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COMPUTER SIMULATIONS OF EVAPORATION OF SESSILE LIQUID DROPLETS ON SOLID SUBSTRATES

by

Sergey Semenov

Thesis submitted in partial fulfilment of the requirements for the award of degree of Doctor of Philosophy of Loughborough University

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   • poster presentation: V.M. Starov, S. Semenov, R.G. Rubio, “Influence of contact angle and temperature on evaporation of sessile liquid droplets”

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   • oral presentation: S. Semenov, V.M. Starov, R.G. Rubio, “Universal behaviour of evaporating sessile water droplets in the presence of contact angle hysteresis”

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   • poster presentation: V.M. Starov, S. Semenov, R.G. Rubio, “Influence of contact angle and temperature on evaporation of droplets”

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• poster presentation: V.M. Starov, S. Semenov, R.G. Rubio, “Dependence of rate of evaporation of sessile liquid droplets on contact angle and temperature”

The International Conference on Multiscale Complex Fluid Flows and Interfacial Phenomena “MULTIFLOW 2010”:

The 24th Conference of the European Colloid and Interface Society “ECIS 2010”:
• poster presentation: V.M. Starov, S. Semenov, R.G. Rubio, “Influence of contact angle and temperature on evaporation of droplets”

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• oral presentation: S. Semenov, N. Ivanova, V.M. Starov, “Spreading of aqueous surfactant solutions over hydrophobic surfaces”

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• poster presentation: K.S. Lee, V.M. Starov, S. Semenov, K. Sefiane, “Kinetics of Simultaneous Spreading and Evaporation of Droplets”
Abstract

Present work is focused on the numerical study of evaporation of sessile liquid droplets on top of smooth solid substrates.

The process of evaporation of a sessile liquid droplet has lots of different applications both in industry and research area. This process has been under study for many years, and still it is an actual problem, solution of which can give answers on some fundamental and practical questions.

Instantaneous distribution of mass and heat fluxes inside and outside of an evaporating sessile droplet is studied in this research using computer simulations. The deduced dependences of instantaneous fluxes are applied for self-consistent calculations of time evolution of evaporating sessile droplets. The proposed theory of evaporating sessile droplets of liquid has been validated against available experimental data, and has shown a good agreement.

Evaporation of surfactant solution droplets is studied experimentally. The theory, proposed for two stages of evaporation, fits experimental data well. An additional evaporation stage, specific for surfactant solutions, is observed and described. Mathematical modelling of this stage requires further research on surfactant adsorption and its influence on the value of receding contact angle.

Numerical study of the evaporation of microdroplets is conducted in order to evaluate the significance of different evaporation mechanisms (diffusive and kinetic models of evaporation) and different physical phenomena (Kelvin’s equation, latent heat of vaporization, thermal Marangoni convection, Stefan flow).

**Key words:** sessile droplet, evaporation, computer simulations, kinetic effects, Marangoni convection, surfactants.
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Introduction

Understanding the evaporation of sessile droplets is essential for many industrial applications. Drying droplets are used in so called molecular combing processes; in cooling systems and heat exchangers; for deposition of suspended colloidal particles; in coating, painting and ink-jet printing; as well as for production of complex functional materials.

From the scientific point of view the problem of evaporating of a sessile droplet is of a substantial interest because of singularity problems arising at the three-phase contact line: singularity of evaporating flux and viscous stress; which contradict to physical reality. The solution of these problems could improve our understanding of molecular interactions in the vicinity of apparent three-phase contact line, and find relevant macroscopic boundary conditions for equations of heat and mass transfer.

The aim of present research is to investigate heat and mass fluxes in the course of sessile droplet evaporation in a self-consistent way: study the interconnected problem of vapour transfer; heat transfer in the vapour, liquid and solid substrate; and Marangoni convection inside the liquid droplet. It will give better understanding of the dynamics of evaporation of sessile drops of pure liquids on smooth solid substrates.

The first part of present work presents literature review in the field of droplets evaporation. The second part describes the problem statement with assumption of quasi-steady state of the evaporation process under consideration. The third part gives results and their comparison with available experimental data in case of contact angle hysteresis. The fourth part presents experimental study of evaporating sessile droplets of surfactant solutions, and application of the proposed theory to those experiments. The last part is about the influence of kinetic effects on evaporation of microdroplets.
1. Literature review

1.1. Evaporation of liquid droplets into gaseous atmosphere

Evaporation of liquid droplets in gas volume has implications in different areas: the Wilson cloud chamber [1], spray drying and production of fine powders [2], fuel preparation [3–7], air humidifying [8], spray cooling [9–11], heat exchangers [8], drying in evaporation chambers of air conditioning systems [8], fire extinguishing [8, 12], fuel spray autoignition [13–15]. Because of such wide range of industrial applications this phenomenon has been under investigation for many years.

Investigations of droplets evaporation were conducted for pure [5, 8], bi-component [13, 16] and multi-component [3, 17] liquids at different conditions: constant temperature and pressure [5, 17], elevated pressure [3], fast compression [4], still gas atmosphere [18] and turbulent reacting flows [6].

In 1950 Kluyver and Endt concluded in [1] that the recovery time in the Wilson cloud chamber determined not only by the heat conduction, but also by the slow evaporation, diffusion, and condensation processes. Since that time many works have been dedicated to studying of the process of thermodynamic equilibration in different types of cloud chambers [19–21].

In the middle of 20th century the combustion process in the Diesel engine already attracted attention of many engineers and scientists [22–25], and at present this problem is still under consideration [26] for both internal combustion engines and turbines. The general process of preparation of fuel-air mixtures was studied in order to overcome the heterogeneity of fuel-air mixtures and to reduce the amount of unburned fuel in fuel gas [22]. The latter produces less pollution of air with harmful exhausts. Alongside with mechanical premixing the evaporation of fuel droplets is considered to be crucial for the formation of fine burning mixtures. The mechanism of the evaporation and combustion of the individual drops of fuel was considered in detail in [23, 25]. Particularly, it was found by Godsav that the rate of change of droplet’s mass is proportional to the first power of its diameter [23]. Hall and Diederichsen [25] presented their experimental results for the burning of single
droplets of fuel in air, which confirm the linear dependence of the rate of change of droplet’s mass on its diameter even during a combustion process.

Since that time different physical processes were taken into account to develop further earlier models of evaporation of sprays and droplets: heat transfer inside droplets [13, 27, 28], mass diffusion in bi- and multi-component liquids [13, 17, 18], droplets interaction in sprays [6, 7], turbulence [6], radiation absorption [12]. Rapid development of computer simulations allowed modelling of complex physical systems, including molecular dynamics simulations [29]. Different models of droplet heating and evaporation are well described in the review work of Sazhin [15]. Particularly it describes Abramzon and Sirignano model [30] and Yao, Abdel-Khalik and Ghiaasiaan model [31], which take into account the effect of convective transport caused by the droplet motion relative to the gas.

1.1.1. Heat transfer inside a droplet

Constant droplet-temperature model (D² law) [23, 32] or infinite conductivity models are often used for simulations of such complex systems as sprays. The main reason for this is the high computational cost of heat transfer simulations inside of each individual spray droplet. However, it has been shown [28] that the accuracy of simulations for heating, evaporation and combustion of sprays could be substantially increased if the model of liquid is endowed with the finite heat conductivity. Balasubramanyam et al. [27, 33] applied in their simulations finite-conductivity spray evaporation model, which accounts for heat transfer inside the liquid phase (based on the two-temperature film theory). It has allowed them to account for droplet internal turbulence effect. Sazhin et al. [5, 13, 14, 34] suggested the usage of analytical solution for the heat conduction inside of droplets coupled with numerical methods of modelling. The latter method according to the authors [13] is more CPU efficient as compared with the model based on the direct numerical simulation of the heat conduction inside droplets.
1.1.2. Diffusion in bi- and multi-component liquid droplets

Classical models are usually based on an assumption that liquid consists of one component only. The latter has been adopted to simplify calculations. One-component assumption, however, is not valid for majority of fuels [15] as well for the case of droplets spreading over solid substrates [35]. In the case of evaporation of multi-component liquids, different components evaporate at different rates. The latter results in the appearance of concentration gradients and diffusive fluxes in the liquid phase. For that reason the evaporation kinetics can differ significantly from that for classical solutions with one-component liquid. For example, evaporation of aqueous salt solution from an open end of a thin capillary results in a crystallisation-dissolution of salt crystals close to the end of the capillary. The latter results in a very special behaviour of time evolution of evaporation flux, which shows decaying oscillation behaviour [36]. There are a number of publications in the literature where models of one-component liquids were extended to multi-component ones [13, 17]. Brenn et al. [17] based their consideration on Abramzon and Sirignano model [30] and the Universal Functional Activity Coefficient (UNIFAC) approach for calculation the vapour pressures of various mixtures. The total evaporation rate was considered as a sum of evaporation rates of all liquid components [17]. Sazhin et al. [13] took into account the analytical solution of the diffusion equation of species inside a liquid droplet, what allowed them to build a simplified model for bi-component droplet heating and evaporation. According to [13] the models of multi-component droplet heating and evaporation could be subdivided into two main groups: those based on the analysis of individual components [37–43]; and those based on the probabilistic analysis of a large number of components, e.g. continuous thermodynamics approach [44–46] and the Distillation Curve Model [3].

1.1.3. Droplet interactions in sprays: Influence on evaporation rate

Modelling of the physical processes involved in droplet interactions is complex, that is, only a few numerical attempts published [6, 7, 47], which directly quantify the effect of droplet interactions on evaporation rate and combustion. Umemura et al. [47] in 1981 studied the interaction between two burning droplets. Later Marberry et al. [48] studied the multiple particle interactions for different geometries of droplets
array. Imaoka et al. [7] studied the effects of droplet interactions in symmetric, multipledroplet arrays, and flame locations for different configuration of droplet arrays. They found that the number of droplets and relative droplet spacing significantly affect the vaporization rate of individual droplets within the array, which can be reduce up to four orders of magnitude. Zoby et al. [6] performed Direct Numerical Simulations of evaporation of droplet arrays in turbulent and reacting flows, using the Level Set approach with the Ghost Fluid method. They compared their results with two commonly used models for RANS (Reynolds-Averaged Navier-Stokes) and LES (Large Eddy Simulations) computations and concluded that for dense sprays those models result in underpredictions of evaporation rates by 20% to 50%.

1.1.4. Molecular dynamics simulations

Molecular dynamic simulations are usually performed for each individual molecule. The advantage of this approach is that it can be used for simulation of systems, which cannot be described using a continuum approach. Such systems include those undergoing significant local fluctuations of thermodynamic parameters (e.g. mass density, temperature). It could be a fluid system with characteristic geometrical size of order of the mean free path of molecules; as well as a fluid under supercritical thermodynamic conditions. The disadvantage of molecular dynamics approach is a high demand for computational resources and, consequently, a demand for highly efficient high performance computers and software. Those restrictions of molecular dynamic simulations do not allow solution of problems with a big number of molecules. Therefore this method is used for modelling of evaporation of submicron droplets [29, 49–55]. Usually the Lennard-Jones potential is adopted for the modelling of intermolecular forces; and three types of problems can be identified: evaporation of nanodroplets into a surrounding vapour of the same species [29, 49–52], a vapour of a different species [53, 54], or a vacuum [55]. Most of the cases investigated show similar qualitative results: (i) for Knudsen numbers (ratio of mean length of free molecular path to the droplet diameter) of order of one or bigger: the droplet diameter decreases linearly with time [29, 50], which is in agreement with predictions of kinetic evaporation models; (ii) for Knudsen numbers of order of $10^{-2}$ or smaller the dependence of the droplet evaporation approaches the $D^2$ law [29, 49],
which is predicted by hydrodynamic models. Supercritical regime of droplet evaporation is characterised by diminishing of the liquid-air surface tension and, consequently, by loss of droplet's spherical shape [53, 54]. Sumardiono et al. [51] showed that there is certain arbitrariness in the calculation of the droplet radius at molecular dynamics simulations, which depends on a method of the calculation.

1.2. Evaporation of sessile droplets

In a number of cases evaporation process of drying droplets develops over a relatively short period of time and, in this case, it is not so straightforward to study the evaporation process and related effects experimentally [56]. There are also lots of other general problems related to evaporating droplets. Some of them require consider a droplet as an integral part of a wider problem of droplets and spray dynamics [15]. Other applications require prediction of solidification in the course of evaporation including formation of hollow shells [57]. The residue from dried drops [58–60] has implications for many applications, including painting, coating processes, ink-jet printing, DNA chip manufacturing [61], formation of pixel arrays of organic materials for video displays and for a variety of micro-electro-mechanical (MEMS) devices [62]. Understanding the evaporation of droplets is essential for premixing of fuel with oxygen in air [3]. The measurements of evaporation rate of droplets on different solid surfaces can be used for production of materials providing optimal regime of work of air conditioners, dryers and cooling systems [63].

1.2.1. Singularities in a vicinity of the three phase contact line

Two singularities have to be coped with simultaneously [64] from the theoretical point of view: the first problem is associated with the well-known problem of a singularity at the moving three phase contact line (a singularity of the viscous stress caused by the incompatibility of no slip condition at the solid substrate and free surface at the liquid-air interface at the three phase contact line), the second problem is associated with the specific behaviour of the evaporation flux at the perimeter of the droplet. The latter singularity is caused by an incompatibility of boundary conditions at the liquid-air interface with those at the solid-liquid and the solid-air at the three phase contact line. Both singularities can be overcome by introducing the Derjaguin’s
(disjoining/conjoining) pressure into the model, which dominates in a vicinity of the apparent three-phase contact line [65, 66]. Note that latent heat of vaporization and Marangoni convection [67] inside the droplets in the course of droplets evaporation has also to be taken into account.

1.2.2. Stages of sessile droplet evaporation

Evaporation starts immediately after the deposition of a liquid droplet on a solid substrate in a non-saturated vapour atmosphere. In the presence of contact angle hysteresis the latter process occurs generally in four steps [68, 69]: (0) quick spreading; (I) evaporation proceeds with a constant radius of the contact line, \( L \), and decreasing contact angle, \( \theta \), until the contact angle reaches the static receding value, \( \theta_r \); (II) evaporation at constant contact angle, \( \theta_r \), and decreasing radius of the contact line, \( L \); (III) both the radius of the contact line, \( L \), and the contact angle, \( \theta \), decrease until the droplet disappears. Stage (I) is usually the longest one and lasts until the contact angle reaches its static receding value, \( \theta_r \). Stage (III) is the shortest one and the most difficult for experimental investigation.

1.2.3. Dependence of the evaporation flux on the droplet size

Theoretical and computer simulation studies [67, 70–74] give the following equation for the evaporation rate of a sessile droplet:

\[
\frac{dV}{dt} = -2\pi \frac{DM}{\rho} \left( c_{\text{sat}}(T_{\text{surf}}) - H c_{\text{sat}}(T_{\infty}) \right) F(\theta)L,
\]

or simply:

\[
\frac{dV}{dt} = -\beta F(\theta)L, \quad \beta = 2\pi \frac{DM}{\rho} \left( c_{\text{sat}}(T_{\text{surf}}) - H c_{\text{sat}}(T_{\infty}) \right),
\]

where \( V \) is the droplet volume, \( t \) is time, \( D \), \( \rho \), and \( M \) are vapour diffusivity in air, density of the liquid and the molecular weight of the evaporating substance, respectively; \( H \) is humidity of the ambient air, \( T_{\text{surf}} \) is the temperature of the droplet-air interface and \( T_{\infty} \) is the temperature of the ambient air, \( c_{\text{sat}}(T_{\text{surf}}) \) and \( c_{\text{sat}}(T_{\infty}) \) are the molar concentrations of saturated vapour at the corresponding temperature; \( F(\theta) \) is a function of the contact angle, \( \theta \), with value 1 at \( \theta = \pi/2 \). Eq. (1.1) was deduced for the model of evaporation which takes into account diffusion only of the vapour in the
surrounding air and ignores the temperature distribution along the droplet-air interface. In the case of $\theta$ independent on $L$ (evaporation stages (I) and (II)) Eq. (1.1) gives an evaporation rate directly proportional to the radius of the contact line, $L$.

Guena et al [75] showed that the surface density of vapour flux, $j$, at the droplet surface is inversely proportional to the radius of the contact line, $L$. As a consequence, the integration of the surface density of the flux, $j$, over the whole droplet surface gives a total vapour flux, $J$, proportional to the radius of the contact line, $L$.

1.2.4. Distribution of the density of vapour flux over the droplet surface

A number of researches in the field showed that in the case of contact angles $\theta < 90^\circ$ the evaporation indeed is more intensive in a vicinity of the three phase contact line. Several different principles were utilised in order to explain this phenomenon: (i) non-uniform distribution of vapour flux over the droplet surface due to the diffusion controlled process of vapour transfer to the ambient air [58–60]; (ii) action of Derjaguin’s (disjoining/conjoining) pressure at the three phase contact line [65, 66, 76, 77]; (iii) evaporative cooling of the liquid-gas interface (due to latent heat of vaporization) and formation of the temperature field leading to a comparatively more intensive evaporation at the three phase contact line [78].

