase fluctuations) cannot come about, although pairs of temperature values and values of the partial pressure of the condensable component suggest the presence of metastability. On the other hand, it is interesting to note that after fog sublayer formation, a further decrease of the isothermal surface temperature does not cause any major change in the temperature and supersaturation ratio on the fog sublayer boundary (although the change is not negligible). Reduction of the water vapour content in the ambient (wherein the temperature in the ambient is unchanged) shifts the temperature on the fog sublayer boundary towards lower values. On the other hand, a decrease of the temperature in the ambient (wherein the water vapour content in the moist air is unchanged) has the reverse effect.

The supersaturation has not been defined for the temperature values of isothermal surface $T_\mathrm{w} > T^{\mathrm{lim}}_\mathrm{w}$ (see Fig. 3). For $T_\mathrm{w} = T^{\mathrm{lim}}_\mathrm{w}$, the supersaturation becomes final in keeping with the theory of nucleation, while for $T_\mathrm{w} < T^{\mathrm{lim}}_\mathrm{w}$, it decreases as the temperature of the isothermal surface decreases, particularly around $T^{\mathrm{lim}}_\mathrm{w}$, but after that the decrease is very slight. The

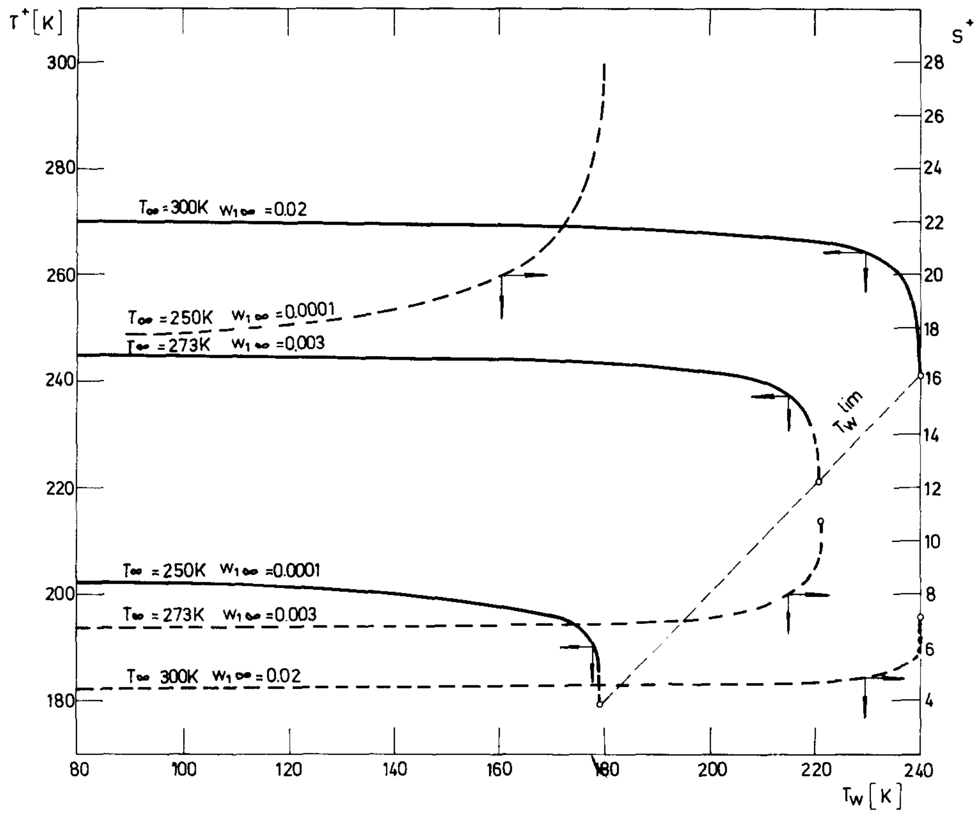

FIG. 3. Temperature and supersaturation on the fog sublayer boundary.

dependence of the supersaturation leads us to the logical and expected conclusion that the fog sublayer forms more easily at lower temperatures of the isothermal surface but that this in no way means a direct proportion between the two.

EXPERIMENTAL OBSERVATIONS

Fog sublayer near cryosurface

An experimental analysis of the fog sublayer phenomenon in the boundary layer was carried out by observing the system in which the moist air of the known parameters ($p = 10^5$ Pa; T_∞, $w_{1\infty}$) was in contact with the vertical isothermal plate (185 × 50 mm) whose temperature was maintained at the level of 160 K by means of a liquid nitrogen freezing system. The schemata of the apparatus used for the phenomenological analysis is shown in Fig. 4.

