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1 Kinetic simulation of the non-equilibrium effects at the
2 liquid-vapor interface

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7 **Abstract**

Phase change phenomena at microscale is important for novel cooling microsystems with intensive evaporation, so the development of reliable models and simulations are challenging. The vapor behaviors near its condensed phase are simulated using the non-linear S-model kinetic equation. The pressure and temperature jumps obtained numerically are in good agreement with the analytical expressions derived from the appropriate Onsager-Casimir reciprocity relations. The results of the evaporation flux are close to those given by the Hertz-Knudsen-Schrage formula, only when the values of the pressure and temperature at the upper boundary of the Knudsen layer are used. Comparison with recently measured temperature jumps are provided and disagreement with some experiments are discussed.

8 *Keywords:* liquid-vapor interface, evaporation rate, Knudsen layer, molecular
9 mean free path, non-equilibrium state, temperature and pressure jumps

10 **1. Introduction**

11 Understanding of heat and mass transfer mechanisms at liquid-vapor interface
12 is important not only from the fundamental point of view, but also for
13 various applications, such as for the design and optimization of the cooling microsystems.
14 During the evaporation process a thin layer, the Knudsen layer, forms near the liquid interface
15 at the vapor side. Inside this layer, which thickness is of the order of several mean free paths,
16 the vapor is in equilibrium state only when the flux of the evaporation molecules is equal to the flux
17 of the condensed molecules. When a net evaporation (or condensation) flux exists a vapor near
18 the interface is in non-equilibrium state and the continuity of the thermodynamic variables,
19 like pressure and temperature, cannot be ensured anymore. This non-equilibrium behavior of a
20 vapor cannot be described by the continuum equations and other approaches, as the gas kinetic
21 theory and molecular dynamics have to be implemented.

22 From a two decades different authors [1], [2], [3], [4] have measured the liquid and vapor
23 properties namely the temperature profiles and the temperature

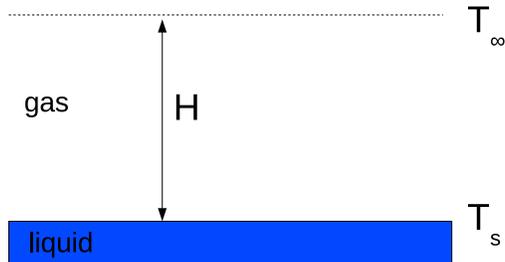


Figure 1: Problem configuration.

26 jump at the liquid-vapor interfaces. In all these experiments the temperature
 27 jump measured on the interface was found surprisingly large, much larger than
 28 that predicted by the kinetic theory of gases. Only recently, the new series of
 29 measurements [5], [6] have appeared, where the temperature jump was found
 30 of the same order as that predicted by the kinetic theory. However, still in re-
 31 cent papers [6], [7] the temperature in vapor near interface was measured higher
 32 compared to the interface temperature. The positive values of the temperature
 33 difference between liquid and vapor temperatures at interface (vapor tempera-
 34 ture is lower than the interface temperature) were measured only by the authors
 35 of Ref. [5].

36 To go forward in the understanding of the flow behavior at liquid-vapor
 37 interface the gas flow evaporating from its condensed phase is investigated on
 38 the basis of the kinetic approach. The non-linear S-model kinetic equation
 39 [8] is solved numerically by the Discrete Velocity Method (DVM) [9]. The
 40 structure of the Knudsen layer is analyzed and the macroscopic temperature
 41 and pressure jumps, obtained from the numerical simulations, are compared
 42 with the analytical expressions derived by the authors of Ref. [10] from the
 43 kinetic theory of gases and the thermodynamics of irreversible processes. The
 44 experimental data of Refs. [4] and [6] are used as input parameters for the
 45 numerical analysis.

46 2. Problem statement

47 We consider a plane condensed phase at rest occupying the half space ($y' <$
 48 0), and the gas (vapor) evaporating from this infinite planar surface kept at
 49 constant and uniform temperature T_s . The interface is located at $y' = 0$, where
 50 y' is the variable normal to the condensed phase surface, see Fig. 1. The steady
 51 one-dimensional flow is considered.

52 When a gas is near a surface (liquid or solid) a thin layer, the Knudsen layer,
 53 forms in the vicinity of the surface. The thickness of this layer is usually of the
 54 order of several molecular mean free paths. To estimate the thickness of this
 55 layer we use the equivalent mean free path defined as [11]:

$$\ell_s = \frac{\mu_s v_s}{p_s}, \quad (1)$$

56 using the reference parameters with subscript s , corresponding to the vapor
 57 characteristics at the condensed phase surface. In Eq. (1) $\mu_s = \mu(T_s)$ is the
 58 dynamic viscosity of the vapor phase

$$\mu(T') = \mu_s \sqrt{\frac{T'}{T_s}} \quad (2)$$

59 at temperature T_s , v_s is the most probable molecular speed,

$$v(T') = \sqrt{2\mathcal{R}T'}, \quad (3)$$

60 calculated also at the temperature T_s : $v_s = v(T_s)$, $\mathcal{R} = k_B/m$ is the specific gas
 61 constant, k_B is the Boltzmann constant, m is the molecular mass.

62 The upper boundary of the computational domain is far from the evaporation
 63 surface, at the distance H , see Fig. 1. Different values of H are tested and finally
 64 $H = 25\ell_s$ is retained to do all the simulations.