Deegan et al [58, 59] studied the distribution of vapour flux density over the spherical cap of a sessile droplet neglecting the latent heat of vaporization and the thermocapillary flow inside the droplet. The obtained solution for droplets with contact angles $\theta < 90^\circ$ shows an infinite increase of the vapour flux in a vicinity of the three-phase contact line. Such distribution of the flux over the droplet surface, according to the authors, generates the flow inside the droplet, which transports suspended solid particles to the edge of the droplet thus leading to a ring-like stain formation (coffee rings).

Starov and Sefiane [78] suggested a physical mechanism of redistribution of evaporation flux which is controlled by the temperature field rather than by the process of vapour diffusion into air. According to their model, there is convection in
the ambient air, so that vapour diffusion occurs only in a boundary layer. If the thickness of the boundary layer, $\delta$, is constant then the vapour diffusion across the layer is controlled by the difference of vapour concentrations in the ambient air and at the droplet surface. The latter is a function of the local temperature at the surface. In the model under consideration [78] the surface of a droplet is cooled by the evaporation; meanwhile due to the high heat conductivity of the substrate the temperature of the contact line is stayed equal to the ambient one. As a result the higher temperature at the three phase contact line gives the higher vapour concentration and more intensive evaporation flux at the droplet’s perimeter (see Fig. 1.1).

![Temperature distribution over the droplet surface](image)

Fig. 1.1: Temperature distribution over the droplet surface, $T_s(r)$. $r$ is the radial coordinate; $T_0$ is the temperature of the substrate; $T_s,\infty$ is the temperature of the droplet surface at which the evaporation flux vanishes; $L$ is the droplet base radius; $\Delta$ is a tiny area within the vicinity of the three phase contact line, where evaporation mostly takes place [78].

### 1.2.5. Influence of Marangoni convection

Investigations of evaporation of droplets with contact angles $\theta < 120^\circ$ were performed by Girard et al. [67, 71–74] and Hu and Larson [79–82]. Girard et al. investigated the influence of substrate heating [73, 74], air humidity [73] and Marangoni convection.
They concluded that contribution of Marangoni convection to the total vapour flux is negligible, whereas heating of the substrate is important. Hu and Larson investigated the process of particles deposition and ring-like stain formation during the droplet evaporation [79–81]. They concluded that the density profile of the particles deposit substantially depends on the Marangoni convection within the sessile droplet [82]. If Marangoni convection is present, then it results in a particle deposition at the droplet centre rather than at the edge. According to authors, the suppression of Marangoni convection is one of the important conditions for ring-like deposit formation.

Ristenpart et al. [83] investigated the influence of the substrate conductivity on the reversal of Marangoni circulation within an evaporating sessile droplet. They neglected the thermal conductivity of the surrounding air. Authors used predefined distribution of evaporation flux over the droplet surface:

\[ j(r) = j_0 \left[ 1 - \left( \frac{r}{L} \right)^2 \right]^{-1/2 + \theta/\pi}, \]

where \( j_0 \) is a constant determined by the ambient humidity and diffusivity of vapour in the ambient air, \( r \) is the radial coordinate. This expression for \( j(r) \) is not applicable for contact angles \( \theta > \pi/2 \), and automatically introduces the singularity at the three phase contact line: \( j(L) \big|_{\theta > \pi/2} = \infty \). Despite of those assumptions made by authors, their quantitative criteria for the circulation direction was experimentally confirmed.

1.2.6. Influence of the heat conductivities of droplet’s liquid and substrate material

It is well known that evaporation process consumes heat due to the latent heat of vaporization. Because of that the droplet’s surface cools down and generates heat flux towards the surface. As the heat conductivities of the droplet liquid and substrate material are much higher than that of air then the major part of the heat flux goes through the droplet and substrate. Thus the heat conductivities of liquid and substrate define the temperature drop at the droplet surface which is necessary to maintain a certain heat flux. On the other hand the temperature of the droplet surface defines the value of saturated vapour concentration (in case of diffusive model of evaporation) and hence the evaporation rate. Dunn et al. [84, 85] solved the coupled
problem of vapour diffusion and heat transfer for the evaporation of sessile droplets of different liquids on substrates with different thermal properties. They demonstrated both experimentally and numerically that the heat conductivity of the substrate strongly influences the evaporation rate. Decreasing the heat conductivity of the substrate causes the decrease of the evaporation rate.

1.2.7. Complete wetting

In case of complete wetting droplets spread out completely over a solid substrate, and contact angle decreases down to zero value. Lee et al. [86] considered the process of simultaneous spreading and evaporation of sessile droplets in the case of complete wetting. In order to model the spreading they [86] considered Stokes equations under a low slope approximation. A linear proportionality of the total evaporation flux, \( J \), to the contact line radius, \( L \), was assumed. The whole process of spreading/evaporation was divided into two stages: (i) the first, fast but short spreading stage, when evaporation can be neglected, and the droplet volume, \( V \), is approximately constant; (ii) the second slower stage, when the spreading process is almost over, contact angle is approximately constant, and evolution is determined by the evaporation. On the basis of this analysis the radius of the contact line, \( L \), is considered as a function of the droplet volume, \( V \), and contact angle, \( \theta \). Time derivative of \( L(V, \theta) \) gives two velocities of the contact line:

\[
\frac{dL(V, \theta)}{dt} = \frac{\partial L(V, \theta)}{\partial \theta} \frac{d\theta}{dt} + \frac{\partial L(V, \theta)}{\partial V} \frac{dV}{dt} = v_+ - v_-, \tag{1.3}
\]

where \( v_+ \) is the spreading velocity, and \( v_- \) is the velocity due to the evaporation:

\[
v_+ = \frac{dL(V, \theta)}{dt} \bigg|_{\theta \text{ const}} = \frac{\partial L(V, \theta)}{\partial \theta} \frac{d\theta}{dt}, \tag{1.4}
\]

\[
v_- = \frac{dL(V, \theta)}{dt} \bigg|_{V \text{ const}} = -\frac{\partial L(V, \theta)}{\partial V} \frac{dV}{dt}. \tag{1.5}
\]

The spreading velocity of the contact line, \( v_+ \), is obtained by Starov et al. in [87]:

\[
v_+ = 0.1 \left( \frac{4V}{\pi} \right)^{0.3} \left( \frac{10\rho\omega}{\mu} \right)^{0.1} \frac{1}{(t + t_0)^{0.9}}, \tag{1.6}
\]

where \( \gamma \) is the surface tension of the liquid; \( \mu \) is the dynamic viscosity of the liquid; \( \omega \) is the effective lubrication parameter [88]; \( t_0 \) is the duration of the initial stage of
spreading when the capillary regime of spreading is not applicable [87]. Eq. (1.6) is derived from Eq. (1.4) using the formula for $L(t)$ obtained by Starov et al. in [88]:

$$L(t) = L_0 \left(1 + \frac{t}{\tau}\right)^{0.1},$$

where $L_0$ is the droplet base radius after the very fast initial stage is over;

$$\tau = \frac{3\mu L_0}{10\gamma} \left(\frac{\pi \lambda L_0^3}{4\gamma}\right)^{-1}; \lambda$$ is the dimensionless constant [88] connected to the effective lubrication parameter $\omega$ [88]. The velocity $v_-$ is obtained from Eq. (1.5) using the Eq. (1.2):

$$v_- = \frac{\beta F(\theta)L^2}{3V}. \quad (1.7)$$

Substituting Eqs. (1.6) and (1.7) into Eq. (1.3) leads to the following equation:

$$\frac{dL}{dt} = 0.1 \left(\frac{4V}{\pi}\right)^{0.3} \left(\frac{10\gamma\omega}{\mu}\right)^{0.1} \frac{1}{(t + t_0)^{0.9}} - \frac{\alpha L^2}{3V}. \quad (1.8)$$

Fig. 1.2: A dimensionless radius against dimensionless time curve for the behaviour of the droplet radius comparing different liquids spreading/evaporating on solid substrates extracted from literature and theoretical prediction [86].

The latter gives a system of two differential Eqs. (1.2) and (1.8) with following boundary conditions [86]:

$$V(0) = V_0, \quad (1.9)$$
where $V_0$ is the initial droplet volume and $L_0$ is the droplet base radius after the very fast initial stage is over. Solution of this system of equation in non-dimensional form gives a universal law of process of simultaneous spreading and evaporation for the case of complete wetting, which is confirmed by experimental data from various literature sources [86] (see Figs. 1.2 and 1.3).

One can see that all experimental data for reduced times from 0.2 to 1 are below the model curve in Fig. 1.2 (for reduced radius) and above the model curve in Fig. 1.3 (for reduced contact angle). One can infer that those deviations in Figs. 1.2 and 1.3 are interconnected. Indeed, if we reduce the value of the reduced radius, preserving the droplet volume, then the reduced contact angle will increase correspondingly. It means that there is a possibility to improve the fitting of experimental data in Figs. 1.2 and 1.3 preserving the same droplet volume, that is, not making any changes to the theoretical fitting of experimental data for the droplet volume.
1.2.8. Ring-like stain formation

The formation of ring-like stains during the droplet drying has been studied by a number of scientists. Deegan et al. [59] studied contact line deposits and reasons of its formation. The authors concluded that formation of ring-like stains requires “a weakly pinning substrate and evaporation”. Hu and Larson [82] reported that formation of such deposits requires not only a pinned contact line but also the suppression of Marangoni flow. They demonstrated both theoretically and experimentally the possibility of Marangoni flow reverse and formation of deposit at the centre of the droplet.

Bhardwaj et al. [60] solved numerically a complex problem of drying of droplets of colloidal solutions and deposits formation. Their model takes into account the Navier-Stokes equations, convective and conductive heat transfer, Marangoni convection and receding of the three phase contact line. The interaction of the free surface with the peripheral deposit and eventual depinning were also simulated. The diffusion of vapour in the atmosphere was simulated, providing an exact boundary condition for the evaporative flux at the droplet-air interface. The formation of different deposit patterns obtained experimentally is explained by their simulations.

1.3. Derjaguin’s (disjoining/conjoining) pressure as a way to cope with singularity problems

In order to get rid of the problem of singularities at the three-phase contact line it is necessary to replace mathematically inconsistent boundary conditions by physically correct ones. It can be done using Derjaguin’s (disjoining/conjoining) pressure concept. This approach does not introduce a three-phase contact line and, therefore, rules out any singularity problems in a vicinity of the otherwise apparent three-phase contact line [65].

Surface forces (Derjaguin’s pressure) act in a vicinity of the apparent three-phase contact line. The latter disturb the initial profile of the liquid droplet in a vicinity of the three phase contact line. It is also known that a very thin adsorbed film is formed on a solid surface, which is at the thermodynamic equilibrium with the vapour in the
surrounding atmosphere. That is, in the humid air, water vapour forms a thin water film on the surface of a solid substrate. Thus, a liquid-air interface of a sessile liquid droplet is actually in a contact with this adsorbed water film (or a film of other substance); thus, in this approach there is no true three-phase contact line.

First models of evaporation in a vicinity of the three phase contact line based on consideration of Derjaguin’s (disjoining/conjoining) pressure action were developed by Potash and Wayner [76], and Moosman and Homsy [66], who used the Derjaguin’s pressure to model the transport phenomena in an evaporating two-dimensional meniscus. In Ref. [76] the authors calculated the meniscus profile, heat flux profile, and pressure gradient profile. Ajaev et al. [77] deduced a meniscus profile changes relative to the static isothermal one, as well as an evaporation flux from the interface using a perturbation theory. Both Refs. [76] and [77] demonstrated that a large heat and evaporation fluxes occur in the transition region between the capillary meniscus and the adsorbed layer. Stephan et al. [89] investigated experimentally evaporation in heat pipes with grooved walls. They confirmed the theoretical conclusions by Moosman and Homsy [66] on prediction that significant part of the evaporation flux is localized at the three-phase contact line.

Ajaev et al. [77] studied both static and dynamic values of the apparent contact angle for gravity-driven flow of a volatile liquid down of a heated inclined plane. The authors investigated macroscopic boundary conditions which could be used with a conventional continuum approach and agree with the micro scale phenomena at the contact line. They found the profile of the liquid-vapour interface in the region of the apparent three-phase contact line and determined the dependence of the macroscopic contact angle on the temperature of the contact line and the velocity of its motion. The interface profile in the region was determined by a disjoining pressure action and asymptotically approaches the adsorbed thin liquid film. It was found that the curvature of the interface at that transition region is very high. Authors [77] also investigated the effect of evaporation on moving contact line in the case of partial wetting. They proposed a generalization of the approach of Moosman and Homsy [66] and Ajaev et al. [90, 91].
Diaz et al. [92] studied a static puddle taking into account capillarity, gravity and disjoining pressure. They found an analytical solution for the shape of the vapour-liquid interface in the transition zone between adsorbed liquid layer and capillary region.

All the above examples of disjoining pressure action at the apparent three-phase contact line give the evidence of possibility to construct physically consistent macroscopic boundary conditions at the contact line taking into account microscopic phenomena.

1.4. Conclusions and problems to be solved

It was observed experimentally, that the rate of evaporation of a sessile droplet is proportional to the perimeter of the droplet. Different authors suggested several different mechanisms to explain this fact. Some of them utilize the idea, that evaporation is really occurs mainly at the perimeter of the droplet due to different phenomena: vapour diffusion, cooling of the droplet's surface, action of surface forces (disjoining/conjoining Derjaguin’s pressure) within the three-phase contact line.

Present work is focused on numerical modelling of the process of evaporation of sessile liquid droplets on top of smooth solid substrates in order to understand what physical processes are most important in this phenomenon. Our objective is to study the influence of different parameters of the system under consideration (such as ambient temperature and humidity, substrate conductivity, droplet size and shape, properties of liquid) on the rate of droplet’s evaporation. Computer simulations can help studying temperature, velocity and concentration fields, which are not available from experiments. It will clarify the main mechanism of droplets evaporation, and bring better understanding of the phenomenon.

We aim to build a mathematical model of this phenomenon, based on our computer simulations, which can predict the evolution of evaporating sessile droplets, observed experimentally.
The influence of surfactants on the evaporation process is poorly studied. Therefore we will experimentally study the evolution of sessile droplets of surfactant solutions. The mathematical model will be validated against obtained experimental data.

Another important question is: which model of evaporation (diffusive or kinetic) is dominant for evaporating droplets of different size? The numerical study will allow us to answer this question and to estimate the influence of kinetic effects on evaporation. Also it is important to understand the role of other effects (Kelvin’s equation, Stefan flow in gas, thermal Marangoni convection inside of the droplet, latent heat of vaporization) and estimate their impact on the evaporation rate.

Solving above stated problems will allow us to move forward in our understanding of the whole phenomena, and apply the new knowledge in future studies of more complex phenomena in the area of research.

Particularly, in industry, the obtained mathematical model of a single evaporating sessile droplet would be very useful for the modelling of spray cooling, which is of interest in the field of cooling of electronic devices. Studying the temperature field in the system under consideration and relating the temperature drop at the droplet surface to the system parameters will help optimizing the spray cooling devices.

2. Modelling of evaporation of millimetre-size pinned sessile droplets

2.1. Introduction

Here we study the evaporation of sessile liquid droplets. Thus the problem under consideration is a pinned sessile droplet of a liquid on a solid substrate open to ambient air, so that it can evaporate. The most often encountered evaporating substance in nature is water.

![Fig. 2.1: Parameters of sessile evaporating droplets.](image-url)
Evaporation of sessile droplets of water without substantial substrate heating is not much intensive and doesn’t produce rotational liquid motion around the axis of droplet’s symmetry.

Thus the axial symmetry is the first assumption, which we adopt in all models considered below. It is convenient to describe axisymmetric problems with a cylindrical system of coordinates \( r \) and \( z \) (Fig. 2.1). Further, to simplify, the attention is focused on relatively small droplets, that is contact line radius, \( L << a \), where

\[
a = \sqrt{\frac{\gamma}{\rho g}}
\]

is the capillary length, \( \gamma \) is the liquid-air interfacial tension, \( \rho \) the liquid density and \( g \) is the gravitational acceleration. In this case, the static Bond number, \( \text{Bo} \), is very small: \( \text{Bo} = \frac{\rho g L^2}{\gamma} << 1 \). Indeed, for aqueous droplets: \( \rho = 10^3 \text{ kg/m}^3 \), \( \gamma = 0.073 \text{ N/m} \), \( L = 0.001 \text{ m} \), \( g \approx 10 \text{ m/s}^2 \) and \( \text{Bo} \approx 0.1 << 1 \). It means that gravity force (body force) is negligible comparing to the capillary forces (surface forces).

Domination of capillary forces results in a spherical cap shape of a sessile droplet with a fixed contact angle, \( \theta \). It should also be assumed that the evaporation rate is slow enough that the evaporating droplet remains spherical in spite of the non-uniformity of the evaporating flux.

The local evaporation rate at the droplet’s surface can be limited by two processes: vapour diffusion into the ambient air in the vicinity of the evaporating surface, and molecules transfer from the liquid phase to the gaseous one [72].