The stand of the optical system, used to control thickness of the fog sublayer, was placed on the optical bench so that it had two degrees of freedom of movement. The optical system consisted of a light tube which carried in homogeneous light from the monochromator, a system for collimating and turning the light beam into the tangential plane parallel to the isothermal surface, and a phototransistor which controlled the attenuation of the beam as it reached the fog sublayer boundary.

The fog sublayer was photographed with a high speed camera placed on the lateral side of the isothermal surface. By directly observing and studying the films, it was established that the sublayer is formed as a stable quasi-steady structure. The sublayer is laminar under experimental conditions until frost

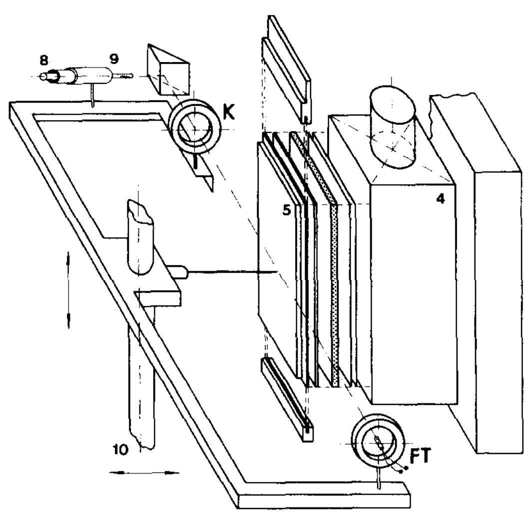

FIG. 4. Experimental apparatus (liquid nitrogen freezing system 4, 5; optical system 8, 9, K, FT; the stand of the optical system 10).

crystals disturb the conditions of flow. The sublayer consists of randomly distributed particles of condensed water vapour. It was not possible, with the methods applied, to determine their phase state. The theoretical analysis carried out here (following the idea of refs. [9, 12 and 16] for calculating the free energies of the liquid and solid phase formation), taking into account the variable density of the condensed phase according to [17], the surface tension according to [17, 18] and extrapolation into the subcooled area (although this extrapolation carries a risk because ignorance of true behaviour of the surface tension of the subcooled phase [19]), shows that the inversion of Ostwald's rule moves to an area of temperatures even lower than those shown in [12]. Therefore, the liquid phase state is formed during the new phase nuclei formation, immediately after which the crystal structure is formed as well. This then is mostly 'icy' fog.

The fog sublayer particles are $r < 10^{-5}$ m in size and possess a pronounced velocity component parallel with the experimental surface in the flow direction within the boundary layer. The theoretically calculated flow velocity in the boundary layer [according to relation (11) at location $x = 0.05$; $y = 0.002$, under the following conditions: $T_\infty = 293$ K, $T_w = 160$ K, $w_{1\infty} = 0.0086$, $p = 10^5$ Pa], is 0.234 m s^{-1}. The experimentally determined particle velocity in the fog sublayer under the same conditions is 0.2 m s^{-1}.

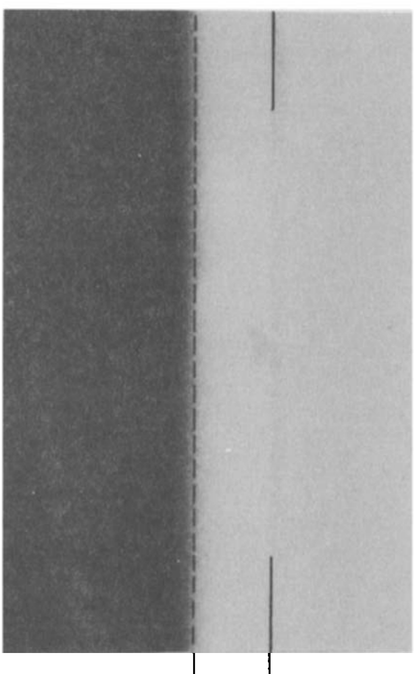

FIG. 5. Fog sublayer ($T_\infty = 302$ K, $T_w = 160$ K, $w_{1\infty} = 0.0115$).

The fog sublayer consists of two regions invisible to the naked eye. Moving from the sublayer boundary to the isothermal surface, in the first area, the fog density increases and along the surface a dense layer of condensed particles is formed.