65 3. S-model kinetic equation

66 To model the evaporation process of a monoatomic gas from its condensed
 67 phase the S-model kinetic equation [8] is used. The evaporation phenomenon
 68 is considered here as one dimensional in physical space, so the S-model kinetic
 69 equation is written as

$$\frac{\partial f}{\partial t'} + v_y \frac{\partial f}{\partial y'} = v' (f^S - f), \quad (4)$$

70 where $f(t', y', \mathbf{v})$ is the one particle velocity distribution function, t' is the time,
 71 $\mathbf{v} = (\mathbf{v}_x, \mathbf{v}_y, \mathbf{v}_z)$ is the molecular velocity vector, v' is the collision frequency,
 72 $v' = p'/\mu'$, p' is the gas pressure. In the frame of the S-model the equilibrium
 73 distribution function f^S in Eq. (4) is defined as following

$$f^S(t', y', \mathbf{v}) = f^M \left[1 + \frac{2m\mathbf{V}\mathbf{q}'}{15n'(y')(k_B T'(y'))^2} \left(\frac{m\mathbf{V}^2}{2k_B T'(y')} - \frac{5}{2} \right) \right], \quad (5)$$

74 here $T'(y')$ is a gas temperature, $n'(y')$ is a gas number density, $\mathbf{u}' = (0, u'_y, 0)$ is
 75 a bulk velocity vector, $\mathbf{V} = \mathbf{v} - \mathbf{u}'$ is the peculiar velocity vector, $\mathbf{q}' = (0, q'_y, 0)$
 76 is a heat flux vector, f^M is the Maxwellian distribution function [12]. The
 77 macroscopic parameters are defined as follows:

$$\begin{aligned} n'(y') &= \int f(y', \mathbf{v}) d\mathbf{v}, & u'_y(y') &= \frac{1}{n'} \int f(y', \mathbf{v}) v_y d\mathbf{v}, \\ T'(y') &= \frac{m}{3k_B n'} \int f(y', \mathbf{v}) V^2 d\mathbf{v}, & q'_y(y') &= \frac{m}{2} \int f(y', \mathbf{v}) V^2 (v_y - u'_y) d\mathbf{v} \end{aligned} \quad (6)$$

78 The evaporation flow rate, expressed in the number of molecules evaporating
 79 per seconds and per unit area, J'_n , and the evaporation mass flow rate, expressed

80 in mass of vapor (in kilogram) per second evaporating from a unit area, J'_m , are
 81 defined as following:

$$J'_n = \int v_y f(y', \mathbf{v}) d\mathbf{v}, \quad J'_m = m \int v_y f(y', \mathbf{v}) d\mathbf{v}. \quad (7)$$

82 The second definition of the evaporation mass flow rate is usually provided from
 83 the experiments. It is clear that previous relations represent the conservation
 84 of the number of particles and the mass conservation. Additionally, the y mo-
 85 mentum and energy conservation are written as

$$J'_{v_y} = \int v_y^2 f(y', \mathbf{v}) d\mathbf{v}, \quad J'_E = m \int v_y v^2 f(y', \mathbf{v}) d\mathbf{v}. \quad (8)$$

86 The constancy of J'_m , J'_{v_y} , and J'_E will be used for the accuracy test of the
 87 applied numerical method.

88 4. Boundary conditions

89 The distribution function of evaporating molecules is assumed to be a half-
 90 range Maxwellian:

$$f(t, 0, \mathbf{v}) = (\sigma n_s + (1 - \sigma) n_r) \left(\frac{m}{2\pi k_B T_s} \right)^{3/2} \exp(-mv^2/(2k_B T_s)), \quad v_y > 0, \quad (9)$$

91 were

$$n_r = -\sqrt{\frac{2\pi m}{k_B T_s}} \int_{v_y < 0} f v_y d\mathbf{v}. \quad (10)$$

92 Here n_s is the number density, calculated from the saturated surface temper-
 93 ature and pressure as $n_s = p_s/(k_B T_s)$. The coefficient σ that is a part of the
 94 incident molecules evaporating immediately from the condensed surface, while
 95 $(1 - \sigma)$ part of molecules is assumed to be reflected diffusively from the interface.

96 The uniform equilibrium vapor state (subscript ∞) is described by the equi-
 97 librium Maxwellian distribution function

$$f(t, H, \mathbf{v}) = \frac{p_\infty}{k_B T_\infty} \left(\frac{m}{2\pi k_B T_\infty} \right)^{3/2} \exp(-m(\mathbf{v} - \mathbf{u}_\infty)^2/(2k_B T_\infty)), \quad v_y < 0, \quad (11)$$

98 where $\mathbf{u}_\infty = (0, u_{y\infty}, 0)$. As it was discussed in Refs. [13], [14], [15], in the case
 99 of evaporation, a solution of the boundary value problem exists only when some
 100 relations between the parameters are satisfied. In the case of evaporation these
 101 relations are given by [14]

$$\frac{p_\infty}{p_s} = h_1(Ma_{y\infty}), \quad \frac{T_\infty}{T_s} = h_2(Ma_{y\infty}). \quad (12)$$

102 The functions h_1 and h_2 are obtained numerically and their tabulated values can
 103 be found in Ref. [14]. In the case of weak evaporation conditions, that means

104 that the variation from the uniform equilibrium state at rest with pressure and
 105 temperature is small (or where the evaporation is weak, *i.e.* evaporation Mach
 106 number is small compared to 1), the relations between three parameters become

$$\frac{p_\infty}{p_s} = 1 + C_4^* \frac{u_{y\infty}}{\sqrt{2\mathcal{R}T_s}}, \quad \frac{T_\infty}{T_s} = 1 + d_4^* \frac{u_{y\infty}}{\sqrt{2\mathcal{R}T_s}}, \quad (13)$$

107 where $C_4^* = -2.13204$ and $d_4^* = -0.44675$, obtained with Boltzmann-Krook-
 108 Welander (BKW) model in Ref. [16]. The previous relations give the boundary
 109 conditions for the Euler equations. However, for the Navier-Stokes equations
 110 more complete boundary conditions have to be used on the liquid-vapor interface,
 111 which are discussed in Section 6.