Let us estimate those rates for millimetre-size droplets. The characteristic time required for a molecule to move from the liquid to the gaseous phase, \( t_r \), can be estimated as \( \varepsilon / \overline{v} \), where \( \varepsilon \) is the width of the transition zone between the phases, and \( \overline{v} \) is the mean square velocity of molecules. If we estimate the width of the transition zone, \( \varepsilon \), between two phases equal to several mean free molecular paths, then \( t_r \sim 10^{-10} \text{ s} \). The time scale required for diffusion, \( t_{\text{diff}} \), of a molecule over the
distance $L$ is $t_{\text{dif}} = L^2 / D \sim 10^{-2} \text{s}$, where $D$ is the molecular diffusion coefficient. As $t_{\nu} \ll t_{\text{dif}}$, the process of transition of molecules across the interface is much faster than the vapour diffusion. Hence, the evaporation rate is limited by vapour diffusion into ambient air.

Assuming that, we impose a lower limit on the value of contact line radius, $L$. This limit can be calculated from the condition of equality of the rate of diffusion to the rate molecules transition across the interface. In other words, characteristic times of these two processes become equal: $t_{\text{dif}} = t_{\nu}$; from where we calculate the lower limit for the contact line radius: $L = \sqrt{t_{\nu} \cdot D} \sim \sqrt{10^{-10} \text{s} \cdot 2.4 \cdot 10^{-5} \text{m}^2/\text{s}} \approx 5 \cdot 10^{-8} \text{m}$.

Droplets with $L < 5 \cdot 10^{-8} \text{m}$ are not considered in current section, as for those droplets the kinetic regime of evaporation tends to dominate. This regime of evaporation will be considered later in a different section.

In view of the above, here diffusion-dominated evaporation will be considered only. The time scale of molecular diffusion, $t_{\text{dif}}$, is much smaller than the characteristic time scale of evaporation, $t_{\text{evap}}$, which is usually of order $10^2 \text{s}$ [86]. Consequently, the vapour diffusion process can be considered as a quasi-steady process.

Heat and momentum transfer processes inside of a droplet also can be accepted as quasi-steady ones, because the characteristic time scales for those processes, $t_{\text{heat}}$ and $t_{\text{mom}}$, are smaller than the droplet evaporation time, $t_{\text{evap}}$, at least by one order of magnitude. Indeed, $t_{\text{heat}}$ and $t_{\text{mom}}$ approximately equal: $t_{\text{heat}} = L^2 / \kappa \sim 10 \text{s} \sim 0.1 \cdot t_{\text{evap}}$, where $\kappa$ is the thermal diffusivity of water and $L=10^{-3} \text{m}$ as above; $t_{\text{mom}} = \rho L^2 / \mu \sim 1 \text{s} \sim 0.01 \cdot t_{\text{evap}}$, where $\mu$ is the dynamic (shear) viscosity of water.

Experiments [86] did not reveal any difference in evaporation rates with and without forced convection in the ambient air. It means that air convection does not affect the evaporation rate of sessile aqueous droplets and, therefore, will be neglected in corresponding computer simulations. Such assumption is justified below.
2.2. Mathematical model

Let us start considering the particular case of contact angle \( \theta = \pi / 2 \). In this case we can solve the isothermal problem of evaporation of a spherical droplet in three dimensions. The half of that droplet gives a solution for a sessile droplet on a solid substrate with contact angle \( \theta = \pi / 2 \) and a zero flux through the solid because of symmetry (Fig. 2.2). In this case, the equation which governs the diffusive evaporation in spherical coordinates is:

\[
\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c}{\partial r} \right) = 0.
\]

Corresponding boundary conditions are \( c(L) = c_{\text{sat}}(T_{\text{surf}}) \) and \( c(\infty) = c_\infty \), where \( c_{\text{sat}}(T_{\text{surf}}) \) is the concentration of the saturated vapour on the droplet surface and we neglect the deviation of the latter from the actual one (according to the Kelvin’s equation [93]). \( c_\infty \) denotes the vapour concentration in the ambient air far away from the droplet. The solution of the latter equation with its boundary conditions is

\[
c(r) = c_\infty + \left( c_{\text{sat}}(T_{\text{surf}}) - c_\infty \right) \frac{L}{r}.
\]

The local molar vapour flux in normal direction to the droplet surface is

\[
j_{\pi/2}(L, T_{\text{surf}}) = D \left( c_{\text{sat}}(T_{\text{surf}}) - c_\infty \right) \frac{1}{L}.
\] (2.1)

The latter equation shows that the local flux is uniform along the spherical surface of the droplet and inversely proportional to \( L \). The total molar flux through the liquid-air interface of a sessile droplet with contact angle \( \theta = \pi / 2 \) (half of the droplet in Fig. 2.2) is

\[
J_{\pi/2}(L, T_{\text{surf}}) = 2\pi D \left( c_{\text{sat}}(T_{\text{surf}}) - c_\infty \right) L,
\] (2.2)

which is proportional to the radius of the droplet (not to the area of its surface) in spite of the uniformity of the local normal flux \( j_{\pi/2}(L, T_{\text{surf}}) \) along the surface. This analytical solution, obtained for \( \theta = \pi / 2 \), will be used to validate the computer simulations below.
Let us demonstrate, that the inverse proportionality of the local flux to \( L \), similar to Eq. (2.1), and the direct proportionality of the total flux to \( L \), similar to Eq. (2.2), remain valid in the general case of an arbitrary contact angle and has nothing to do with a flux distribution over the droplet surface. Cylindrical system of coordinates is used below.

Under quasi-steady conditions the distribution of vapour concentration in the ambient air, \( c(z, r) \), is governed by the following diffusion equation:

\[
\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c}{\partial r} \right) + \frac{\partial^2 c}{\partial z^2} = 0. \tag{2.3}
\]

The local molar flux, \( j \), in normal direction to the surface of the droplet

\[
j = -D \frac{\partial c}{\partial n} \bigg|_{z=h(r)} = -D \left[ \frac{\partial c}{\partial r} \bigg|_{z=h(r)} \cos \alpha + \frac{\partial c}{\partial z} \bigg|_{z=h(r)} \sin \alpha \right], \tag{2.4}
\]

where \( \alpha \) is the angle shown in Fig. 2.1. Let us introduce dimensionless variables using the same symbols as the original dimensional ones but with an overbar: \( \bar{z} = z / L, \quad \bar{r} = r / L, \quad \bar{c} = c / c_\infty, \quad \bar{h} = h / L \), then

\[
j = -D \frac{\partial c}{\partial n} \bigg|_{z=h(r)} = -\frac{Dc_\infty}{L} \left( \frac{\partial c}{\partial \bar{r}} \bigg|_{z=\bar{h}(\bar{r})} \cos \alpha + \frac{\partial c}{\partial \bar{z}} \bigg|_{z=\bar{h}(\bar{r})} \sin \alpha \right) = \frac{Dc_\infty}{L} A(\bar{r}, \bar{z}), \tag{2.5}
\]

where \( A(\bar{r}, \bar{z}) = -\left( \frac{\partial c}{\partial \bar{r}} \bigg|_{z=\bar{h}(\bar{r})} \cos \alpha + \frac{\partial c}{\partial \bar{z}} \bigg|_{z=\bar{h}(\bar{r})} \sin \alpha \right). \) The total molar flux is

\[
J = 2\pi \int_0^L r j \sqrt{1 + \left( \frac{\partial \bar{h}}{\partial \bar{r}} \right)^2} \, dr = 2\pi LDc_\infty \int_0^1 \bar{r} A(\bar{r}, \bar{z}) \sqrt{1 + \left( \frac{\partial \bar{h}}{\partial \bar{r}} \right)^2} \, d\bar{r}. \tag{2.6}
\]

Hence, according to Eqs. (2.5) and (2.6), the local flux is \( j \sim \frac{1}{L} \) and the total flux is \( J \sim L \). The latter property does not depend on the distribution of the flux over the droplet surface, because this distribution is unnecessary for the above derivation.

2.2.1. Assumptions

As already mentioned above, we:

- assume axial symmetry of the problem;
• neglect gravity force (capillary forces dominate over gravitational one for 
\( L < 1 \text{ mm} \));

• assume that for \( L > 5 \cdot 10^{-8} \text{ m} \) the evaporation rate is limited by vapour diffusion 
into ambient air, which means that diffusion is much slower than the process 
of molecules transition across the liquid-air interface (kinetic effects are 
neglected);

• neglect the influence of the curvature of the droplet’s surface on the value of 
concentration of saturated vapour immediately above this surface (Kelvin’s 
equation is neglected): a noticeable influence of the curvature on the vapour 
concentration appears only for very small droplets, the change constitutes 
more than 1% if the droplet size is less than \( 10^{-7} \text{ m} \);

• based on the conducted estimations, we assume that process of vapour 
diffusion into ambient air and processes of heat and momentum transfer 
inside of the droplet are quasi-steady ones, which allows us neglecting time 
derivatives in governing equations.

Now let us estimate in more detail the influence of air convection on the evaporation 
process. We will consider only that air convection, generated by evaporation (Stefan 
flow) and by thermal Marangoni convection inside of the droplet. The air velocity 
above the liquid-air interface has both tangential (caused by Marangoni convection) 
and normal (due to evaporation) components. Consequently, the tangential 
component is determined by the velocity of Marangoni convection, which is of order 
of \( 10^{-3} \text{ m/s} \) (according to computer simulations). The normal component is defined by 
the local evaporation rate \( j \). Let us denote the surface density of the molar flux of 
vapour as \( j_c \) \((\text{mol/m}^2\text{s})\) and the surface density of the mass flux of vapour as \( j_m \) 
\((\text{kg/m}^2\text{s})\). Then the normal air velocity, \( u_{a,n} \), at the droplet surface can be calculated as

\[
 u_{a,n} = \frac{j_m}{\rho_a} = \frac{j_c M}{\rho_a},
\]

where \( \rho_a \) is the density of air, and \( M \) is the molar mass of vapour. For the case of 
contact angle \( \theta = \pi / 2 \), humidity \( H = 70\% \), contact line radius \( L = 10^{-3} \text{ m} \) and surface 
temperature \( T_{surf} = 293 \text{ K} \) we can estimate the local molar vapour flux \( j_{c2} \) using Eq. 
(2.1). The result is \( u_{a,n} \sim 10^{-4} \text{ m/s} \). Hence, the characteristic convection velocity of air
is $u_a = 10^{-3}$ m/s. Using that characteristic velocity, the characteristic droplet size $L = 10^{-3}$ m, as well as the vapour diffusion coefficient $D = 2.4 \cdot 10^{-5}$ m$^2$/s and the thermal diffusivity of air $\kappa = 2.0 \cdot 10^{-5}$ m$^2$/s, we can calculate the thermal, $Pe_\kappa$, and the diffusive, $Pe_D$, Peclet numbers: $Pe_\kappa = L u / \kappa = 0.05$; $Pe_D = L u / D \approx 0.04$. Such low values of Peclet numbers mean that the convective fluxes of heat and mass are negligible in comparison with diffusive ones.

From the above estimations we can conclude that air convection can be neglected. A numerical experiment was conducted to cross-check it by considering evaporation of a sessile droplet with air convection and without it. The result shows that the change of temperature at the droplet apex (minimal temperature in the system) is very small:

$$\frac{T_{\text{conv}}^{\text{apex}} - T_{\text{apex}}^{\text{apex}}}{T_\infty - T_{\text{apex}}} < 0.01,$$

where $T_{\text{conv}}^{\text{apex}}$ and $T_{\text{apex}}^{\text{apex}}$ are the temperature of the droplet apex with and without air convection, respectively, $T_\infty$ is the ambient temperature far away from the droplet.

The quasi-steady-state solution of the problem corresponds to solving the problem with vanishing time-derivatives. Hence, the problem is solved only for the instantaneous field values and for the fluxes in the system.

The above statement implies that the problem must be solved with a fixed droplet volume. Accordingly, in order to preserve the mass conservation law as the droplet evaporates, the rate of change of the droplet’s volume must be non-zero. In this case the liquid-gas interface must have non-zero normal velocity, in accordance with the evaporation rate. The order of magnitude of this interface velocity, $u_\Gamma$, is:

$$u_\Gamma \approx \frac{1}{A_t} \frac{dV}{dt},$$

where $A_t$ is the droplet surface area. Using the Eq. (1.1) and formula for the surface area $A_t = \frac{2\pi L^2 (1 - \cos \theta)}{\sin^2 \theta}$, we get:

$$u_\Gamma \approx -\frac{\sin^2 \theta}{L(1-\cos \theta)} \frac{DM}{\rho} c_{sat}(T_\infty)(1-H)F(\theta).$$

Using the known analytical expression for $F(\theta)$ derived in Ref. [70], for the isothermal case:
it can be concluded, that \( \frac{\sin^2 \theta}{(1-\cos \theta)} \cdot F(\theta) \) in the expression for \( u_1 \) is finite and less than 1.316 for all values of the contact angle in the interval \( 0 \leq \theta \leq 2\pi \). Thus, \( |u_1| < \frac{DM}{\rho L} c_{sw}(T_\infty)(1-H) \cdot 1.316 \). For an evaporating water droplet in a completely dry air atmosphere \((H=0)\) at \( T_\infty = 293K \) we get: \(|u_1| < \frac{5.6 \cdot 10^{-10} \text{ m}^2/\text{s}}{L} \). For \( L > 10^{-6} \text{ m} \) it gives the interfacial velocity \(|u_1|\) lower than the velocity of Marangoni flow inside of the droplet, which is about \( 10^{-3} \text{ m/s} \). Accordingly, the interfacial velocity of the liquid-air interface can be neglected in our computations for millimetre-size droplets.

Summarizing the above, we:

- neglect convective heat and mass transfer in the air domain and consider only vapour diffusion and heat conduction in that domain;
- neglect the interfacial velocity of the liquid-air interface.

### 2.2.2. Bulk equations

Based on the above assumptions, the following quasi-steady bulk equations are used in present model:

1) Eq. (2.3) describes the vapour diffusion in ambient air;

2) The Navier-Stokes (momentum transfer) equations together with the continuity equation in the liquid bulk:

\[
\begin{align*}
   u \frac{\partial u}{\partial r} + v \frac{\partial u}{\partial z} &= -\frac{\partial p}{\partial r} + \mu \left( \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial u}{\partial r} \right) + \frac{\partial^2 u}{\partial z^2} - \frac{u}{r^2} \right) , \\
   u \frac{\partial v}{\partial r} + v \frac{\partial v}{\partial z} &= -\frac{\partial p}{\partial z} + \mu \left( \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial v}{\partial r} \right) + \frac{\partial^2 v}{\partial z^2} \right) , \\
\end{align*}
\]

\( \left(2.7\right) \)

\[
1 \frac{\partial (ru)}{r \partial r} + \frac{\partial v}{\partial z} = 0 ,
\]

\( \left(2.8\right) \)
where $u$ and $v$ are radial and vertical components of the velocity vector, respectively; $p$ is the hydrodynamic pressure; and $\mu$ is the dynamic (shear) viscosity;

3) The equation of conductive (Fourier) and convective heat transfer in all three phases (solid support, liquid droplet, and the ambient air):

$$
\left(\frac{u}{r} \frac{\partial T}{\partial r} + \frac{v}{\partial z} \right) = \kappa \left(1 \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r}\right) + \frac{\partial^2 T}{\partial z^2}\right),
$$

where $T$ is the temperature, $\kappa$ is the thermal diffusivity of the corresponding phase. Note that $u = v = 0$ in vapour and solid phases.

### 2.2.3. Boundary conditions

At the **liquid-solid** interface:
- no-penetration and no-slip boundary conditions are used for Navier-Stokes equations:
  $$u = 0, \quad v = 0;$$
- continuity conditions for the temperature and heat fluxes:
  $$T_l = T_s, \quad -k_l (\nabla T)_l \cdot \vec{n}_{l,s} = -k_s (\nabla T)_s \cdot \vec{n}_{l,s},$$
  where subscripts $l$ and $s$ refer to liquid and solid phase, respectively, $k$ is the thermal conductivity, $\nabla T$ is the temperature gradient, $\vec{n}_{l,s}$ is the unit normal vector, to the liquid-solid interface.

At the **air-solid** interface:
- no-penetration condition is used for the diffusion equation:
  $$\vec{j} \cdot \vec{n}_{a,s} = 0,$$
  where subscripts $a$ and $s$ refer to air and solid phase, respectively, $\vec{n}_{a,s}$ is the unit vector, normal to the air-solid interface;
- continuity for the temperature and the heat fluxes is assumed:
  $$T_a = T_s, \quad -k_a (\nabla T)_a \cdot \vec{n}_{a,s} = -k_s (\nabla T)_s \cdot \vec{n}_{a,s}.$$
• **Symmetry** demands:

\[ \frac{\partial c}{\partial r} \bigg|_{r=0} = 0, \quad \frac{\partial T}{\partial r} \bigg|_{r=0} = 0, \quad \frac{\partial v}{\partial r} \bigg|_{r=0} = 0, \quad \frac{\partial p}{\partial r} \bigg|_{r=0} = 0, \quad u = 0. \quad (2.15) \]

• At the **outer boundaries** of the system the following conditions are applied:

\[ c(\infty) = c_* , \quad T(\infty) = T_* . \quad (2.16) \]

At the **liquid-air** interface (droplet’s surface):

• As already was discussed, one of the assumptions accepted here is that the velocity component, normal to the liquid-air interface, is negligible in comparison with its tangent component, caused by thermal Marangoni stress. Hence in our quasi-steady approach we set:

\[ \vec{u} \cdot \vec{n}_{i,a} = 0 , \quad (2.17) \]

where \( \vec{n}_{i,a} \) is the unit vector perpendicular to the liquid-air interface.