Figure 5 shows a detail of the fog sublayer within the boundary layer. It gives the theoretically obtained values of the fog sublayer boundary. A strong compatibility can be seen.

Comparison between theoretical and experimental results

Here we shall only compare the theoretically and experimentally determined values of the fog sublayer thickness. Figure 6 shows the comparison between theoretical and experimental results for fog sublayer thickness.

The calculations indicate that the maximum deviation between the theoretically and experimentally determined values is less than 30%, and that the mean is less than 15%.

It is easily observable that as a rule, the experimental data give a greater thickness of the fog sublayer than the theoretical results. This is only to be expected! Namely, the theoretical approach is based on the theory of homogeneous heterophase fluctuations [relation (8)], and the experiment was performed under conditions significantly closer to heterogeneous heterophase fluctuations. This means that real conditions for the spontaneous phase change are considerably easier to achieve and that the sublayer thickness must be greater (the fog sublayer boundary moves towards the region of higher temperatures, i.e. towards lower supersaturation values).

A change in the theoretical approach, in the case of accepting heterogeneous heterophase fluctuations, is analytically simple. Namely, instead of the rule for the new phase nuclei rate under homogeneous conditions (8) and (8a), an expression for the new phase nuclei rate at heterophase heterogeneous fluctuations needs to be used. Of course expression of this dependence in an explicit form, in keeping with the given experimental conditions, still poses a special problem ($S \to 1$) [20–23].

The behaviour of experimentally obtained data in accordance with our expectations reinforces our conviction that introduced Hypotheses 1 and 2 and the approximations, regardless of their radical influence on the mathematical model, present satisfactory theoretical material for following some phenomena during fog sublayer formation within the laminar boundary layer.

CONCLUSIONS

A simplified theoretical model has been elaborated for determining the thermodynamic conditions attending the fog sublayer phenomenon in the laminar binary, free convective boundary layer on the vertical isothermal surface. The model is valid in cases when the

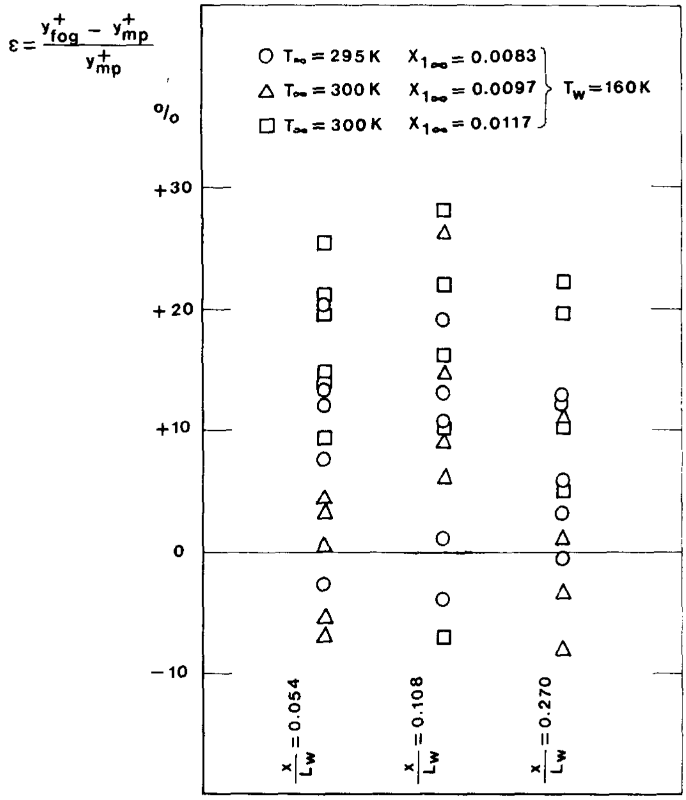

FIG. 6. Comparison between theoretical and experimental results.

inert component of the binary mixture is dominant and homogeneous.

The conditions necessary for fog sublayer formation by homogeneous heterophase fluctuations consist of a combination of the following parameters: the binary mixture temperature (T_∞), isothermal surface temperature (T_w) and condensable component content in the binary mixture ($w_{1\infty}$), along with the fixed total pressure value (p). Temperature decreases in the ambient and an increase of the condensable component content enhance the fog sublayer phenomenon. A rising isothermal surface temperature hinders the fog sublayer phenomenon.

The temperature and supersaturation on the fog sublayer boundary change very little with the isothermal surface temperature change (other conditions being unchanged) until surface temperatures approach the temperature limit T_w^{lim}, when a stable fog sublayer is formed.