112 The number and the nature of conditions (12) are different for evaporation
 113 and condensation flows [14], [15].

114 5. Dimensionless form

115 For further derivation we introduce the following dimensionless quantities:

$$y = \frac{y'}{\ell_s}, \quad \mathbf{c} = \frac{\mathbf{v}}{v_s}, \quad \mathbf{u} = \frac{\mathbf{u}'}{v_s}, \quad t = t' \frac{v_s}{\ell_s}, \quad n = \frac{n'}{n_s}, \quad T = \frac{T'}{T_s}, \quad \mathbf{q} = \frac{\mathbf{q}'}{p_s v_s}. \quad (14)$$

116 Now the dimensionless S-model kinetic equation can be written in the form:

$$\frac{\partial f}{\partial t} + v_y \frac{\partial f}{\partial y} = n\sqrt{T} (f^S - f). \quad (15)$$

117 The dimensionless boundary conditions for the distribution function of the re-
 118 flected molecules at the liquid-vapor interface can be written as

$$y = 0, \quad t > 0, \quad c_y > 0, \\ f(t, 0, \mathbf{c}) = (\sigma n_s + (1 - \sigma)n_r) f_s^M, \quad f_s^M = \frac{1}{\pi^{3/2}} \exp(-c^2). \quad (16)$$

119 The number density n_r can be calculated from the impermeability condition on
 120 the condensed surface:

$$n_r = -2\sqrt{\pi} \int_{c_y < 0} c_y f d\mathbf{c}. \quad (17)$$

121 As it was mentioned in previous section far from the condensed surface the gas is
 122 supposed in equilibrium steady-state, so for the molecules coming from infinity
 123 two parameters from three in the Maxwellian depend on the third one. Here we
 124 fix the macroscopic flow velocity in the Maxwellian distribution function as

$$y = H, \quad t > 0, \quad c_y < 0, \quad f_\infty^M = \frac{1}{\pi^{3/2}} \frac{p_\infty}{p_s} \left(\frac{T_s}{T_\infty} \right)^{5/2} \exp\left(-\frac{T_s}{T_\infty} (u_{y\infty} - c)^2 \right). \quad (18)$$

125 At the upper boundary initially, at $t = 0$, all three parameters, p_∞ , T_∞ and $u_{y\infty}$
 126 are fixed, and the distribution function for the incoming molecules is calculated

127 from Eq. (18), then only the macroscopic velocity is still kept constant, but
 128 other two parameters are obtained from previous time step.

129 To minimize the computational efforts, the c_z variable is eliminated by intro-
 130 ducing the reduced distribution functions as in Ref. [17]. The Discrete Velocity
 131 Method [9] was used to solve Eq. (15) with the boundary conditions Eqs. (16),
 132 (17) and (18). The details of the numerical realization can be found in [18].

133 6. Jump boundary conditions

134 In this Section we present the jump boundary conditions by following the
 135 approach based on the Onsager-Casimir reciprocity relations, as it was presented
 136 in Ref. [19] for the case of evaporation and condensation of a gas between two
 137 parallel condensed phases. In the case of evaporation from a plate liquid surface
 138 we can introduce, by analogy with [19], the thermodynamic "forces" as following

$$X_P = \frac{p_\infty - p_s}{p_s}, \quad X_T = \frac{T_\infty - T_s}{T_s}. \quad (19)$$

139 We assume then that the deviations between the temperature of the condensed
 140 surface and that far from it and the corresponding pressures are small: $X_P \ll 1$
 141 and $X_T \ll 1$. For a given gas the pressure and temperature differences are
 142 coupled by the relation

$$p_s - p_\infty = \beta(T_s - T_\infty), \quad (20)$$

143 where β is a positive constant corresponding to the slop of the Clausius-Clapeyron
 144 curve at T_s , so X_P and X_T are not independent quantities. However, here we
 145 will consider two forces separately, to see clearly the impact of each force on the
 146 evaporation process.

147 Following [19] we introduce the "fluxes" corresponding to the driving "forces"
 148 as:

$$J'_P = -n_s u'_y, \quad J'_T = -\frac{1}{k_B T_s} q'_y, \quad (21)$$

149 where u'_y and q'_y do not depend on y . The thermodynamic fluxes are related to
 150 the thermodynamic forces in the matrix form:

$$\begin{bmatrix} J'_P \\ J'_T \end{bmatrix} = \begin{bmatrix} \Lambda'_{PP} & \Lambda'_{PT} \\ \Lambda'_{TP} & \Lambda'_{TT} \end{bmatrix} \times \begin{bmatrix} X_P \\ X_T \end{bmatrix}. \quad (22)$$

151 The Onsager-Casimir relation $\Lambda'_{PT} = \Lambda'_{TP}$ in this case yields the coupling be-
 152 tween the mass flux caused by temperature drop and the thermal flux caused
 153 by the pressure drop [19].

154 Previous equation allows to express the thermodynamic fluxes in function of
 155 the thermodynamic forces. In this way the expressions analogous to the Hertz-
 156 Knudsen equation are obtained in the end of this Section. However, first we are

157 interested to express the thermodynamic forces in function of fluxes, so we can
 158 write

$$\begin{bmatrix} X_P \\ X_T \end{bmatrix} = \begin{bmatrix} \Lambda'_{PP} & \Lambda'_{PT} \\ \Lambda'_{TP} & \Lambda'_{TT} \end{bmatrix}^{-1} \times \begin{bmatrix} J'_P \\ J'_T \end{bmatrix} = \begin{bmatrix} a'_{11} & a'_{12} \\ a'_{21} & a'_{22} \end{bmatrix} \times \begin{bmatrix} J'_P \\ J'_T \end{bmatrix}. \quad (23)$$

159 The elements $a'_{ij} = a_{ij}/(n_s v_s)$ in previous relation are obtained in [10], [20],
 160 from gas kinetic theory for the case of the diffuse reflection of the molecules
 161 from a surface. The coefficients a_{ij} have the following values:

$$a_{11} = 2\sqrt{\pi} \left(\frac{1}{\sigma} - b_{11} \right), \quad a_{12} = a_{21} = 2\sqrt{\pi} b_{12}, \quad a_{22} = 2\sqrt{\pi} b_{22}, \quad (24)$$

162 where

$$b_{11} = \frac{1}{\pi} - \frac{23}{32}, \quad b_{12} = \frac{1}{16} + \frac{1}{5\pi}, \quad b_{22} = \frac{1}{8} + \frac{13}{25\pi}. \quad (25)$$

163 The numerical values of a_{ij} coefficients for $\sigma = 1$ are the following

$$a_{11} = 2.125, \quad a_{12} = a_{21} = 0.447, \quad a_{22} = 1.030. \quad (26)$$

164 In Ref. [10] a particular approximation method was used to evaluate the nu-
 165 merical values of a_{ij} coefficients. Other approximation methods have also been
 166 used and give slightly different values, see Ref. [14].