• The condition of thermal Marangoni stress is used at the liquid-air interface:

\[ \mathbf{T} \cdot \vec{n}_{i,a} = -\gamma K \vec{n}_{i,a} + \gamma' \nabla_{\text{surf}} T, \quad (2.18) \]

where \( \mathbf{T} \) is the full stress tensor, \( \gamma \) is the liquid-air interfacial tension, \( K \) is the curvature of the liquid-air interface (positive for a droplet), \( \gamma' \) is the derivative of \( \gamma \) with temperature, \( \nabla_{\text{surf}} T = \left( \frac{\partial T}{\partial r} \sin \alpha - \frac{\partial T}{\partial z} \cos \alpha \right) \vec{t}_{i,a} \) is the surface gradient of the temperature, \( \vec{t}_{i,a} \) is the unit tangent vector at the liquid-air interface.

• The concentration of saturated vapour, \( c_{\text{sat}} \), at the droplet surface is defined by the local temperature according to the Clausius-Clapeyron equation and the ideal gas law:

\[ \ln \left( \frac{p_{\text{sat}}}{p_{\text{ref}}} \right) = -\frac{\Lambda}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right), \quad (2.19) \]

\[ p_{\text{sat}} = c_{\text{sat}} RT, \quad (2.20) \]

where \( p_{\text{sat}} \) is the pressure of saturated vapour at temperature \( T \), \( p_{\text{ref}} \) is the pressure of saturated vapour at temperature \( T_{\text{ref}} \), \( \Lambda \) is the latent heat of vaporization of the liquid and \( R \) is the universal gas constant. As already mentioned above, the influence of curvature on the concentration of saturated vapour is neglected.

• The temperature at the liquid-air interface is continuous:
\[ T_i = T_a. \] (2.21)

- However the heat flux experiences discontinuity because of the latent heat of vaporization:
\[ k_a(\nabla T)_a \cdot \hat{n}_{f,a} - k_i(\nabla T)_i \cdot \hat{n}_{i,a} = j \cdot \Lambda. \] (2.22)

### 2.3. Computer simulations

The numerical solution of the steady state problem described above is obtained using the commercial software COMSOL Multiphysics v 3.5a. The numerical technique employed by that software by default is the Finite Element Method (FEM). The shape functions, chosen for the simulation, are Lagrange quadratic shape functions. All the equations are automatically converted into their weak form. All boundary conditions are fulfilled using constraints with Lagrange multipliers (the calculus of variations is applied).

The shape of the computational domain is a sphere with its centre in the origin of coordinates, position of which is determined by the intersection of the axis of problem symmetry with the upper surface of the substrate. Boundary conditions, Eq. (2.16), are applied at its outer boundary. The radius of this sphere is chosen to be one hundred times bigger than the contact line radius \( L \). This choice prevents numerical artefacts caused by the proximity of the outer boundary [73], and provides a good approximation (less than 1% error bar) for the problem of droplet evaporation into a semi-infinite space.

The generated computational mesh consists of triangular elements, whose size is changing gradually from the smallest value at the droplet edge to the biggest one at the outer boundary of the computational domain.

Further mesh refinement is done in order to reduce the influence of singularities at the droplet edge. The evaporation flux and viscous stress both diverge to infinity at the droplet edge (for \( \theta \neq \pi/2 \)), which is due to the incompatibility of boundary conditions at the liquid-air interface with those at the liquid-solid and air-solid interfaces. Therefore, to reduce the influence of these singularities on the problem
solution, the size of mesh elements at the droplet edge is selected to be one hundred times smaller than the contact line radius, $L$. Thus the numerical artefacts, caused by the singularities, are enclosed within the smallest computational elements adjacent to the three-phase contact line.

In all computer simulations of the present study the liquid is water and the solid substrate is copper if other materials are not mentioned. Ambient temperature $T_\infty=20^\circ$C is used below.

### 2.3.1. Mesh resolution study

It is well known that the resolution of the computational mesh influences the accuracy of a numerical solution. Reducing the mesh size we can reduce the error of discretization of equations. At the same time, decreasing the size of mesh elements leads to the increase of the number of mesh elements, which can substantially slow down the computational process and require much greater amount of machine memory. Therefore the optimal size of mesh elements must be determined for the numerical calculations.

The mesh resolution study was performed, results of which are shown below. We studied the influence of the computational mesh resolution on the macroscopic parameter: the total molar vapour flux at the droplet surface, $J_c$, obtained by the numerical integration of the local vapour flux over the whole droplet surface.

![Fig. 2.3: Total molar vapour flux at the droplet surface, $J_c$, as a function of the number of elements of the computational mesh. Left: contact line radius $L = 1E-5$ m. Right: contact line radius $L = 1E-3$ m. See M1, M2, and M3 in Fig. 2.4.](image)
Fig. 2.4: Computational meshes for different mesh resolutions. M1 is for 15000 mesh elements; M2 is for 60000; and M3 is for 130000.

Fig. 2.3 shows the dependence of $J_c$ on the number of mesh elements for two different droplet sizes: $L = 10^{-5}$ m, and $L = 10^{-3}$ m. For three particular numbers of
mesh elements (marked as M1, M2, and M3) corresponding computational meshes are shown in Fig. 2.4.

It is clearly seen in Fig. 2.3 that the value of the macroscopic parameter $J_c$ is gradually approaching some upper limit as the number of mesh elements is growing (numerical solution is converging).

Based on the above study, the optimal number of mesh elements is chosen to be approximately $6 \cdot 10^4$. This mesh resolution will be used throughout the rest of present work.

2.4. Results: instantaneous distribution of fluxes in the course of evaporation

Unlike lab experiments computer simulations allow to switch on/off any physical effects in the system under consideration. Switching off both the Marangoni convection and the effect of latent heat of vaporization allows comparing our simulation results with earlier published results on isothermal evaporation of droplets.

In all computer simulations presented below the cell Reynolds number in liquid droplet did not exceed 1, which means that flow regime is far from the turbulent one. Cell Peclet number for heat transfer in liquid droplet did not exceed 5. As the thermal Peclet number can reach value of 5, then convective heat flux can be 5 times more intensive than conductive one, therefore the convective heat transfer in the droplet it is taken into account.

2.4.1. Temperature filed

Temperature field for the particular case of evaporating sessile droplet is presented below, Fig. 2.5. Results show that highly heat conductive substrate (copper) has almost the same temperature through the bulk, which equals the ambient one. Temperature changes mostly within the droplet bulk, from the highest value at the liquid-solid interface to the lowest value at the apex of the droplet.
The lowest temperature in the system is at the liquid-air interface, because heat is consumed by the process of evaporation. Both the value of vapour concentration in ambient atmosphere (humidity) and its saturated value above the droplet surface determine the intensity of evaporation. Note that saturated vapour concentration depends on local temperature. In turn, the intensity of evaporation and the latent heat of vaporization define the intensity of the heat sink on the droplet’s surface. Thus Fig. 2.5 represents the numerical solution of the coupled problem of heat transfer and diffusive evaporation.

As one can see from the figure above, the temperature drop for that particular case constitutes about one degree. This is enough to generate thermal Marangoni convection inside of the droplet with typical velocity of liquid motion of order of 1 mm/s.

Fig. 2.5: Temperature field in an evaporating droplet of water on top of a copper substrate for particular values of contact angle $\theta = 40$ deg and contact line radius $L = 1$ mm. White lines are contour lines of temperature, ambient temperature is 293 K, and ambient air humidity is 70%.
2.4.2. Thermal Marangoni convection

As already mentioned above, the thermal Marangoni convection inside of the evaporating sessile droplet is generated by the gradient of temperature on the droplet’s surface. The temperature on that surface is higher at the droplet edge because of the proximity of a highly heat conductive substrate (copper) which delivers ambient heat and supports the evaporation process. The coldest point on the droplet’s surface is its apex, which is the most distant point from the heat conducting substrate. Thus, having a temperature gradient, $\nabla T$, on the surface introduces also the surface tension gradient, $\nabla \gamma$, because surface tension is the function of temperature:

$$\nabla \gamma = \gamma' T,$$

where $\gamma'$ is the derivative of surface tension with respect to temperature.

Gradient of surface tension gives a tangential Marangoni stress on the liquid surface, which drives adjacent layers of liquid underneath the surface. As a result we observe Marangoni convection inside of the droplet, which looks like an eddy (see Fig. 2.6).

![Diagram showing velocity field inside the droplet with $\theta = \pi/2$ and $L = 1$ mm. Both LHV and MC are taken into account.](image)

Fig. 2.6: Velocity field inside the droplet with $\theta = \pi/2$ and $L = 1$ mm. Both LHV and MC are taken into account.
2.4.3. Local normal vapour flux over the droplet surface

As the density of vapour flux, $\bar{j}$, in the air phase is governed by the diffusion process, then its value is directly determined by the gradient of vapour concentration: $\bar{j} = -D \nabla c$. In turn, the gradient of vapour concentration above the droplet’s surface is affected by the concentration of saturated vapour, $c_{\text{sat}}$, on that surface. The value of $c_{\text{sat}}$ is determined by the local temperature; and its dependence on the surface curvature is ignored here, because this effect is negligible, as already mentioned.

Thus, the local evaporation flux at the droplet’s surface is determined by local temperature and by vapour concentration field around the point where evaporation flux is evaluated.

![Graph](image.png)

Fig. 2.7: Calculated distributions of local normal vapour flux, $j$, over the droplet surface, $\theta = \pi/2$, $L = 1\, \text{mm}$. Circles - both Marangoni convection (MC) and latent heat of vaporization (LHV) are taken into account; squares - LHV is included, but MC is excluded; triangles - both MC and LHV are excluded. The insertion represents the shaded rectangle with a changed scale.
Our computer simulations give the distribution of evaporation flux, \( j \), over the droplet surface presented in Fig. 2.7. It shows normalised vapour flux \( j / j_\pi/2(L, T_\infty) \), where \( j_\pi/2(L, T_\infty) \) is the isothermal flux for \( \theta = \pi / 2 \) and \( T_{\text{surf}} = T_\infty \) according to Eq. (2.1), when only diffusion of the vapour is taken into account.

There are three different cases presented in Fig. 2.7: 1) evaporation when both Marangoni convection (MC) and latent heat of vaporization (LHV) are included – circles; 2) evaporation with LHV included but without MC – squares; 3) evaporation without both MC and LHV – triangles. The latter case corresponds to the above mentioned analytical solution, \( j_\pi/2(L, T_\infty) \), Eq. (2.1). Therefore the numerically obtained and normalised evaporation flux (triangles in Fig. 2.7) equals 1 within the simulation error bar: \( j / j_\pi/2(L, T_\infty) = 1 \). This confirms the validity and enough accuracy of our numerical model with respect to modelling of the vapour diffusion process.

Introducing the latent heat of vaporization into the isothermal problem results in appearance of the cooling of the droplet’s surface, as evaporation consumes heat. The cooling is not uniform (see Fig. 2.8) due to the presence of the heat conductive substrate. As expected, the coldest point in the system is located at the apex of the droplet. It gives the lowest value of the saturated vapour concentration, \( c_{\text{sat}}(T_{\text{apex}}) \), and consequently the lowest evaporation rate, \( j \), at the droplet apex (squares in Fig. 2.7).

The highest temperature (due to the proximity of the substrate, see Fig. 2.8), and consequently the highest saturated vapour concentration, \( c_{\text{sat}}(T_{\text{edge}}) \), and the highest local evaporation flux, \( j \) (squares in Fig. 2.7), are at the droplet edge.

One can see that switching on the LHV (squares in Fig. 2.7) increased the evaporation rate at the droplet edge (comparing to the isothermal case: triangles in Fig. 2.7). This seems counterintuitive, because LHV usually causes cooling of the liquid-gas interface (Fig. 2.8) and decrease of the evaporation rate. However, there
is no mistake here, and a simple physical explanation can be given to the observed numerical result: (i) there is almost no decrease of temperature at the droplet’s edge (Fig. 2.8) because of the proximity of a heat conductive substrate; (ii) the evaporation at the droplet’s edge is increased due to the appearance of an additional vapour flux along the droplet surface (from the edge to the apex), which is caused by the gradient of vapour concentration along the surface. This vapour flux along the droplet surface is absent in the isothermal problem, because in that case the saturated vapour concentration, \( c_{sat}(T_{\infty}) \), does not change along the droplet surface. As a result there is up to 10% decrease of \( j \) over the bigger part of the droplet surface (due to temperature decrease), and up to 30% increase of \( j \) at the droplet edge (due to unchanged temperature at the edge and vapour concentration redistribution along the droplet surface), as illustrated by Fig. 2.7.

Switching on the Marangoni convection inside of the droplet generates a liquid flow, as shown in Fig. 2.6, which introduces a convective heat flux in addition to the conductive one. The flow along the droplet surface from its edge (where temperature is higher) to the apex (where temperature is lower) increases the overall temperature of the surface (see Fig 2.8, compare circles and squares). However, the convective heat flux from the droplet apex down to the substrate along the axis of droplet’s symmetry results in a comparative apex cooling (plot of the surface temperature is more concave at the centre of the droplet: see circles in Fig. 2.8). This insignificant temperature reduction at the droplet’s apex results in a quite noticeable decrease of the local evaporation flux, \( j \) (circles in Fig. 2.7).

The above consideration of the distribution of local evaporation flux, \( j \), over the droplet surface is carried out only for a particular value of contact angle: \( \theta = \pi / 2 \). This is done on purpose in order to exclude the influence of the contact angle (in an isothermal model the evaporation flux for \( \theta = \pi / 2 \) is uniform over the droplet surface) and to be able to show the effects of latent heat of vaporization and Marangoni convection. Below we consider the influence of the contact angle on the distribution of \( j \) over the droplet surface. This effect is stronger and it masks the
above considered weaker effects of the latent heat of vaporization and Marangoni convection.

Fig. 2.9 shows the distribution of the local vapour flux, \( j \), for three different contact angles \( \theta \). When \( \theta < \pi / 2 \), the local flux increases towards the three-phase contact line. However, if \( \theta > \pi / 2 \), the behaviour is opposite: local flux decreases towards the three-phase contact line. This distribution is the result of solving the diffusion Laplace equation for vapour concentration in surrounding air. Results are in qualitative agreement with the results of Deegan et al [59], who calculated the vapour flux taking into account the vapour diffusion only in an isothermal case.

Fig. 2.8: Calculated temperature distributions over the droplet surface: \( \theta = \pi / 2 \), \( L = 1 \) mm. \( T_{\infty} \) is the ambient temperature. Circles - MC and LHV are taken into account; squares - LHV is included, but MC is excluded; triangles - both MC and LHV are excluded.
Fig. 2.9: Calculated distributions of local normal vapour flux, \( j \), over the droplet surface, \( L = 1 \text{ mm} \), both LHV and MC are taken into account. Circles - \( \theta = \pi/2 \); squares - \( \theta = 2\pi/3 \); triangles - \( \theta = 2\pi/9 \).

\[ j / j_{\pi/2}(L,T_\infty) \]

Fig. 2.10: Calculated dependences of a local vapour flux at the droplet apex, \( j_{\text{apex}} \), on radius of the contact line, \( L; \theta = \pi/2 \). Circles - MC and LHV are taken into account; squares - LHV is included, but MC is excluded; triangles - both MC and LHV are excluded.
The part of the curve for $\theta = 2\pi/3$ in Fig. 2.9 (squares) appears in the range $r/L > 1$, which corresponds to the part of the droplet surface appearing in that range for contact angles $\theta > \pi/2$.

To check the validity of the earlier given dependence of the local vapour flux on contact line radius, $j \sim 1/L$, Eq. (2.5), the ratio of fluxes $j_{\text{apev}}/j_{\pi/2}(L,T_\infty)$ is plotted against the inverse value of $L$ (Fig. 2.10) for $\theta = \pi/2$. In Fig. 2.10 one can see that proportionality $j_{\text{apev}}/j_{\pi/2}(L,T_\infty) \sim \text{const}$ (which means $j_{\text{apev}} \sim 1/L$) is valid only when effect of Marangoni convection is switched off. The presence of Marangoni convection makes that dependence non-linear (circles in Fig. 2.10).

### 2.4.4. Total vapour flux from the droplet surface

Let us now study the dependence of the total vapour flux, $J$, on the radius of the contact line, $L$, and the contact angle, $\theta$ (Fig. 2.11). It appears that $J$ increases nonlinearly with the increase of the contact angle. All calculations were performed with both LHV and MC included. The results (Fig. 2.11) were obtained for substrates with parameters of different materials and compared to those calculated for the isothermal case by H. Hu and R.G. Larson [79] and F. Schonfeld et al [94]. In the case of highly heat conductive solid support (copper) the difference between the present simulations and the results from [79, 94] for isothermal case do not exceed 3%. The latter is because of a small temperature change at the droplet surface: this regime is close to the isothermal one (Fig. 2.8). However, if other materials are used with lower heat conductivity (down to the heat conductivity of air), then the evaporation flux is substantially reduced (Fig. 2.11). This flux reduction is related to the noticeable temperature reduction of the droplet surface.
Fig. 2.11: Rescaled dependence of the total vapour flux from the droplet surface, $J$, on contact angle $\theta$, $L = 1\text{ mm}$. Both LHV and MC are taken into account.