The theoretical model has been phenomenologically and quantitatively compared with findings in observing the fog sublayer formed after moist air comes into contact with the isothermal surface at low temperatures. The fog sublayer consists of particles in a liquid and solid state, chaotically distributed within the self-similar sublayer boundary. Concurrence between the theoretically and experimentally obtained values for the thickness of the fog sublayer is within the range of 30%.

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CONDITIONS DE CONDENSATION IRREVERSIBLE PRES D'UNE CRYOSURFACE

Résumé—Les circonstances conduisant à la condensation irréversible par le mécanisme des fluctuations hétérophasiques dans la couche limite sont discutées théoriquement à travers 'l'approximation de couche limite monophasique' (MBL). La théorie classique de nucléation et la théorie de la couche limite binaire monophasique sont toutes deux utilisées pour prédire le changement de phase spontané dans le gaz binaire de la couche limite laminaire de convection naturelle. En opposition à ce qui est appelé 'modèle de sursaturation critique' (CSM), dans l'approximation MBL les champs de température et de concentration du composant condensable ne sont pas déterminés a priori mais plutôt de façon à satisfaire à la fois le système d'équations aux dérivées partielles de la couche limite avec leurs conditions aux limites d'une part, et la condition thermodynamique additionnelle sur la frontière de la sous-couche de brouillard en accord avec la théorie des fluctuations hétéorophasiques, d'autre part. Les résultats de cette analyse sont illustrés par l'exemple d'un mélange binaire d'air et de vapeur d'eau en contact avec une surface verticale isotherme à température cryogénique. Les prévisions théoriques sont comparées avec les données expérimentales.

IRREVERSIBLE KONDENSATION IN DER NÄHE EINER KRYO-OBERFLÄCHE

Zusammenfassung—Die Umstände, welche die irreversible Kondensation in Gestalt der Fluktuation der unterschiedlichen Phasen innerhalb der Grenzschicht begleiten, werden theoretisch beschrieben, mit dem Ziel einer sogenannten 'monophase boundary layer approximation' (MBL). Die klassische Theorie der Keimbildung und die Theorie der einphasigen binären Grenzschicht werden benutzt, um den spontanen Phasenwechsel innerhalb der laminaren Grenzschicht aus binärem Gas bei freier Konvektion vorherzusagen. Im Gegensatz zum 'critical supersaturation model' (CSM) sind bei der MBL-Näherung das Temperaturfeld und die Konzentration der kondensierenden Komponenten nicht von vornherein bestimmt. Dennoch kann das System der partiellen Differentialgleichungen der Grenzschicht und die dazugehörigen Randbedingungen einerseits und die zusätzliche thermodynamische Bedingung für die Grenze der Dampfunterschicht andererseits in Übereinstimmung mit der Theorie der Fluktuation der unterschiedlichen Phasen bestimmt werden. Die Ergebnisse dieser Analyse werden am Beispiel des binären Gemisches aus Luft und Wasserdampf beim Kontakt mit einer vertikalen isothermen Oberfläche von sehr tiefer Temperatur erläutert. Die theoretischen Ergebnisse wurden mit experimentellen Werten verglichen.

УСЛОВИЯ НЕОБРАТИМОЙ КОНДЕНСАЦИИ НА КРИОПОВЕРХНОСТИ

Аннотация—В рамках аппроксимации, называемой 'аппроксимацией многофазного пограничного слоя' (МПС), проведено теоретическое исследование условий, сопутствующих необратимой конденсации, для механизма гетерофазных флуктуаций внутри пограничного слоя. При расчетах мгновенных фазовых изменений в свободноконвективном ламинарном пограничном слое бинарного газа применяются как классическая теория нуклеации, так и теория многофазного бинарного пограничного слоя. В противоположность модели, называемой 'моделью критического перенасыщения' (МКП), при МПС-аппроксимации поля температуры и концентрации конденсирующегося компонента не определяются заранее, а должны удовлетворять как системе дифференциальных уравнений в частных производных для пограничного слоя и соответствующим граничным условиям, с одной стороны, так и дополнительному термодинамическому условию, выполняющемуся на границе подслоя, в соответствии с теорией гетерофазных флуктуаций, с другой. Результаты этого анализа проиллюстрированы на примере контакта бинарной смеси, состоящей из воздуха и водяного пара, с вертикальной изотермической поверхностью, поддерживаемой при низкой температуре. Дано сравнение теоретических расчетов с экспериментальными данными.