167 Finally the pressure and temperature jumps can be expressed as following:

$$\frac{p_s - p_\infty}{p_s} = a_{11} \frac{J'_m}{mn_s v_s} + a_{12} \frac{q'}{p_s v_s}, \quad (27)$$

168

$$\frac{T_s - T_\infty}{T_s} = a_{21} \frac{J'_m}{mn_s v_s} + a_{22} \frac{q'}{p_s v_s}. \quad (28)$$

169 In previous expressions J'_m and q' are the evaporation mass flux (7) and the
 170 heat flux (6) outside from the Knudsen layer in the continuum part of the flow.
 171 As it is clear from the previous relations that the intensity of pressure and
 172 temperature jumps is proportional to both mass and heat fluxes. It is worth
 173 to note that this form of jumps expression is similar to Eqs. (13), but in the
 174 present form the heat exchange is also considered.

175 As it was pointed out in [21] if one uses as the surface temperature the tem-
 176 perature of the adjacent liquid, the results found using non-equilibrium ther-
 177 modynamics and the results obtained from the kinetic theory are in perfect
 178 agreement with each other.

179 We can also express the fluxes in the function of forces from Eq. (22) as

$$\begin{bmatrix} J'_P \\ J'_T \end{bmatrix} = \begin{bmatrix} \Lambda'_{PP} & \Lambda'_{PT} \\ \Lambda'_{TP} & \Lambda'_{TT} \end{bmatrix} \times \begin{bmatrix} X_P \\ X_T \end{bmatrix} = \begin{bmatrix} a''_{22} & -a''_{12} \\ -a''_{21} & a''_{11} \end{bmatrix} \times \begin{bmatrix} X_P \\ X_T \end{bmatrix}, \quad (29)$$

180 where $a''_{ij} = a_{ij} n_s v_s / \mathcal{D}$ and $\mathcal{D} = a_{11} a_{22} - a_{12} a_{21}$. From (29) we have

$$\frac{J'_m}{mn_s v_s} = \frac{1}{\mathcal{D}} \left(a_{22} \frac{p_s - p_\infty}{p_s} - a_{12} \frac{T_s - T_\infty}{T_s} \right), \quad (30)$$

181

$$\frac{q'}{p_s v_s} = \frac{1}{\mathcal{D}} \left(-a_{21} \frac{p_s - p_\infty}{p_s} + a_{11} \frac{T_s - T_\infty}{T_s} \right). \quad (31)$$

182 Previous relations are analogous to that obtained from non-equilibrium ther-
 183 modynamics [21], [22]. We can provide the explicite expressions for the surface
 184 resistivities

$$\begin{aligned} \frac{a_{22}}{\mathcal{D}} &= \frac{\sigma}{2\sqrt{\pi}(1 + \sigma(b_{11} - b_{12}^2/b_{22}))} = \frac{\sigma}{2\sqrt{\pi}(1 - 0.455\sigma)}, \\ \frac{a_{12}}{\mathcal{D}} &= \frac{\sigma b_{12}}{2\sqrt{\pi}b_{22}(1 + \sigma(b_{11} - b_{12}^2/b_{22}))} = \frac{0.434\sigma}{2\sqrt{\pi}(1 - 0.455\sigma)}, \\ \frac{a_{11}}{\mathcal{D}} &= \frac{1 + \sigma b_{11}}{2\sqrt{\pi}b_{22}(1 + \sigma(b_{11} - b_{12}^2/b_{22}))} = \frac{1 - 0.4\sigma}{2\sqrt{\pi}0.291(1 - 0.455\sigma)}. \end{aligned} \quad (32)$$

185 The numerical values of the coefficients provided above for evaporation coeffi-
 186 cient equal to 1 are:

$$\frac{a_{22}}{\mathcal{D}} = 0.517, \quad \frac{a_{12}}{\mathcal{D}} = 0.225, \quad \frac{a_{11}}{\mathcal{D}} = 1.068. \quad (33)$$

187 6.1. Hertz-Knudsen-Schrage formula

188 More than one hundred year ago Hertz and Knudsen [23], considering only
 189 the fluxes balance near the liquid interface, proposed the equation which relate
 190 the evaporation flux to the liquid temperature (and pressure) and to the pa-
 191 rameters on the upper boundary of the Knudsen layer. The flux of the particles
 192 evaporated from a surface was estimated from the gas kinetic theory as

$$J'_n = \frac{n_s v_{ms}}{4}, \quad \text{where} \quad v_{ms} = \sqrt{\frac{8k_B T_s}{\pi m}}, \quad (34)$$

193 where v_{ms} is the average molecular velocity at the interface temperature. The
 194 same molecular flux comes to the interface from the Knudsen layer with the
 195 parameters n_∞ and T_∞ . The balance of the fluxes allows to derive the Hertz-
 196 Knudsen formula

$$J'_m = \sqrt{\frac{m}{2\pi k_B}} \left(\frac{p_s}{\sqrt{T_s}} - \frac{p_\infty}{\sqrt{T_\infty}} \right). \quad (35)$$

197 This expression was improved by Kucherov and Rikenglas [24], [25] and then
 198 by Schrage [26] by taking into account the macroscopic vapor velocity and by
 199 introducing the evaporation coefficient as:

$$J'_m = \frac{2\sigma}{2 - \sigma} \sqrt{\frac{m}{2\pi k_B}} \left(\frac{p_s}{\sqrt{T_s}} - \frac{p_\infty}{\sqrt{T_\infty}} \right). \quad (36)$$

200 Later, many various modifications of this expression were proposed to much it
 201 with the measurements. However, this formula provides the evaporation flux

202 much larger than one found in experiments [4] for measured large value of the
 203 temperature jump. We show in the next Section that this expression works well
 204 only when the p_∞ and T_∞ are taken in the upper boundary of the Knudsen
 205 layer, where it is very difficult to make the measurements because of the very
 206 thin thickness of this layer.