$J/J_{\pi/2}(L, T_{\infty})$

Fig. 2.12: Rescaled dependence of the total vapour flux from the droplet surface, $J$, on contact angle $\theta$, $L = 1\text{ mm}$. Both LHV and MC are taken into account.
Let us now introduce the mean temperature of the droplet surface: 

$$T_{av} = \frac{1}{S} \int_{S} T dS,$$

where $S$ is the droplet surface area. The dimensionless total flux $J/J_{π/2}(L,T_{av})$, (Fig. 2.12), has been plotted. All calculated total fluxes for all substrates appeared on one universal dependence of total vapour flux, $J$, versus contact angle, $θ$. Accordingly, the variation of the surface temperature is important phenomenon influencing the evaporation rate.

Let us check if the singularity at the droplet edge affects the dependence, presented in Fig. 2.12. The following procedure was adopted: the singularity region (close to the three-phase contact line) was excluded from the integration of the local vapour flux, $j$. That is the integration was performed over the part of the surface corresponding to the following range of radial coordinate values: $0 ≤ r < 0.95L$; after that the total vapour fluxes $J$ and $J_{π/2}(L,T_{av})$ were calculated by integration over a truncated area of the droplet. As a result a deviation from the dependence, presented in Fig. 2.12 was found to be not more than 2%. That means that the influence of the singularity in the present simulations is negligible.

The total vapour flux, $J$, varies linearly with $L$ only in the case of absence of Marangoni convection. That can be seen from Fig. 2.13, where the triangles show the ratio $J(L)/J_{π/2}(L,T_{∞})$ to be constant for the isothermal model while the squares illustrate the constancy for the model with LHV and without MC. The difference between these two is only quantitative: the total evaporation rate is smaller, if LHV is included into the model. The addition of Marangoni convection changes the character of the above dependence. It becomes non-linear (circles in Fig. 2.13). For any value of $L$ the evaporation is enhanced if Marangoni convection is included. This evaporation enhancement is due to surface temperature increase (Fig. 2.8).
Fig. 2.13: Dependence of the total vapour flux from the droplet surface, $J$, on radius of the contact line, $L$, at $\theta = \pi/2$. Circles - MC and LHV are taken into account; Squares - LHV is included, but MC is excluded; Triangles - both MC and LHV are excluded from the model.

Fig. 2.14: Dependence of the temperature at the apex of the droplet, $T_{\text{apex}}$, on the radius of the contact line, $L$, at $\theta = \pi/2$. Circles - MC and LHV are taken into account; squares - LHV is included, but MC is excluded; triangles - both MC and LHV are excluded.
For the case with MC, as the size of the droplet decreases, the total evaporation flux, \( J \) (circles in Fig. 2.13), tends to the value attained in case of “switched on” LHV and “switched off” MC (squares in Fig. 2.13). In order to understand such behaviour let us compare the two types of heat transfer in the system: conductive and convective.

In the first approximation, when convection is absent, the conductive heat flux from the substrate to the droplet surface is spent on evaporation (see Eq. (2.22)). If the heat flux to air is neglected, then we get from Eq. (2.22): 

\[ -k_j(\nabla T)_j \cdot \hat{n}_{ia} = j \cdot \Lambda, \]

that is

\[ \frac{T_\infty - T_{apex}}{L} \sim j_{apex} \frac{\Lambda}{k_j}, \]

where \( T_{apex} \) is the temperature and \( j_{apex} \) is the local vapour flux at the droplet apex. According to Eq. (2.5) \( j_{apex} \sim \frac{1}{L} \). Comparing the latter two equations we conclude that \( T_\infty - T_{apex} \) does not depend on the droplet size \( L \). However, that latter is true only for the case of no MC (Fig. 2.14).

According to the Newton’s law of viscous flow, the velocity gradient in the droplet is proportional to the surface stress, Eq. (2.18):

\[ \frac{u_{surf} - u_{sub}}{L} \sim \nabla u \frac{T_\infty - T_{apex}}{L}, \]

where \( u_{surf} \) is the velocity at the droplet surface, and \( u_{sub} = 0 \) is the velocity at the solid substrate. Consequently, \( u_{surf} \sim T_\infty - T_{apex} \), which does not depend on the droplet size \( L \).

Thus, in the first approximation the velocity inside the droplet is constant, leading to a constant convective heat flux. At the same time the conductive heat flux is proportional to the temperature gradient \( \frac{T_\infty - T_{apex}}{L} \). Therefore as the droplet size decreases the conductive regime of heat transfer becomes dominant. As a result (see Fig. 2.13) the reduction of the contact line radius, \( L \), changes the value of total vapour flux, \( J \), to that corresponding to the regime of heat conduction only.
Fig. 2.15: Dependence of total vapour flux from the droplet surface, $J$, on contact angle, $\theta$, in the case of substrate heating, $L = 1$ mm. Both LHV and MC are taken into account. Normalized by $J_{\pi/2}(L, T_s)$. $T_s$ is the temperature of the substrate far from the droplet.

$$J/J_{\pi/2}(L, T_s)$$

Fig. 2.16: Dependence of total vapour flux from the droplet surface, $J$, on contact angle, $\theta$, in the case of substrate heating, $L = 1$ mm. Both LHV and MC are taken into account. Normalized by $J_{\pi/2}(L, T_{av})$. $T_s$ is the temperature of the substrate far from the droplet.
Evaporation of a droplet placed on a heated substrate reveals similar dependencies of the total vapour flux, $J$, on the contact angle, $\theta$, as shown in Fig. 2.15. In this case the total vapour flux, $J$, is related to the theoretical value, $J_{\pi/2}$, according to Eq. (2.2), at a surface temperature equal to the temperature of the heated substrate. As before, the result in the case of a copper substrate is close to the theoretical curve because of the high heat conductivity of copper and, consequently, the small difference in the temperatures of the droplet surface and the heated substrate. But for materials with poor heat conductivity the deviation from the isothermal curve is even bigger than that in case of absence of substrate heating (Fig. 2.11).

Fig. 2.16 shows the same simulation results as shown in Fig. 2.15, but comparing with the theoretical value (Eq. (2.2)), $J_{\pi/2}$, calculated with the mean temperature of the droplet surface, $T_{\text{av}}$. It is clearly seen that all curves fall in one universal relationship. Thus, it can be concluded that together with contact line radius, $L$, and contact angle, $\theta$, the mean surface temperature of the droplet, $T_{\text{av}}$, is an important parameter describing the evaporation rate.

**2.5. Conclusions**

Under a number of reasonable approximations the evaporation of small enough sessile droplets has been investigated in a self-consistent way by considering the interconnected problem of vapour transfer; heat transfer in solid substrate, liquid and surrounding air; and thermal Marangoni convection inside the liquid droplet. The influence of the thermal conductivity of the solid substrate on the evaporation rate has been analysed. The calculated total evaporation flux has been compared with the one in case of isothermal evaporation. It has been shown that the lower the thermal conductivity of the solid support the higher the deviations from the isothermal curve.

It has also been found that the latent heat of vaporization does not change the qualitative dependence of the total vapour flux, $J$, on the droplet size, $L$, which remains linear: $J \sim L$. The latent heat of vaporization affects only the distribution of
the local flux over the droplet surface due to temperature changes and reduces the value of the total vapour flux, \( J \). This effect however does not change the proportionality of the local normal vapour flux at the apex of the droplet to the inverse value of droplet size: \( j_{\text{apex}} \sim 1/L \).

The presence of the thermal Marangoni convection inside of the droplet makes all relationships non-linear. Consequently, the proportionality of the rate of change of the droplet volume to the radius of the droplet base, \( L \), is affected by the thermal Marangoni convection inside of the droplets.

When the rescaled dimensionless total flux is plotted, \( J/J_\pi (L, T_{av}) \) where \( T_{av} \) is the mean surface temperature, then all calculated total fluxes for solid substrates of different heat conductivity fall on a single universal relationship between the total vapour flux, \( J \), and the contact angle, \( \theta \). It was found out that this universal curve coincides with the one known for the isothermal case. Accordingly, the variation of the surface temperature is an important element influencing the evaporation rate.

Finally, we can safely say that the deduced expressions of the instantaneous fluxes can be applied for self-consistent calculations of the time evolution of the evaporation processes of sessile droplets.

3. Evaporation of sessile water droplets: universal behaviour in presence of contact angle hysteresis

3.1. Introduction

The time evolution of an evaporating sessile droplet can be reconstructed using the deduced expressions of the instantaneous fluxes. In presence of contact angle hysteresis the whole duration of the spreading/evaporation process can be subdivided into four stages:

0) A spreading until the value of static advancing contact angle, \( \theta_{\text{adv}} \), is reached.

1) Radius of the contact line remains constant and equal to its initial value \( L_0 \), which is the maximum value of the radius of the contact line. At the same time the
contact angle, $\theta$, decreases from the initial value, which is equal to a static advancing contact angle, $\theta_{ad}$, to the final value, which is a static receding contact angle, $\theta_r$. The moment when the first stage started is adopted below as a zero moment, $t = 0$. At this moment the radius of the contact line reaches its maximum value and the contact angle is equal to the static advancing contact angle, $\theta_{ad}$.

II) Contact angle remains constant and equal to $\theta_r$, while the radius of the contact line decreases from $L_0$ to almost zero value.

III) Both contact angle, $\theta$, and contact line radius, $L$, decrease to zero values.

Stages (0) and (III) are not covered by the theory presented below; only stages (I) and (II) are considered, which below are referred to as stage one and stage two respectively. Two contact angles $\theta_{ad}$ and $\theta_r$ are considered to be determined independently.

### 3.2. Theory

Let us assume that during both stages of evaporation the droplet surface retains the spherical cap shape. That is, the volume of the droplet, $V$, can be presented as follows:

$$V = L^3 f(\theta), \quad f(\theta) = \frac{(1 - \cos \theta)^2}{3 \sin^3 \theta} (2 + \cos \theta). \quad (3.1)$$

During both stages of evaporation the mass conservation law has the form given by Eq (1.1), where

$$F(\theta) = \begin{cases} 
0.6366 \cdot \theta + 0.09591 \cdot \theta^2 - 0.06144 \cdot \theta^3, & \theta < 10^\circ \\
0.00008957 + 0.6333 \cdot \theta + 0.116 \cdot \theta^2 - 0.08878 \cdot \theta^3 + 0.01033 \cdot \theta^4, & \theta > 10^\circ
\end{cases} \quad (3.2)$$

derived by R.G.Picknett and R.Bexon [70] and later used by F.Schonfeld et al. [94] (see Figs. 2.12 and 2.16). Let us rewrite Eq. (1.1) in the following form:

$$\frac{dV}{dt} = -\beta F(\theta)L, \quad (3.3)$$

where

$$\beta = 2\pi \frac{DM}{\rho} \left( c_{sat} \left( T_{surf} \right) - H_{c_{sat}} \left( T_s \right) \right). \quad (3.4)$$
Note that in this equation, the temperature of the droplet surface, $T_{surf}$, is supposed to be uniform, because formula for $F(\theta)$ is obtained in [70] for an isothermal problem. However, according to the results of our computer simulations, we can apply this formula in non-isothermal case by substituting the average temperature, $T_{av}$, of the droplet surface instead of $T_{surf}$. In what follows we analyse the behaviour of the average temperature of the droplet surface, $T_{av}$.

3.2.1. Average temperature of the surface of a sessile droplet

Let us estimate the variation of the average temperature of the droplet surface, $T_{av}$, in the course of droplet evaporation. Our computer simulations show (see Fig. 3.1) the dependence of the average temperature of the surface of an aqueous drop, $T_{av} - T_\infty$, on: (1) the substrate temperature, $T_s$, far away from the droplet; (2) the thermal conductivity, $k_s$, of the substrate; (3) the contact angle, $\theta$. Fig. 3.1 clearly shows that dependence of $T_{av}$ on contact angle, $\theta$, is much less pronounced than its dependence on $T_s$ and $k_s$.

We conclude from Fig. 3.1 that if heat conductivity and temperature of the substrate remain constant during the evaporation of a droplet, then the average temperature, $T_{av}$, of the droplet surface is almost constant. It can only vary within the range of 1 degree (Fig. 3.1) in the course of evaporation due to weak dependence on the contact angle.

Experiments by S. David et al. [95] have shown that temperature in the bulk of a sessile evaporating droplet substantially depends on the thermal properties of the substrate and the rate of evaporation. Their measurements (Fig. 3.2) clearly show that temperature of an evaporating droplet is different from the ambient temperature and almost constant in the course of evaporation. We assume that the constancy over time of the droplet bulk temperature (Fig. 3.2) also implies the constancy over time of its average surface temperature.
Fig. 3.1: Simulated dependences of average temperature, $T_{av}$, of the droplet surface on the reciprocal of thermal conductivity of the substrate, $k_s$, and droplet contact angle, $\theta$. Liquid is water. Both latent heat of vaporization and Marangoni convection are taken into account. $T_s$ and $T_\infty$ are the temperatures of the substrate and of the air, respectively, far away from the droplet. Humidity $H = 70\%$. $L = 1 \text{ mm}$, $T_\infty = 293 \text{ K}$.

Fig. 3.2: Evolution of temperature inside the droplet after water droplet is deposited on PTFE substrate. Redrawn from [95].
Above mentioned arguments support the assumption of relative constancy of the average temperature of the droplet surface in the course of evaporation:

\[ T_{av} \approx \text{const}. \]  

(3.5)

Fig. 3.1 shows that the influence of the substrate outer temperature, \( T_s \), on the average temperature of the droplet surface, \( T_{av} \), vanishes as thermal conductivity of the substrate, \( k_s \), tends to zero. That is, there exists a limit for the temperature drop, \( T_{av} - T_{\infty} \), which is identical for all curves in the Fig. 3.1. This limit must depend on ambient temperature, \( T_{\infty} \), and ambient humidity, \( H \), of air. Let us calculate this limit.

When thermal conductivity of the substrate, \( k_s \), is zero, then liquid droplet and air are thermally insulated from the substrate. In this particular case the vaporization process is maintained by the heat flux from the ambient air. Let us show that in case of contact angle \( \theta = \pi/2 \), and \( k_s = 0 \) an analytical solution of the problem under consideration exists. Absence of normal heat and mass fluxes at the flat surface of the substrate allows us to consider this surface as a plane of symmetry. The latter shows that our problem has actually a spherical symmetry. The solution of the latter problem depends only on radial coordinate, \( r \), and gives uniform evaporation and heat fluxes along the droplet surface. As the heat sink (due to vaporization) is distributed over the droplet surface, the spherical symmetry implies uniform temperature field inside of the droplet and on its surface. As a result: there are no Marangoni convection, and no heat fluxes inside of the droplet. Solving Laplace equations for vapour concentration, \( c \), and temperature, \( T \), in infinite air domain gives the following solutions:

\[ c = H c_{sat}(T_s) + \frac{c_{sat}(T_{surf}) - H c_{sat}(T_s)}{r} L, \]  

(3.6)

\[ T = T_{\infty} + \frac{T_{surf} - T_{\infty}}{r} L, \]  

(3.7)

where \( r \) is the radial coordinate in the spherical system of coordinates.

Let us analyse the stability of this regime of evaporation (when \( k_s = 0 \) and \( \theta = \pi/2 \)) by considering a small local disturbance of the evaporation flux on the droplet surface. If evaporation rate is locally increased/decreased then due to increased/decreased
heat consumption (due to latent heat) the latter results in a local temperature
decrease/increase. It leads to a decrease/increase of a local concentration of
saturated vapour, and as a consequence, to a local decrease/increase of
evaporation rate. Thus an initial small disturbance in the system is suppressed. In
addition, local Marangoni stresses always appear on the surface where local
temperature gradient appears: it generates liquid flows along the surface, which
contribute to the elimination of temperature non-uniformity. Thus the system in
question is in a stable regime of quasi-steady process of evaporation.

Let us estimate the relaxation time for the temperature or vapour concentration
fluctuations at the surface of the droplet. The upper limit for the relaxation time of
concentration fluctuation can be estimated as the time required for the vapour to
diffuse across the distance $L$ ($L \sim 10^{-3}$ m, $D \sim 10^{-4}$ m$^2$s$^{-1}$):
$t_{\text{diff}} = L^2 / D \sim 10^{-2}$ s.

Corresponding time for the process of heat conduction: $t_{\text{heat}} = L^2 / \kappa \sim 1$ s,
where $\kappa$ is the thermal diffusivity of water ($\kappa \sim 10^{-6}$ m$^2$s$^{-1}$). Considering the thermal Marangoni
convection gives a similar result: a typical velocity of the thermal Marangoni
convection in water is about $v_{\text{Ma}} \sim 1$ mm/s, which gives us a time for the convective
transport across the distance $L$: $t_{\text{Ma}} = L / v_{\text{Ma}} \sim 1$ s. This demonstrates that times of
fluctuation relaxation are much smaller than the time of the droplet evaporation
(which is about 100 s). It confirms the stability of the evaporation process for the
above considered system with zero thermal conductivity of the substrate.