207 6.2. Comments on Jumps

208 It is worth to discuss first the definition of the temperature jump as it is used
 209 in the kinetic theory. This jump is defined as a difference between the solid (or
 210 liquid) surface temperature, T_s , and the gas temperature near the surface, $T|_{y=0}$.
 211 It is well known [27], [14] that near a surface a very thin layer, the Knudsen
 212 layer, exists, whose thickness is of the order of several molecular mean free paths.
 213 Inside this layer the continuum approach does not hold any more. Therefore
 214 the temperature jump boundary condition is used for the Navier-Stokes (NS)
 215 equations:

$$T|_{y=0} - T_s = \xi_T \ell \frac{dT}{dy}, \quad (37)$$

216 where ξ_T is the temperature jump coefficient [12], [11]. This condition assures
 217 that the solution of the NS equation with the jump condition coincides with the
 218 solution of the Boltzmann equation (or of other kinetic equations) on the upper
 219 boundary of the Knudsen layer. It is clear from Eq. (37) that in the case of
 220 the gas - solid interface the temperature jump ($T|_{y=0} - T_s$) is proportional to
 221 the molecular mean free path. Therefore this jump becomes negligible under
 222 atmospheric conditions where the molecular mean free path is small, of the
 223 order of a micron. This temperature jump has to be taken into account either
 224 under reduced pressure conditions or in the microsystem applications, when the
 225 characteristic length-scale of a flow is of the order of tens of microns.

226 When the liquid-gas interface is considered, this difference between the gas
 227 temperature and surface temperature, $T_s - T|_{y=0}$, exists also. However, his-
 228 torically, the difference between the temperature at the upper boundary of the
 229 Knudsen layer and the surface temperature, $T_s - T|_{y=H}$ is called the tempera-
 230 ture jump. As in the case of the gas-solid interface the NS equations do not hold
 231 inside the Knudsen layer. Therefore, the boundary conditions, Eqs. (27), (28),
 232 are proposed to use for the Navier-Stokes equations [28] to take into account the
 233 Knudsen layer influence. The implementation of these conditions ensures that
 234 both solutions: the solution of the NS equations with temperature and pressure
 235 jump boundary conditions and the solution of the kinetic equation coincide on
 236 the upper boundary of the Knudsen layer.

237 In addition, contrarily to the gas-solid interface, in the case of the gas-liquid
 238 interface one more condition for the pressure jump exists. Both pressure and
 239 temperature jumps are proportional to the mass and heat fluxes, and so depend
 240 on their intensity.

241 Figure 2 schematically demonstrates the temperature profile normal to the
 242 liquid-vapor interface, located at $y = 0$, as it can be obtained from the solution
 243 of a kinetic equation, see also next Section with the numerical results. From

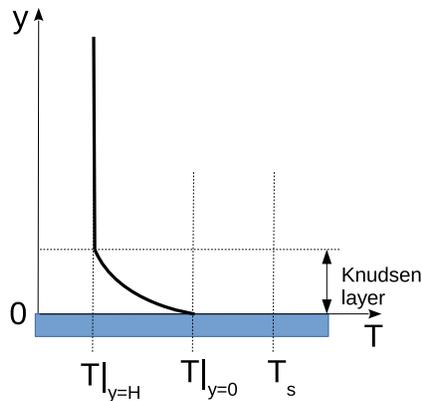


Figure 2: Temperature profile and temperature jump definition at liquid-vapor interface.

244 Fig. 2 it is clear that the strong temperature gradient is observed inside the
 245 Knudsen layer, then the temperature reaches asymptotically its value far from
 246 the Knudsen layer in the continuum region. In adopted here simulations we as-
 247 sume the absence of the macroscopic parameter gradient outside of the Knudsen
 248 layer.

249 7. Results

250 We present here a first step of application of non-linear S-model kinetic
 251 equation for modeling of evaporation process in the case, where the calculations
 252 have been made under assumption of the constant temperature in the vapor
 253 continuum region, so the heat flux in vapor phase is negligible. However, the
 254 model can be adopted to the situation, when the heat flux is important in the
 255 vapor continuum region.

256 7.1. Comparison with experiments

257 Recently several experiments are carried out to measure the temperature
 258 discontinuities on the liquid-gas interfaces in the case of pure substance evap-
 259 oration [3], [4], [6] and in the case of presence of non-condensable gas [5]. We
 260 analyse here the experimental results, provided from Refs. [4] and [6], where
 261 evaporation process of pure substance (water) is considered. To compare with
 262 the measurements of the water evaporation the expressions provided in [29] is
 263 used to calculate the saturation pressure value from the measured liquid water

experimental data	Operating conditions [4]		
	30°C	50°C	80°C
$T_s(^{\circ}C)$	2.65	4.66	-9.76
$p_s(Pa)^1$	738.8	851.2	291.9
$T_v(^{\circ}C)$	6.64	10.91	4.69
$p_v(Pa)$	736.0	847.9	288.1
$J \times 10^4[kg/(m^2s)]$	5.78	7.66	11.9
$q \times 10^4[W/m^2]$	-231.45	-396.63	-650.56

Table 1: Experimental data from Ref. [4]. The saturation pressure p_s^1 is calculated from the saturation temperature by using the expression provided in Ref. [29].

264 temperature:

$$\begin{aligned}
p_{sat}(T) &= k_1 \exp(k_2 - k_3/T + k_4T - k_5T^2 + k_6T^3 - k_7T^4 - k_8 \ln(T)), \\
k_1 &= 611.2 \quad k_2 = 1045.8511577 \quad k_3 = 21394.6662629 \quad k_4 = 1.0969044 \\
k_5 &= 1.3003741 \times 10^{-3} \quad k_6 = 7.747298 \times 10^{-7} \quad k_7 = 2.1649005 \times 10^{-12} \\
k_8 &= 211.3896559.
\end{aligned} \tag{38}$$

265 It is worth to underline that the specific temperature range of the liquid water
266 was used in the experiments, namely, the water was maintained at the liquid
267 state for the temperatures below 0°C, *i.e.* below its triple point. As it was
268 mentioned in [29], the water is metastable in this temperature range and the
269 measurements are impacted by the possibility of ice formation.

270 The S-model allows us to calculate the evaporation properties of the monoatomic
271 gas. However, the numerical results are compared with the experiments made
272 with water evaporation. To do this, first, all the numerical results were obtained
273 in dimensionless form, then, to provide the dimensional values of the parame-
274 ters of interest the water vapor properties are implemented. In addition, it was
275 shown in Refs. [30], [15], that for the small evaporation rate the influence of the
276 internal degree of freedom of a molecule on the temperature and pressure jumps
277 is still negligible, which justifies here the implementation of the monoatomic gas
278 model.

279 Three sets of experimental data from Ref. [4] and three sets from Ref. [6]
280 were used as initial conditions for the numerical calculations and all these data
281 are provided in Tables 1 and 2. The indications 30°C, 50°C and 80°C are used
282 to refer to the operating conditions from Ref. [4]. All simulations have been
283 made with the evaporation coefficient equal to 1.

284 Figures 3 (a)-(d) show the profiles of the pressure in [Pa] and temperature
285 [°C] as a function of a distance (in [μm]) from the liquid surface for two cases,
286 heating 30°C and 50°C, from the experimental data of Ref. [4]. For each Figure
287 the maximum value on the y axis corresponds to the value of saturation pressure
288 (temperature) of the liquid layer. Both temperature and pressure jumps are
289 visible on Figures and they are associated to the difference between the saturated
290 values on the interface and on the upper boundary of the Knudsen layer.

experimental data	Operating conditions [6]		
	case 1	case 4	case 7
$T_s(^{\circ}C)$	-10.82 ± 0.05	-4.52 ± 0.05	4.08 ± 0.05
$p_s(Pa)$	265.7 ± 1.3	435.7 ± 2.2	815.5 ± 4.1
$p_s(Pa)^1$	268.43	437.17	817.28
$J \times 10^4 [kg/(m^2s)]$	3.6350	3.1967	1.9532

Table 2: Experimental data from Ref. [6]. The saturation pressure p_s^1 is calculated from the saturation temperature by using the expression provided in Ref. [29]. The values of the evaporation flux were additionally provided by the authors of Ref. [6].

291 For two surface temperatures, $T_s = 2.65^{\circ}C$ and $T_s = 4.66^{\circ}C$ and correspond-
292 ing saturation pressures, see Table 1, the molecular mean free path, estimated
293 using Eq. (1), is equal to $6.31 \mu m$ and $5.60 \mu m$, respectively, so the Knud-
294 sen layer thickness for both cases is of the order of 2 mean free paths. It is
295 worth to note that here we use the so-called equivalent mean free path, Eq. (1),
296 while various other definitions exist in the literature, which take into account
297 different molecular interaction models. However, all these expressions provide
298 similar order of magnitude of the mean free path. We would like also to un-
299 derline that the calculated numerically Knudsen layer thickness is much smaller
300 than thermocouple bed size, used in experiments [4], which was referred to be
301 of $25 \mu m$.

302 The profiles of the heat flux, in $[W/m^2]$, are also presented on Fig. 3 (e)
303 and (f). The heat flux changes its sign through the Knudsen layer: it is positive
304 near the liquid surface and become negative outside of this layer.

305 From Figure 3 it is clear that all parameters have the gradients inside the
306 Knudsen layer, which thickness is around of $10 \mu m$ for two cases. Outside the
307 Knudsen layer all parameters are quasi constant. It is worth to note that only
308 one dimensional problem is considered here, therefore the constancy of the mass,
309 momentum and full energy fluxes have to be conserved. However, the numerical
310 values of the mass, momentum and full energy fluxes, Eqs. (7) and (8), which
311 should theoretically be constant, show small variations over $0 < y < 1$. To
312 quantify these variations we introduce the deviation, $dev(J)$, of the numerical
313 values of a flux from its average, [31] *i.e.*,

$$dev(J) = \frac{1}{N_y} \sum_{j=1}^{N_y} \frac{|J(y_j) - J_{av}|}{|J_{av}|}, \quad J_{av} = \frac{1}{N_y} \sum_{j=1}^{N_y} J(y_j), \quad (39)$$

314 here N_y is the number of the computational points between 0 and 1 in y direc-
315 tion. These deviations for the evaporation (mass) and energy fluxes are provided
316 in Table 3 and they are used as the accuracy test of the numerical computations.

317 As it is clear from Figure 3 the gradients of all macroscopic parameters
318 exist in the Knudsen layer. As the continuum approach does not allow to
319 simulate the flow behaviors inside the Knudsen layer the values obtained from
320 the numerical solution of the S-model kinetic equation, *i.e.* the value on the
321 upper boundary of the Knudsen layer, must be used as the boundary conditions,

Operating conditions [4]	$\text{dev}(J_m) \times 10^{-5}$	$\text{dev}(J_E) \times 10^{-5}$
30°C	0.203	0.170
50°C	0.237	0.171
80°C	0.303	0.179

Table 3: Deviations, Eq. (39) for the evaporation (mass) and full energy fluxes for different experimental conditions from Ref. [4].

Operating conditions [4]	$J'_m \times 10^4 [kg/(m^2s)]$				
	Eq. (30)	HKS ¹	HKS ²	S-model	[4]
30°C	5.17	179.8	5.49	5.88	5.78
50°C	8.73	281.7	9.39	7.86	7.66
80°C	12.80	261.1	13.74	12.70	11.9

Table 4: Mass flow rate $J'_m \times 10^4$ in $kg/(m^2s)$, obtained from: Eq. (30), second column; HKS¹, Hertz-Knudsen-Schrage formula (36) with experiment data $T_s(p_s)$ and $T_\infty = T_v$, $p_\infty = p_v$ from [4], third column; HKS², Hertz-Knudsen-Schrage formula (36) with experimental data $T_s(p_s)$, T_∞ and p_∞ are taken from numerical solution of the S-model kinetic equation, fourth column; numerical S-model results, fifth column; experimental data [4], sixth column.