Using the obtained solution, Eqns. (3.6) and (3.7), we can calculate the density of
molar vapour flux, $j_c|_{r=L}$, and density of heat influx, $j_h|_{r=L}$ on the droplet surface:

$$j_c|_{r=L} = -D \frac{\partial c}{\partial r} \bigg|_{r=L} = D \frac{c_{\text{sat}}(T_{\text{surf}}) - H c_{\text{sat}}(T_{\infty})}{L}, \quad (3.8)$$

$$j_h|_{r=L} = k_a \frac{\partial T}{\partial r} \bigg|_{r=L} = -k_a \frac{T_{\text{surf}} - T_{\infty}}{L}, \quad (3.9)$$

where $k_a$ is the thermal conductivity of the surrounding air. Boundary condition for
fluxes gives:

$$j_c|_{r=L} \Lambda = j_h|_{r=L}, \quad (3.10)$$
where $\Lambda$ is the latent heat of vaporization in J/mol. It follows from Eqs. (3.8) – (3.10):

$$c_{\text{sat}}(T_{\text{surf}}) = H c_{\text{sat}}(T_\infty) + \frac{k_s}{D \Lambda} (T_\infty - T_{\text{surf}}).$$  \hspace{1cm} (3.11)

We have taken tabulated values of saturation pressure of water vapour ($p_{\text{ref}} = 2337$ Pa) and latent heat of vaporization ($\Lambda = 44320$ J/mol) at temperature $T_{\text{ref}} = 20^\circ$C [96], and have applied the Clausius-Clapeyron equation [97] and ideal gas law to express the dependence of molar concentration of saturated vapour, $c_{\text{sat}}$ (in mol/m$^3$), on temperature, $T$:

$$\ln \left( \frac{p_{\text{sat}}}{p_{\text{ref}}} \right) = -\frac{\Lambda}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right),$$

$$p_{\text{sat}} = c_{\text{sat}}RT.$$  

This dependence, $c_{\text{sat}}(T)$, can be approximated for the temperature range (273 K $< T < 303$ K) with the following quadratic equation:

$$c_{\text{sat}}(T) \approx 1.1951 \cdot 10^{-3} \cdot T^2 - 6.4255 \cdot 10^{-1} \cdot T + 86.636,$$  \hspace{1cm} (3.12)

where temperature, $T$, is in Kelvin and concentration, $c_{\text{sat}}$, is in mol/m$^3$. Taking into account approximation (3.12), Eq. (3.11) can be easily solved with respect to the unknown $T_{\text{surf}}$ within range (273 K $< T_{\text{surf}} < 303$ K). We denote the root of the Eq. (3.11) as $T_{\text{surf}} |_{k_s=0}$, which is the temperature of the droplet surface in case of contact angle $\theta = \pi/2$ and thermal conductivity of the substrate $k_s = 0$.

Thus, using Eq. (3.11) we have calculated the value of $T_{\text{surf}} |_{k_s=0}$ for the humidity $H = 70\%$ and temperature of the ambient air $T_\infty = 293$ K (as in the Fig. 3.1). The result is $T_{\text{surf}} |_{k_s=0} - T_\infty = -3.9$ K. This temperature drop is the limit attained by the curves in Fig. 3.1 as the $k_s^{-1}$ tends to infinity. Using this temperature drop we can write an expression for a dimensionless average temperature of the droplet surface:

$$\chi = \frac{T_{av} - T_{\text{surf}} |_{k_s=0}}{T_s - T_{\text{surf}} |_{k_s=0}}.$$  \hspace{1cm} (3.13)
Fig. 3.3: The same as Fig. 3.1 using non-dimensional temperature Eq. (3.13).

Fig. 3.3 shows the plot of $\chi$ versus non-dimensional thermal conductivity $k_w/(k_w + k_a)$, where subscripts $w$, $a$, and $s$ correspond to “water”, “air”, and “substrate” respectively. Fig. 3.3 shows that for contact angles $10^\circ$ and $40^\circ$ there is almost no difference between calculated values of $\chi$ for two specific temperatures of the substrate, $T_s$, ($T_s$ is specified far away from the droplet). But for contact angles $90^\circ$ and $120^\circ$ there is small difference: in the case $T_s - T_\infty = 5K$ the value of $\chi$ is slightly higher than that in case $T_s - T_\infty = 0K$.

Let us find a semi-empirical approximation for the results of computer simulation presented in Fig. 3.3. If we consider a specific case $k_s = 0$, and accept the assumption that temperature of the droplet surface, $T_{surf}$, is uniform and equal to its average temperature $T_{av}$, then the solution of Laplace equation for temperature in air, $\Delta T = 0$, gives the following total heat flux, $J_h$, from ambient air to the droplet surface:

$$J_h = 2\pi k_a (T_s - T_\infty) F(\theta)L.$$  \hspace{1cm} (3.14)

By analogy with electrical circuits temperature can be considered as the analogue of electrical potential, and total heat flux as the analogue of electrical current. Then it follows from the above formula (3.14) that analogue of the electrical resistance of air domain is
\[ R_a = \frac{T_w - T_{av}}{J_h} = \frac{1}{2\pi k_a F(\theta)L} . \]

The analogue of electrical resistance of the substrate can be represented as
\[ R_s = \frac{1}{2\pi k_s F(0)L} = \frac{1}{4k_s L} . \]

To calculate the analogue of the resistance for water droplet, we assume for simplicity that total heat flux through the droplet:
\[ J_{h,w} \approx J_{h,w} \cdot \pi L^2 \approx k_w \frac{\Delta T_w}{h} \cdot \pi L^2 , \quad (3.15) \]

where \( J_{h,w} \) is the average density of the vertical component of the heat flux through the water droplet, \( \Delta T_w \) is the temperature difference between the bottom and the top surfaces of the droplet, and \( \bar{h} \) is the average height of the droplet, which can be represented as the ratio of droplet volume, \( V \), and the area of droplet base: \( \bar{h} = \frac{V}{\pi L^2} \).

According to Eq. (3.1), droplet volume can be represented as \( V = L^3 f(\theta) \). Thus from Eq. (3.15) we get:
\[ R_w \approx \frac{\Delta T_w}{J_{h,w}} \approx \frac{V}{\pi^2 L^2 k_w} = \frac{f(\theta)}{\pi^2 L k_w} . \]

By analogy with electrical circuits, the total heat flux, \( J_h \), to the droplet surface with temperature \( T_{av} \) comprises the flux from ambient air with temperature \( T_\infty \) and the flux (through the water droplet) from the substrate with far-field temperature \( T_s \):
\[ J_h = \frac{T_w - T_{av}}{R_a} + \frac{T_s - T_{av}}{R_s} . \quad (3.16) \]

Using boundary condition \( J_h = J_A = J_{\pi/2} F(\theta)A \), from Eq. (3.16) we get:
\[ T_{av} = \frac{T_\infty + T_s R_a / (R_w + R_s) - J_{\pi/2} F(\theta)A R_a}{1 + R_a / (R_w + R_s)} . \quad (3.17) \]

From Eq. (3.17) follows:
\[ T_{av} \bigg|_{\theta=0}^{\theta = \pi/2} = \lim_{k \to 0} T_{av} = \lim_{k \to 0} T_{av} = T_\infty - J_{\pi/2} \Lambda R_a \bigg|_{\theta=\pi/2} . \quad (3.18) \]

Note that
\[ R_a \bigg|_{\theta=\pi/2} = \frac{1}{2\pi k_a F(\pi/2)L} = \frac{1}{2\pi k_a L} = F(\theta) R_a . \quad (3.19) \]
Combining equations (3.17), (3.18), and (3.19) we can calculate dimensionless temperature:

\[ \chi = \frac{T_{av} - T_{s, \text{surf}}}{T_s - T_{s, \text{surf}}} \left[ \frac{k_s}{\theta_s - \pi/2} \right] \approx \frac{1}{1 + R_w/R_s + R_s/R_a}. \]  

(3.20)

As the resistances are calculated roughly, we add empirical functions of contact angle \( \omega_w(\theta) \) and \( \omega_s(\theta) \) into Eq. (3.20) to improve approximation:

\[ \chi = \frac{1}{1 + \omega_w(\theta)R_w/R_s + \omega_s(\theta)R_s/R_a}. \]

Substituting expressions for resistances we get:

\[ \chi = \frac{1}{1 + \frac{2}{\pi} \omega_w(\theta)f(\theta)F(\theta) \left( \frac{k_s}{k_w} + \frac{\pi}{2} \frac{\omega_s(\theta)F(\theta)}{k_s} \right)}, \]

or

\[ \chi = \frac{1}{1 + F(\theta) \left( \omega_1(\theta) \frac{k_s}{k_w} + \omega_2(\theta) \frac{k_s}{k_s} \right)}, \]

where \( \omega_1(\theta) = \frac{2}{\pi} \omega_w(\theta)f(\theta) \) and \( \omega_2(\theta) = \frac{\pi}{2} \omega_s(\theta) \) are new empirical functions of contact angle. They have been chosen empirically:

\[ \omega_1(\theta) = \sin \theta, \]

\[ \omega_2(\theta) = \begin{cases} \sin \theta - 0.75 \cdot \theta + 4.61, & \text{for } T_s - T_w = 0 \text{ K} \\ \sin \theta - 0.75 \cdot \theta + 4.09, & \text{for } T_s - T_w = 5 \text{ K} \end{cases}. \]

Thus results of computer simulations in Fig. 3.3 in case \( T_s - T_w = 0 \text{K} \) can be approximated by the following semi-empirical equation (\( \theta \) is in radians):

\[ \chi(k_s, \theta) \bigg|_{T_s - T_w = 0\text{K}} \approx \frac{1}{1 + F(\theta)(k_s/k_w)\sin \theta + (k_s/k_s)(\sin \theta - 0.75 \cdot \theta + 4.61)} \],  

(3.21)

with an approximation error: \( \Delta \chi = \Delta T / \left( T_s - T_{s, \text{surf}} \right)^{\theta - \pi/2} < 0.02 \).

Results of computer simulations in Fig. 3.3 in case \( T_s - T_w = 5\text{K} \) can be approximated by the next equation (\( \theta \) is in radians):
\[
\chi(k_s, \theta)_{\Delta T_s - T_\infty = 5K} \approx \frac{1}{1 + F(\theta)\left[(k_u/k_w)\sin \theta + (k_u/k_s)(\sin \theta - 0.75 \cdot \theta + 4.09)\right]},
\]

with an approximation error: \(\Delta \chi = \Delta T_s \int_{T_s - T_{surf}}^{T_s - T_{surf}} \left| \frac{\partial}{\partial \theta} \right| d\theta < 0.03\).

Fig. 3.4 represents approximating curves (3.21) and (3.22) together with computer simulation points taken from Fig. 3.3.

3.2.2. Two stages of evaporation of a sessile droplet

Assuming the constancy of the average temperature, \(T_{av}\), of the droplet surface (Eq. (3.5)) during the whole process of evaporation, we automatically get the constancy of the parameter \(\beta\) (see Eq. (3.4)):

\[\beta \approx \text{const}.\]

3.2.2.1. The first stage of evaporation

During this stage of evaporation the radius of the contact line, \(L_0\), remains constant and Eq. (3.3) can be rewritten as \(L_0^3 f'(\theta) \frac{d\theta}{dt} = -\beta F(\theta)L_0\), or:
\[ L_0^2 f'(\theta) \frac{d\theta}{dt} = -\beta F(\theta), \quad (3.23) \]

with the initial condition
\[ \theta|_{t=0} = \theta_{ad}. \quad (3.24) \]

Let us introduce the following dimensionless time \( \tau = \frac{t}{t_{ch}} \), where \( t_{ch} = \frac{L_0^2}{\beta} \) is the characteristic time of the process. Eq. (3.23) now takes the following form:
\[ f'(\theta) \frac{d\theta}{d\tau} = -F(\theta). \]

Direct integration of the latter equation with the boundary condition (3.24) results in
\[ A(\theta, \theta_{ad}) = \tau, \quad (3.25) \]
where \( A(\theta, \theta_{ad}) = \int_0^{\theta} \frac{f'(\theta)}{F(\theta)} d\theta \). The latter equation shows that the deduced dependency should be universal and does not depend on the nature of the liquid and the droplet volume. The only parameter left is the initial contact angle (static advancing contact angle), which is supposed to be independently determined.

The first stage proceeds until the contact angle reaches its final value equal to the static receding contact angle. Using Eq. (3.25) we conclude that the end of the first stage, \( \tau_r = \frac{t_r}{t_{ch}} \), is determined as
\[ A(\theta_r, \theta_{ad}) = \tau_r. \quad (3.26) \]

### 3.2.2.2. The second stage of evaporation

During that stage the contact angle remains constant, \( \theta_r \), but the radius of the contact line varies. Hence Eq. (3.3) can be rewritten now as
\[ 3L^2 f(\theta_r) \frac{dL}{dt} = -\beta F(\theta_r)L. \]

Let us introduce the same dimensionless time as before and dimensionless radius of the contact line: \( \ell = L/L_0 \). Hence the latter equation can be rewritten as
\[ \frac{d\ell^2}{d\tau} = -\frac{2}{3} \frac{F(\theta_r)}{f(\theta_r)} \ell, \quad \tau > \tau_r, \]

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with the following initial condition: $\ell(\tau_r) = 1$. Direct integration of the latter equation results in $\ell^2(\tau) = 1 - \frac{2F(\theta_r)}{3f(\theta)}(\tau - \tau_r)$, or:

$$\ell(\tau) = \sqrt{1 - \frac{2F(\theta_r)}{3f(\theta)}(\tau - \tau_r)}.$$  

(3.27)

The latter dependence gives a universal dependence during the second stage of evaporation.

![Graph](image)

**Fig. 3.5:** Dependencies on the dimensionless time: (a) contact angle, (b) non-dimensional radius of the contact line.

Resulting curves are schematically represented in Fig. 3.5. Second stage of evaporation (when $\theta = \theta_r$) is usually finished before $\ell$ reached zero, and the final point of the second stage must belong to curves in Fig. 3.5. Afterwards, the last stage of evaporation starts, when both $\ell$ and $\theta$ are decreasing over time, but this stage is not covered by present model.

### 3.3. Validation against experimental data

Universal laws of evaporation of a sessile droplet represented by Eqs. (3.25) and (3.27) are validated against available experimental data extracted from literature sources [68, 98, 99]. The characteristic time of the process can be calculated using Eq. (3.26): $t_{ch} = t_c / A(\theta_r, \theta_{ad})$. The latter can be calculated using experimental values of $\theta_{ad}$ and $\theta_r$. Obtained value of $t_{ch}$, as well as $\theta_{ad}$ and $\theta_r$ can be used to plot the
dependencies $\theta(\tau)$ and $\ell(\tau)$ corresponding to the first (Fig. 3.6) and second (Fig. 3.7) stages of evaporation respectively. Figures 3.6 and 3.7 show good agreement of proposed theory and available experimental data.

Using the proposed above theory we can estimate the average temperature, $T_{av}$, of the droplet surface. Substituting the experimentally calculated value of $t_{ch} = t_r / A(\theta, \theta_{ad})$ into the theoretical equation $t_{ch} = L_0^2 / \beta$, and using the initial value of contact line radius, $L_0$, we can obtain the value of $\beta$. After that using Eq. (3.4) for $\beta$ and the dependence of concentration of saturated vapour, $c_{sat}(T)$, on temperature (Clausius-Clapeyron equation) [97] we can calculate the average temperature, $T_{av}$, of the droplet surface. Thus for the experimental data represented in Figures 3.6 and 3.7 we calculated the following values of $T_{av}$: for water on PMMA $T_{av} = T_\infty - 2.76$ K, for water on PET $T_{av} = T_\infty - 0.52$ K. Average temperatures of the droplet surface, $T_{av}$, calculated using the above algorithm, are smaller than the ambient temperature, $T_\infty$.
what indicates the surface cooling. We can see that calculated temperature drops, \( T_{av} - T_{\infty} \), are of the same order of magnitude as the experimentally measured temperature drop inside of the droplet bulk [95] (see Fig. 3.2). This confirms the validity of the proposed assumptions.

For the experiments presented in paper [68] (water on polished epoxy surface) it is impossible to calculate \( T_{av} \) because the humidity of ambient air was not specified in their experiments. For water on corning glass, the estimation showed that the average temperature of the droplet surface, \( T_{av} \), is higher than the ambient temperature, \( T_{\infty} \), what is in contradiction with the physics of the phenomenon. But our calculations show that taking relative air humidity 40% or less (instead of 60% reported by authors [98]) gives \( T_{av} < T_{\infty} \), as it should be. The latter result leads us to a conclusion that the relative humidity in experiments by Chen et al. [98] is measured inaccurately, and its value can be much different from the actual one in their experiments.
Note, real substrate used in any experiment is of a finite size, whereas our model is proposed for a semi-infinite substrate. Therefore calculated temperature drop, $T_{av} - T_{\infty}$, can be used for the estimation of the thermal conductivity of an equivalent semi-infinite substrate (see Fig. 3.1), which gives the same cooling as the real substrate of finite thickness.