322 when the continuum approach is applied with the Navier-Stokes equation in
323 order to describe correctly the interface behaviors.

324 Table 4 gives the values of the average over distance evaporation rate J'_m ,
325 obtained by different ways. Second column presents the results derived from the
326 Onsager-Casimir theory, Eq. (30), with the pressure and temperature values, p_∞
327 and T_∞ , obtained numerically from the solution of the S-model kinetic equation;
328 third column, HKS¹, Hertz-Knudsen-Schrage formula (36) with experiment data
329 [4], with $T_s(p_s)$ and $T_\infty = T_v$, $p_\infty = p_v$ given in Table 1; fourth column HKS²,
330 Hertz-Knudsen-Schrage formula (36) with T_∞ and p_∞ obtained from numerical
331 solution of the S-model kinetic equation; fifth column presents the numerical
332 S-model results, sixth column contains the experimental data [4].

333 Analyzing the results presented in Table 4 we can conclude that the nu-
334 merical solution of the S-model kinetic equation provides the results on the
335 evaporation mass flow rate which are very close to the measured values. In ad-
336 dition, expression (30), obtained from Onsager-Casimir theory gives also very
337 similar values of the evaporation flow rate, when the values p_∞ and T_∞ are
338 taken from the numerical results. The Hertz-Knudsen-Schrage expression for
339 mass flow rate, Eq. (36), calculated also with the numerical S-model results
340 gives also similar values. However, when the same Hertz-Knudsen-Schrage ex-
341 pression, Eq. (36), is used but with $p_\infty = p_v$ and $T_\infty = T_v$ (see Table 1) much
342 larger values for the evaporation mass flow rate is obtained. It means that the
343 temperature T_v and pressure p_v , measured in Ref. [4], do not correspond to
344 the upper boundary of a Knudsen layer. Therefore, Eq. (36) overestimates the
345 evaporation rate, when temperature and pressure of vapor are taken at some
346 distance outside the Knudsen layer.

347 One additional comment related to the extraction of the evaporation coeffi-

Operating conditions [4]	$T_s - T_\infty$ [$^{\circ}C$]			
	[4]	Eq. (28) ¹	Eq. (28) ²	S-model
30 $^{\circ}C$	-3.99	-0.15	0.025	0.036
50 $^{\circ}C$	-6.25	-0.23	0.029	0.028
80 $^{\circ}C$	-14.44	-1.09	0.131	0.124

Table 5: Temperature jump $T_s - T_\infty$ in $^{\circ}C$, obtained from: experiments [4], second column; Eq. (28)¹, with experimental values of J'_m and q' from [4], third column; Eq. (28)², where numerical values of J'_m and q' from numerical solution using S-model equation are used, fourth column; numerical S-model results, fifth column.

348 cient can be done. Usually, to extract the values of this coefficient, the Hertz-
349 Knudsen-Schrage expression for evaporation rate, Eq. (36), is implemented.
350 But usually the experimental values of the vapor temperature and pressure far
351 from the liquid interface are used. Therefore, in order to much the measured
352 evaporation rate given by Eq. (36) very small evaporation coefficient have to be
353 used. In our opinion the large amount of the experimental data on the evapo-
354 ration coefficient, where its value was found very small, can be related to this
355 error.

356 The values of the temperature jump, *i.e.* the difference between the inter-
357 face temperature, T_s , and the vapor temperature at the upper boundary of the
358 Knudsen layer, T_∞ , are given in Table 5. Second column provides the measured
359 values of this jump; third column gives the values, calculated from Onsager-
360 Casimir relation, Eq. (28), but using the measured in [4] evaporation rate and
361 heat flux; forth column presents the value obtained from the same Onsager-
362 Casimir relation, Eq. (28), but with evaporation rate and heat flux, obtained
363 numerically from the solution of the S-model kinetic equation; forth column
364 gives the temperature jump obtained numerically. One can see that the exper-
365 imental values are very large compared to the values obtained numerically for
366 very similar evaporation rate.

367 Table 6 provides the values of the temperature jump obtained for three sets
368 of the experimental conditions from Ref. [6] (see also Table 2). As for the
369 experimental data from Ref. [4] the calculated temperature jump is notably
370 smaller than the measured one, despite the fact that the evaporation flux is
371 reproduced numerically with very good accuracy, see Table 7. In addition, for
372 two experimental data Refs. [4] and [6], the calculated vapor temperature near
373 the liquid interface is found lower than that measured one. This fact could be
374 partially explained by the formulation of the boundary condition on the upper
375 boundary of the Knudsen layer. In both experiments the negative (directed
376 to the liquid interface) heat flux exists in the vapor phase outside the Knudsen
377 layer, while in the present form of the boundary condition at the upper boundary
378 of the Knudsen layer the constant vapor temperature is assumed.

379 The values of the pressure jump, *i.e.* $p_s - p_\infty$ are provided in Table 8. Second
380 column gives the jump values calculated from Eq. (27) using numerical values
381 of the evaporation rate and heat flux; third column provides the values obtained
382 directly from the numerical solution of the S-model kinetic equation. The values

Operating conditions [6]	$T_s - T_\infty$ [$^{\circ}C$]	
	[6]	S-model
case 1	-0.36	0.039
case 4	-0.24	0.022
case 7	-0.14	0.0075

Table 6: Temperature jump, $T_s - T_\infty$, in [$^{\circ}C$], comparison with the measured values from Ref. [6].

Operating conditions [6]	$J'_m \times 10^4$ [$kg/(m^2s)$]	
	[6]	S-model
case 1	3.6350	3.6329
case 4	3.1967	3.1957
case 7	1.9532	1.9530

Table 7: Evaporation flux J'_m in [$kg/(m^2s)$], comparison with measured values from Ref. [6].

383 of the pressure jump obtained from both approaches are very similar.

384 Finally, the validation and improvement of the presented kinetic approach
385 should be done by the detailed comparison with the precise measurements for
386 different operating conditions requiring different rarefaction regimes. Such ex-
387 perimental data are practically missing. Such kind of data can be obtained by
388 the contact methods which use the microthermocouples as well as by the more
389 difficult in the realization non-contact methods. As it was pointed out above,
390 the pressure and temperature discontinuities on the vapor-liquid interface are
391 proportional to the evaporation rate and the heat flux through the interface.
392 Therefore, for the future experiments this point should be taken into account
393 to develop a new measurement system.

394 8. Conclusions

395 The kinetic approach is developed for numerical simulation of the evapora-
396 tion process from a liquid surface. This approach allows the detailed simulations
397 of the vapor flow behaviors above its condensed phase. The temperature jumps
398 obtained numerically for different experimental conditions were found of the

Operating conditions [4]	$p_s - p_\infty$ [Pa]	
	Eq. (27)	S-model
$30^{\circ}C$	0.32	0.29
$50^{\circ}C$	0.43	0.46
$80^{\circ}C$	0.69	0.67

Table 8: Pressure jump $p_s - p_\infty$ in [Pa], obtained from: Eq. (27), where numerical values of J'_m and q' from numerical solution using S-model equation are used, second column; numerical S-model results, third column.

399 same order as that measured recently and presented in Refs. [6], [5], but much
400 smaller than that found previously in Ref. [4]. The comparison with the ex-
401 perimental data from Ref. [4] shows that the vapor parameters are measured
402 in [4] very far from the upper boundary of the Knudsen layer and therefore the
403 application of the Knudsen-Hertz-Schrage formula predicts much higher mass
404 flow rate as it was really measured. In addition, if the values of the pressure
405 and temperature at the upper boundary of the Knudsen layer, obtained from
406 the numerical solution of the S-model kinetic equation, are implemented in the
407 Knudsen-Hertz-Schrage formula the evaporation rate is in excellent agreement
408 with the measured one. The proposed approach could be used for the measure-
409 ments of the evaporation coefficient.

410 In addition, the measured and calculated evaporation fluxes are very close
411 each other. However, the calculated vapor temperature is found to be lower
412 than that of the liquid interface, while in the analyzed experiments [4], [6] the
413 measured near the liquid surface vapor temperature is higher than that of the
414 liquid phase. This fact could be partially explained by the assumption of the
415 constant vapor temperature made in the numerical simulations. To improve
416 the simulations the boundary conditions could be modified to take into account
417 the presence the heat flux in the vapor phase. In addition, to account more
418 precisely the heat and mass exchanges between two phases the coupling between
419 the continuum and kinetic approaches could be also realized.

420 In practice very often the evaporation of one substance in the presence of a
421 non-condensable takes place, as in many cooling devices. Therefore, the next
422 step will be the simulation of the fluid evaporation into a mixture of the evapo-
423 rated fluid and non-condensable gas by using the kinetic approach. The numer-
424 ical results will be compared to the available experimental data [5].

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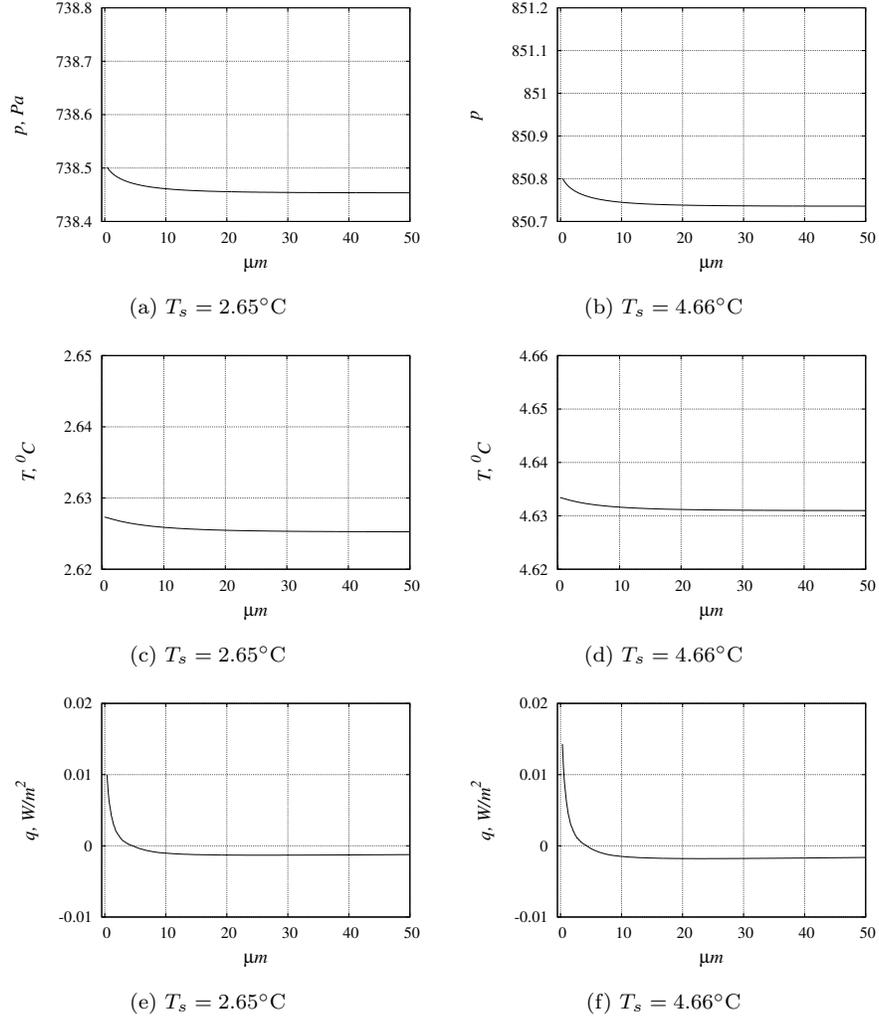


Figure 3: (a) and (b) pressure profiles, (c) and (d) temperature profiles, (e) and (f) heat flux profiles. All the profiles are obtained numerically using the experimental data [4], provided in Table 1, which correspond to heating 30°C and 50°C , for (a),(c),(e) and (b),(d),(f), respectively. For figures (a)-(d) the maximal value on y axis corresponds to the saturation pressure (a),(b) and temperature (c),(d) of the interface.