Let us introduce new dimensionless times. Eq. (3.25) can be rewritten as:

$$\int_0^{\pi/2} f'(\theta) \, d\theta = \tau + \int_{\theta_{ad}}^{\pi/2} f'(\theta) \, d\theta,$$

\[ \theta, \text{ rad} \]

![Graph showing dependence of contact angle, $\theta$, on dimensionless time, $\tilde{\tau}$.](image)

Fig. 3.8: First stage of evaporation, Eq. (3.28). Dependence of contact angle, $\theta$, on dimensionless time, $\tilde{\tau}$.
\[ B(\theta) = \tilde{\tau}, \ \ \ \ \text{(3.28)} \]

where \( B(\theta) = \int_{0}^{\pi/2} \frac{f'(\theta)}{F(\theta)} d\theta = A(\theta, \pi/2) \), and \( \tilde{\tau} = \tau + B(\theta_{ad}) \) is a new dimensionless time.

Function \( A(\theta_1, \theta_2) \) now can be expressed as follows: \( A(\theta_1, \theta_2) = B(\theta_1) - B(\theta_2) \).

According to its derivation Eq. (3.28) is supposed to be the universal curve describing the first stage of evaporation.

The latter is completely confirmed by comparison with available experimental data in Fig. 3.8. For the range of contact angle \( 0 \leq \theta \leq 2.967 \) the dependence \( B(\theta) \) can be approximated with the following function:
\[
B(\theta) \approx \begin{cases}
-0.3714 \cdot \theta^3 + 0.3921 \cdot \theta^2 - 1.358 \cdot \theta + 2.623, & 0 \leq \theta \leq \pi \\
-37.13 \cdot \theta^3 + 358.5 \cdot \theta^4 - 1387 \cdot \theta^3 + 2680 \cdot \theta^2 - 2585 \cdot \theta + 995.9, & \pi < \theta \leq 2.618 \\
-8.404 \cdot 10^4 \cdot \theta^3 + 1.151 \cdot 10^6 \cdot \theta^4 - 6.302 \cdot 10^6 \cdot \theta^3 + 1.726 \cdot 10^7 \cdot \theta^2 - 2.363 \cdot 10^7 \cdot \theta + 1.294 \cdot 10^7, & 2.618 < \theta \leq 2.967
\end{cases}
\]

Hence,
\[
\theta(\bar{\tau}) \approx \begin{cases}
-4.143 \cdot 10^{-15} \cdot \bar{\tau}^6 - 2.3891 \cdot 10^{-10} \cdot \bar{\tau}^5 - 5.6799 \cdot 10^{-9} \cdot \bar{\tau}^4 - 7.2288 \cdot 10^{-8} \cdot \bar{\tau}^3 - 5.3674 \cdot 10^{-4} \cdot \bar{\tau}^2 - 2.4122 \cdot 10^{-2} \cdot \bar{\tau} + 2.3596, & -149.95 \leq \bar{\tau} \leq -27.76 \\
-1.4194 \cdot 10^{-8} \cdot \bar{\tau}^6 - 1.5219 \cdot 10^{-6} \cdot \bar{\tau}^5 - 6.7149 \cdot 10^{-5} \cdot \bar{\tau}^4 - 1.5884 \cdot 10^{-3} \cdot \bar{\tau}^3 - 2.2204 \cdot 10^{-2} \cdot \bar{\tau}^2 - 1.9676 \cdot 10^{-1} \cdot \bar{\tau} + 1.6933, & -27.76 \leq \bar{\tau} \leq -3.27 \\
2.5116 \cdot 10^{-4} \cdot \bar{\tau}^6 + 1.0479 \cdot 10^{-3} \cdot \bar{\tau}^5 - 1.8704 \cdot 10^{-3} \cdot \bar{\tau}^4 - 1.9189 \cdot 10^{-2} \cdot \bar{\tau}^3 - 7.715 \cdot 10^{-2} \cdot \bar{\tau}^2 - 3.1528 \cdot 10^{-1} \cdot \bar{\tau} + 1.5708, & -3.27 \leq \bar{\tau} \leq 2.61
\end{cases}
\]

Introduction of the new dimensionless time \( \bar{\tau} = \frac{2F(\theta)}{3f(\theta)}(\tau - \tau_r) \) to the Eq. (3.27) gives:
\[
\ell(\bar{\tau}) = \sqrt{1 - \bar{\tau}}. \tag{3.29}
\]

Again according to its derivation Eq. (3.29) is supposed to represent the universal curve describing the second stage of evaporation. Experimental data in Fig. 3.9 confirm that conclusion.

3.4. Conclusions

The deduced expressions of the instantaneous fluxes are applied for self-consistent calculations of the time evolution of the evaporation processes of sessile droplets in case of contact angle hysteresis. The theory proposed is in good qualitative and quantitative agreement with experimental data from literature.

4. Evaporation of surfactant solution droplets: experiment and theory

4.1. Introduction

The experimental studies of evaporating droplets of aqueous solutions of surfactant (Silwet L-77) on top of smooth solid hydrophobic substrate were carried out by our colleagues, Mr Hezekiah Agogo and his supervisor Prof Ramon G. Rubio, at the University Complutense in Madrid, Spain.
The above proposed theory for evaporation of sessile droplets of pure water is applied here to original experimental data for evaporating droplets of surfactant solutions. Results demonstrate that for different initial concentrations of the surfactant in the droplet, two different cases are possible: (i) the experimentally observed time evolution of the droplet shape is well described by the proposed theory; and (ii) more complex time evolution of the droplet shape is observed, which requires further complication of the theory in order to obtain an accurate theoretical description. In the last case, the theory modification requires additional knowledge about adsorption of the surfactant on interfaces (liquid-air, liquid-solid, solid-air).

A detailed experimental study of the time dependence of the contact angle, the volume and the contact line radius of aqueous surfactant solution droplets onto a hydrophobic TEFLON-AF substrate is performed. We have used drops of an aqueous solution of a super-spreader surfactant (Silwet L-77) over a wide concentration range both below and above the critical aggregation concentration (CAC). Below the experimental data obtained for the quasi-steady evaporation stages (initial spreading stage and final stage of fast evaporation are not considered) are compared with the earlier proposed mathematical model.

4.2. Experimental technique

Our colleagues (Complutense University in Madrid, Spain) purchased SILWET L-77 from Sigma-Aldrich (Germany) and used as received. Poly[4,5-difluoro-2,2-bis(trifluoromethyl)-1,3-dioxole-co-tetrafluoroethylene], hereinafter TEFLON-AF, was purchased from Sigma-Aldrich (Germany) as powder, the Fluorinert F77 solvent was bought from 3M (USA), and the silicon wafers were obtained from Siltronix (France). Ultrapure deionized water (Younglin Ultra 370 Series, Korea) with a resistivity higher than 18 MΩ and TOC lower than 4 ppm was used for preparing all the surfactant solutions.

All the surfactant solutions were prepared by weight using a balance precise to ±0.01 mg. A pH = 7.0 buffer was used as solvent to prevent hydrolysis of the SILWET
L-77. It was checked that the buffer did not change the surface tension of water and that fresh SILWET L-77 solutions with and without buffer had the same surface tension. The solutions were used immediately after preparation. The silicon wafers were cleaned using piranha solution for 20 min. The solid substrates were prepared as follows: the TEFLON-AF powder was suspended in the Fluorinert F77 and spin-coated onto the silicon wafers. The average roughness of the 20 µm x 20 µm surface was ≈ 1.0 nm as measured by AFM (tapping mode). The macroscopic contact angle of pure water was (104 ± 2)° on those substrates. Drops of 4 mm³ were deposited onto the substrate for measurements. Five independent measurements were performed for each experimental point reported and the average was used.

The experimental technique used was similar to the one used earlier by Ivanova et al. [100, 101] with some modifications that allowed us to monitor continuously the temperature and the relative humidity inside the experimental setup. Fig. 4.1 shows a diagram of the experimental device. The cameras were calibrated using a micrometer with a precision of ± 0.5 µm.

![Diagram of the experimental device used. CCD1 and CCD2 are the cameras to capture the drop profiles from the top and side view. Inside the chamber both the temperature and the relative humidity were controlled and continuously monitored.](image)

Sessile droplets were deposited onto the substrate inside a chamber attached to a thermostat, and its shape and size were captured by the CCD camera (side view) at 30 frames per second. The initial drop volumes used were about 4 mm³ in order to
ensure that gravity effects can be neglected and the drop always had a spherical cap shape. The images captured were analysed using the drop tracking and evaluation analysis software (Micropore Technologies, UK) that allowed us to monitor the time evolution of the droplet base diameter, height, radius of the curvature, and contact angle. The precision of the contact angle measurements was $\pm 2^\circ$ under dynamic conditions, i.e. spreading and evaporation; those of height and diameter were $\pm 1 \mu m$; and that of temperature was $\pm 0.5^\circ C$. The relative humidity was maintained constant ($\pm 2 \%$) by placing a saturated salt solution inside the measuring chamber. The salts used to maintain the humidity are given in Table 4.1.

Table 4.1: Inorganic salts used to maintain the relative humidity (RH) constant in the measuring cell.

<table>
<thead>
<tr>
<th>Temp</th>
<th>RH</th>
<th>30 %</th>
<th>55 %</th>
<th>90 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>18°C</td>
<td>MgCl$_2$·6H$_2$O/CaCl$_2$·6H$_2$O</td>
<td>NaBr+KBr</td>
<td>KCl+KBr</td>
<td></td>
</tr>
<tr>
<td>24°C</td>
<td>CaCl$_2$·6H$_2$O</td>
<td>NaBr</td>
<td>KCl</td>
<td></td>
</tr>
<tr>
<td>30°C</td>
<td>MgCl$_2$·6H$_2$O</td>
<td>KBr</td>
<td>KCl+KBr</td>
<td></td>
</tr>
</tbody>
</table>

4.3. Validation of the proposed theory against experimental data

Fig. 4.2 gives a schematic representation of possible stages of spreading/evaporation process. Stage (0) corresponds to the initial spreading of a droplet over a solid substrate. Stage (I) is the first evaporation stage with constant contact line radius, $L$. Stage (II) is the second evaporation stage with constant receding contact angle, $\theta_r$. Stages (0) and (III) are not considered in the proposed theory, and therefore will be ignored in what follows. Depending on the experiment the depinning jump between stages (I) and (II) can be observed, but in most cases stage (II) immediately follows stage (I).
Fig. 4.2: Stages of the process of sessile droplet spreading/evaporation.

Fig. 4.3 shows the typical behaviour of contact angle, $\theta$; the contact line radius, $L$; and the volume to the power $2/3$ ($V^{2/3}$) for a SILWET L-77 solution of concentration $C = 0.25 \text{ CAC}$ (CAC being the critical aggregation concentration of the surfactant, CAC = 0.1 g/l, [101, 102]) at ambient temperature $18^\circ\text{C}$ and 90% relative humidity (RH). The end of each of the three first stages of the spreading/evaporation process is marked by a vertical bar in Fig. 4.3.
Fig. 4.3: Process of spreading/evaporation of a sessile droplet, time dependence of (a) contact angle, (b) contact line radius, (c) droplet volume to the power 2/3 for a surfactant concentration 0.25 CAC at ambient temperature 18°C and 90% relative humidity. The vertical bars mark ends of stages (0), (I) and (II) of the spreading/evaporation process.

The experimental results for the droplet volume show that $V^{2/3}$ decreases linearly with time during stages (0), (I) and (II) of the process, thus it can be inferred that evaporation is diffusion controlled. It allows us to apply the above proposed theory for the diffusion limited evaporation.
Fig. 4.4: Time dependence of the contact angle (a), droplet radius (b) and (c) volume ($V^{2/3}$) for different concentrations of SILWET L-77 surfactant at 24°C and 55% relative humidity.

Fig. 4.4 shows the time dependence of contact angle, $\theta$, radius of the contact line, $L$, and volume to power 2/3, $V^{2/3}$, for the SILWET L-77 solutions over the studied concentration range. As expected, the increase of surfactant concentration reduces the initial contact angle and increases the maximum spreading radius, $L$, of the droplet. Similar trends were found for the data measured at all the temperatures ($18^\circ$C, $24^\circ$C, and $30^\circ$C) at three different relative humidities (30%, 55%, and 90%).

The condition $L = \text{const}$ for the first evaporation stage, (I), is found for all the solutions studied. Even though for pure fluids the second evaporation stage, (II), is characterized by $\theta = \theta_r = \text{const}$, this is not observed for the surfactant solutions at all the values of surfactant concentration. Thus in Fig. 4.4 (a) one can see that receding contact angle, $\theta_r$, is not constant during the stage (II) if initial surfactant concentration is less than CAC.

This behaviour is easy to explain from the qualitative point of view. As the droplet evaporates, it loses solvent molecules through evaporation, and therefore the surfactant concentration in the droplet increases over time (in this reasoning we
assume that loss of surfactant molecules on adsorption at different interfaces has minor influence on its bulk concentration, though it may be important for a quantitative modelling of the process). This is the main reason of changing receding contact angle, because contact angle depends on surfactant concentration.

Thus, the inconstancy of the receding contact angle does not actually allow us to call this evaporation stage as “stage (II)”. Virtually, it is a stage with simultaneously decreasing contact angle, \( \theta_r \), and contact line radius, \( L \). Though it looks like stage (III), in fact it is different, because it is not a final stage of evaporation and it is caused by the change of surfactant concentration, rather than by a fast dynamics of the droplet at the very end of evaporation process. Let us call this stage as “stage (S)”, because the evolution of the droplet shape is determined by the change of surfactant concentration.

Stage (S) can be followed by stage (II). Indeed, at some moment during the stage (S), the surfactant concentration in the droplet can reach the CAC level, and then the receding contact angle becomes constant, which formally corresponds to stage (II).

Thus, the complete sequence of possible spreading/evaporation stages for surfactant solution droplets looks as follows:

- **stage (0)** - Initial spreading;
- **stage (I)** - evaporation with constant contact line radius, \( L = \text{const} \);
- **depinning (jump)** - contact line starts receding;
- **stage (S)** - evaporation, when both \( L \) and receding contact angle, \( \theta_r \), are not constant. \( \theta_r \) is determined by the changing surfactant concentration;
- **stage (II)** - evaporation with constant receding contact angle, \( \theta_r = \text{const} \), (CAC is reached);
- **stage (III)** - final stage of evaporation with fast decrease of both \( L \) and \( \theta_r \).

In order to validate the proposed theory of evaporation, the experimental measurements (time \( t \), contact line radius \( L \), and volume \( V \)) have to be nondimensionalized.
The only parameter, needed for nondimensionalization of the experimental data is the coefficient $\beta$ from Eq. (3.3): $dV/dt = -\beta F(\theta)L$. This coefficient, see Eq. (3.4), characterizes the intensity of evaporation. It depends on the conditions of an experiment (ambient humidity and temperature, vapour diffusivity), and therefore is different for individual experimental runs.

The following technique is adopted for determination of the coefficient $\beta$. Eq. (3.3) is integrated over time with the assumption of constancy of $\beta$:

$$V(t) - V_o = -\beta \int_0^t F[\theta(i)]L(i)dt.$$ \hspace{1cm} (4.1)

Let us denote $x(t) = \int_0^t F[\theta(i)]L(i)dt$, then Eq. (4.1) takes the following form:

$$V(t) = -\beta x(t) + V_o.$$ \hspace{1cm} (4.2)

![Graph](image)

**Fig. 4.5:** Example of the experimentally obtained dependence of $V(t)$ on $x(t)$, and its linear fit.

Value of $x(t)$ is calculated using experimental values of $\theta(t)$ and $L(t)$, and applying numerical integration over time (second order integration method). Plotting
experimental $V(t)$ versus calculated $x(t)$ (see Fig. 4.5) and fitting it with the linear dependence gives us the value of $\beta$ parameter for each particular experiment.

We plotted the fitting parameter $\beta$ as function of surfactant concentration for SILWET L-77 and for SDS solutions [103], see Fig. 4.6. The surfactant concentration is expressed in terms of the critical aggregation concentration (CAC) for SILWET L-77, and in terms of the critical micelle concentration (CMC) for SDS in order to make the abscissa axis comparable for both surfactants.

Fig. 4.6 shows that within the limits of experimental errors it can be concluded that $\beta$ does not depend on surfactant concentration for all the temperatures and relative humidities studied. According to Eq. (3.4) this can be understood if both the liquid density and the vapour pressure of the solutions remain almost constant. This is reasonable considering that the surfactant mole fraction is very low for all the solutions studied, and therefore both $\rho$ and $c_{sat}$ are almost unaffected by the presence of the surfactant.
Fig. 4.6: Surfactant concentration dependence of the $\beta$ parameter for SILWET L-77 (a) and SDS [103] (b) solutions at similar experimental conditions (55% RH, 24°C for SILWET L77 and 55% RH, 21.7°C for SDS), (c) is an enlargement of the SDS results to show the $C < C_{\text{MC}}$ region.
Obtained values of coefficient $\beta$ have been subsequently used for nondimensionalization of corresponding experimental data. Fig. 4.7 (a) shows a comparison of the theoretical curve for the evaporation stage (I) with the nondimensionalized experimental data from the interval of time when $L = \text{const}$. A very good agreement is observed for all the temperatures, relative humidities and concentrations studied (72 sets of data).

Fig. 4.7 (b) shows a comparison of the theoretical curve for the evaporation stage (II) with the nondimensionalized experimental data for the interval of time when the receding of the contact line occurs (stage (III) is excluded from consideration). Note that experimental data from the interval of time, when contact line recedes, in fact can correspond to one of two possible stages of evaporation discussed above: stage (II) with constant receding contact angle, or stage (S) with the receding contact angle as a function of surfactant concentration. Indeed, Fig. 4.7 (b) demonstrates that not all experiments follow the theoretical stage (II). Some of them deviate from the theory, and therefore are suspected to belong to a stage (S), which is not yet studied theoretically. In order to analyse this deviation, we plotted the difference between the theoretical for stage (II) and the experimentally obtained values of nondimensional contact line radiuses, $\Delta \ell = \left| \ell_{\text{theory, stage (II)}} - \ell_{\text{experiment}} \right|$, versus the initial SILWET L-77 surfactant concentration in the droplet for a particular nondimensional moment of time, $\bar{\tau} = 0.2$, see Fig. 4.7 (c). One can see that this deviation, $\Delta \ell$, occurs mainly within the concentration range $0 < C < CAC$, where the contact angle strongly depends on the surfactant concentration.

It means that those experimental curves (for $0 < C < CAC$), which deviate from the theoretical one for the stage (II), actually belong to stage (S). Fig. 4.7 (c) roughly shows that difference $\Delta \ell$ approaches zero value for $C = 0$ and for $C > CAC$, which means that evaporation follows stage (II) for $C = 0$ (pure liquid, receding contact angle is constant) and for $C > CAC$ (receding contact angle is constant).
Fig. 4.7: Comparison of the experimental results for SILWET L-77 solutions (over the wide concentration range, at three different temperatures and three relative humidities) with the universal curves predicted by the theory, for the (a) first stage and (b) second stage of evaporation. (c) concentration dependence of the difference, $\Delta \ell$, between the experimental and the theoretical values of $\ell$ for a given value of $\tau$.

4.4. Conclusions

It can be concluded that experimental data follow the predicted universal curve of the stage (II) only for pure liquids or surfactant solutions with surfactant concentration, $C$, above the critical aggregation concentration: $C > CAC$.

Apparently the situation is more complex for the evaporation stage (S), which occurs for surfactant concentration range $0 < C < CAC$, when the liquid-air and liquid-solid interfacial tensions would change as the evaporation progress due to the increase of concentration. In turn, the change of interfacial tensions changes the receding contact angle.
In order to build a theory for the evaporation stage (S), it is necessary to study the kinetics of adsorption of surfactant molecules on interfaces (liquid-gas, liquid-solid, gas-solid), as well as the influence of the adsorption concentration (surface excess) on the value of a receding contact angle. This complex problem is not considered in present work and will be studied in future researches.

5. Influence of kinetic effects on evaporation of pinned sessile droplets: computer simulations

5.1. Introduction

From the previously considered model of diffusion limited evaporation we found out that the density of evaporation flux (local evaporation flux) at the droplet surface is inversely proportional to the droplet size, \( j \sim 1/L \). Thus, following that model, we conclude that diminution of the droplet size leads to an increase of the local evaporation rate on the droplet surface, and at some point it should reach its physical limit: evaporating molecules cannot move with the velocity higher than their thermal velocity. In general, the effects, which are the consequence of a molecular motion and which require a consideration of kinetic theory of gases, are called kinetic effects.

The aim of subsequent computer simulations is to show how the evaporation of pinned sessile submicron size droplets of water on a solid surface is affected by kinetic effects.

The model used below includes both diffusive and kinetic models of evaporation simultaneously. Our model differs from a purely diffusive model, because the Hertz-Knudsen-Langmuir equation [104, 105] is used as a boundary condition at the liquid-gas interface instead of a saturated vapour condition. The adopted model also differs from a purely kinetic model of evaporation, because it also includes the vapour diffusion into the surrounding gas similar to the diffusion model. In this way the evaporation rate is controlled by both the rate of vapour diffusion into ambient gas and the rate of molecules transfer across the liquid-gas interface. Thus the resulting evaporation rate is limited by the slower process.
In this hybrid model, the vapour concentration at the liquid-gas interface falls in between its saturated value and its value in ambient gas. This intermediate value of vapour concentration at the liquid-gas interface drives both transition of molecules from liquid to gas (kinetic flux across the interface) and vapour diffusion into ambient gas (diffusive flux from the interface to ambient air). According to the mass conservation law these two fluxes are equal locally (at the droplet interface), but the intensity of a resulting flux is always less than that predicted by either pure diffusive or pure kinetic models.

5.2. Improved mathematical model

As previously, the problem is solved under a quasi-steady state approximation. That is, all time derivatives in all equations are neglected. The quasi-steady solution of the problem gives simultaneous distribution of heat and mass fluxes in the system.

A volume of the droplet decreases over time, which is caused by the evaporation. Therefore, a certain velocity is ascribed to the liquid-gas interface in order to satisfy the mass conservation law in the quasi-steady state approximation. This velocity is calculated in such a way to preserve the spherical-cap shape of the liquid-gas interface, to have zero velocity of the contact line, and to match the evaporation rate of the droplet.

The parameters of the following materials are used in the present computer simulations: copper as a substrate, water as liquid inside of droplets, and humid air as a surrounding medium. The pressure in the surrounding gas equals to the atmospheric pressure, the ambient temperature is 20°C, and the ambient air humidity is 70%.

In the improved model we consider the influence of some additional effects on the process of evaporation of submicron droplets: kinetic effects, influence of the curvature of the droplet surface on the value of the saturated vapour (effect of Kelvin’s equation), effect of Stefan flow in the gaseous phase generated by evaporation (as the local evaporation rate can be very high for small droplets). In
order to be able to incorporate these effects into our model, we slightly changed bulk equations and added new boundary conditions at the droplet surface.

We accept the same bulk equations as in the previously considered model for diffusion limited evaporation: heat transfer equation, diffusion equation for vapour in air, Navier-Stokes equations; but this time we add convective components of heat and mass fluxes in equations of heat and mass transfer for gaseous phase. This means that equations for heat and vapour transfer (in gaseous phase) become diffusive-convective ones. Thus, it requires the knowledge of the velocity field in the gaseous phase. For this reason the improved model includes also Navier-Stokes equation for the gaseous phase.

5.2.1. Governing equations in the bulk phases

This section presents the problem statement, which is based on that one proposed by Krahl et al [106]. The following governing equations describe the heat and mass transfer in the bulk phases:

- heat transfer in a solid phase:
  \[ \Delta T = 0, \]
  where \( \Delta \) is the Laplace operator, and \( T \) is the temperature;

- heat transfer inside of fluids (liquid and gas):
  \[ \vec{u} \cdot \nabla T = \kappa \Delta T, \]
  where \( \vec{u} \) is the fluid velocity, \( \nabla \) is the gradient operator, and \( \kappa \) is the thermal diffusivity of the fluid;

- incompressible Navier-Stokes equations are used to model hydrodynamic flows in both fluids (liquid and gas):
  \[ \rho \vec{u} \cdot \nabla \vec{u} = \nabla \cdot \mathbf{T}, \]
  where \( \rho \) is the fluid density, \( \nabla \vec{u} \) is the gradient of the velocity vector, \( \mathbf{T} \) is the full stress tensor, and \( \nabla \cdot \mathbf{T} \) is the dot-product of nabla operator and the full stress tensor. The full stress tensor is expressed via hydrodynamic pressure, \( p \), and the viscous stress tensor, \( \pi \), as:
  \[ \mathbf{T} = -\rho \mathbf{I} + \pi, \]
  where \( \mathbf{I} \) is the identity tensor.
• Continuity equation for fluids is used:
  \[ \nabla \cdot \vec{u} = 0. \]

• The convection-diffusion equation for vapour in gas phase:
  \[ \vec{u} \cdot \nabla c = D \Delta c, \quad (5.1) \]
  where \( c \) is the molar concentration of the vapour, \( D \) is the diffusion coefficient of vapour in air, \( \Delta \) is the Laplace operator, and \( \nabla \) is the nabla operator. Note: if the effect of Stefan flow is “switched off” in the model, that is \( \vec{u} = 0 \) in gas phase, then Eq. (5.1) transforms into a Laplace equation for vapour concentration: \( \Delta c = 0 \).

Let us show the range of droplet sizes, for which the buoyancy force in gas phase can be neglected. Assuming a contact angle \( \theta = \pi/2 \), a dry ambient atmosphere (zero vapour humidity: \( H = 0 \)), neglecting the temperature change at the droplet surface, \( T_{\text{surf}} = T_\infty \), and using the equation (3.8) we can estimate the surface density of the molar vapour flux at the droplet surface: \( j_c \big|_{r=L} = D c_{\text{sat}}(T_\infty) / L \). This provides a rough estimation of the gas velocity at the droplet surface in normal direction to the surface: \( u_g \big|_{r=L} \approx j_c \big|_{r=L} M / \rho_g = D c_{\text{sat}}(T_\infty) M / (L \rho_g) \), where \( M \) is the molecular weight of the evaporating substance (0.018 kg/mol for water), subscript \( g \) corresponds to ‘gas’, \( \rho_g \) is the gas (ambient atmosphere) density. Next, assuming the spherical symmetry of the gas flow, we can write the equation for the velocity field in gas:
  \[ \vec{u}_g = u_g \hat{r} = u_g \big|_{r=L} (L/r)^2 \hat{r} \approx \frac{D c_{\text{sat}}(T_\infty) M L}{\rho_g r^2} \hat{r}, \]
  where \( \hat{r} \) is the unit vector in radial direction. Using this velocity field we can estimate the modulus of the volume density of the inertial force in the Navier-Stokes equation for the gaseous phase:
  \[ f_{\text{inertia}} = \rho_g \left[ \vec{u}_g \cdot \nabla \vec{u}_g \right] = \rho_g \left[ u_g \hat{r} \cdot \nabla (u_g \hat{r}) \right] = \rho_g \left[ u_g \frac{\partial}{\partial r} (u_g \hat{r}) \right] = \rho_g \left[ u_g \frac{du_g}{dr} \hat{r} \right] = \rho_g \left[ u_g \frac{du_g}{dr} \right] \approx \rho_g \left[ \frac{D c_{\text{sat}}(T_\infty) M L}{\rho_g} \right] \frac{1}{r^2} \cdot \frac{1}{r^2} = 2 \frac{(D c_{\text{sat}}(T_\infty) M L)^2}{\rho_g L^2} \frac{1}{r^2}. \]

At the droplet surface \( r = L \), and the above expression will take form:
  \[ f_{\text{inertia}} \approx 2 \frac{(D c_{\text{sat}}(T_\infty) M L)^2}{\rho_g L^2}. \]
Thus for water droplets we have: $D = 2.4 \cdot 10^{-5} \text{ m}^2/\text{s}$, $M = 0.018 \text{ kg/mol}$, $c_{\text{sat}}(293^\circ \text{K}) = 0.959 \text{ mol/m}^3$, $\rho_g = \rho_{\text{air}} = 1.184 \text{ kg/m}^3$, and thus:

$$f_{\text{inertia}} = 2 \left( 2.4 \cdot 10^{-5} \cdot 0.959 \cdot 0.018 \right) \frac{\text{N}}{1.184 \cdot L^3} = 2.899 \cdot 10^{-13} \text{ N}.$$ 

Now let us derive an expression for the volume density of the buoyancy force, arising from the difference of densities of the dry, $\rho_{g,H=0}$, and humid, $\rho_{g,H=1}$, air:

$$f_{\text{buoyancy}} = \Delta \rho_g g = (\rho_{g,H=0} - \rho_{g,H=1}) g,$$

where $g = 9.81 \text{ m/s}^2$ is the standard gravitational acceleration.

In order to calculate the densities of dry and humid air we use partial pressures of water vapour, $p_{\text{H}_2\text{O}}$, and dry air, $p_{\text{dry}}$, and represent the atmospheric pressure, $p_{\text{atm}} = 101.3 \text{ kPa}$, as follows: $p_{\text{atm}} = p_{\text{H}_2\text{O}} + p_{\text{dry}}$. In case of zero air humidity, $H = 0$, the partial pressure of the water vapour is zero, $p_{\text{H}_2\text{O}}|_{H=0} = 0$, and therefore $p_{\text{dry}}|_{H=0} = p_{\text{atm}}$.

In case of a humid air at ambient temperature $T_\infty = 293^\circ \text{K}$, for 100% humidity ($H = 1$) we have: $p_{\text{H}_2\text{O}}|_{H=1} = 2.337 \text{ kPa}$, and therefore:

$$p_{\text{dry}}|_{H=1} = p_{\text{atm}} - p_{\text{H}_2\text{O}}|_{H=1} = 101.3 \text{ kPa} - 2.337 \text{ kPa} = 98.963 \text{ kPa}.$$ 

Using the ideal gas law, $pV = \frac{m}{M} RT$ ($m$ is the gas mass), for dry air we obtain:

$$\rho_{g,H=0} = \frac{m_{\text{H}_2\text{O}} + m_{\text{dry}}}{V} = \frac{M_{\text{H}_2\text{O}} p_{\text{H}_2\text{O}}|_{H=0} + M_{\text{dry}} p_{\text{dry}}|_{H=0}}{RT_\infty} = \frac{M_{\text{dry}} p_{\text{atm}}}{RT_\infty} = 1.206 \frac{\text{kg}}{\text{m}^3},$$

where $M_{\text{dry}} = 0.029 \text{ kg/mol}$ is the molecular weight of dry air and $R$ is the universal gas constant. For the humid air we obtain:

$$\rho_{g,H=1} = \frac{m_{\text{H}_2\text{O}} + m_{\text{dry}}}{V} = \frac{M_{\text{H}_2\text{O}} p_{\text{H}_2\text{O}}|_{H=1} + M_{\text{dry}} p_{\text{dry}}|_{H=1}}{RT_\infty} = 1.195 \frac{\text{kg}}{\text{m}^3},$$

where $M_{\text{H}_2\text{O}} = 0.018 \text{ kg/mol}$ is the molecular weight of water vapour. As a result we get the volume density of the buoyancy force:
Relating the buoyancy force to the inertia force we can determine the range of droplet sizes, for which the buoyancy force can be neglected:

\[
\frac{f_{\text{buoyance}}}{f_{\text{inertia}}} = \frac{0.11 \text{ N/m}^3}{2.899 \cdot 10^{-3} \text{ N}} L^3 \ll 1,
\]

or

\[
L^3 \ll 2.635 \cdot 10^{-12} \text{ m}^3,
\]

\[
L \ll 1.38 \cdot 10^{-4} \text{ m}.
\]

The last expression clearly shows that buoyancy force in the gas phase can be neglected for droplets of size less than 0.1 mm. The last infers that buoyancy is definitely negligible for microdroplets, which are of main interest in this section. Below we neglect the buoyancy force in the Navier-Stokes equations for the whole range of droplet sizes studied.

### 5.2.2. Improved boundary conditions

No-slip and no-penetration boundary conditions are used for Navier-Stokes equations at the liquid-solid and gas-solid interfaces, resulting in zero velocity at these interfaces:

\[
\bar{u} = 0.
\]

Let \( \Gamma \) be the liquid-gas interface. Let also \( j_c \) be a density of a molar vapour flux across the liquid-gas interface, then a density of mass vapour flux across this interface is \( j_m = j_c M \), where \( M \) is the molar mass of an evaporating substance (water).

Let the normal velocity of the interface itself be \( u_\Gamma \), see Fig. 5.1. Then the boundary condition for the normal velocity of liquid at the liquid-gas interface reads:

\[
\rho_l (\bar{u}_l \cdot \bar{n} - u_\Gamma) = j_m,
\]

where \( \rho_l \) is the liquid density, subscript \( l \) stands for liquid. Expressions for evaporation flux, \( j_m \), and normal interfacial velocity, \( u_\Gamma \), are specified below. A condition of the stress balance at the liquid-gas interface is used to obtain boundary conditions for the pressure and tangential velocity:

\[
(T \cdot \bar{n})_l - (T \cdot \bar{n})_g = -\gamma (\nabla \cdot \bar{n})_l \bar{n} + \gamma' (\nabla_\Gamma T),
\]

(5.3)
where subscripts \( l \) and \( g \) stand for liquid and gas, respectively; \( \mathbf{T} \) is the full stress tensor; \( \gamma \) is the interfacial tension of the liquid-gas interface; \( \gamma'_T \) is the derivative of the interfacial tension with the temperature; \( \nabla_T T \) is the surface gradient of temperature; \( (\nabla \cdot \vec{n})_T \) is the divergence of the normal vector at the liquid-gas interface, which is equal to the curvature of the interface. Boundary condition (5.3) is a vector one, and therefore can split into two scalar boundary conditions: in normal and tangential direction. They are deduced as follows: (i) the tangent component of the velocity vector (which determines the boundary condition for the thermal Marangoni convection) is obtained by multiplying Eq. (5.3) by the tangential vector \( \vec{\tau} \) (see Fig. 5.1) and neglecting the viscous stress in the gas phase (due to small gas viscosity compared to the liquid viscosity); (ii) the similar procedure results in a boundary condition for pressure in the liquid at the liquid-gas interface using the normal vector \( \vec{n} \) (see Fig. 5.1).

![Fig. 5.1: Notations at the liquid-vapour interface.](image)

The normal flux of vapour at the gas-solid interface is zero because there is no penetration into the solid surface:

\[
\nabla c \cdot \vec{n} = 0,
\]

where \( c \) is the molar concentration of the vapour in the air; and \( \vec{n} \) is the unit vector, perpendicular to the solid-gas interface.

We consider gas phase as the mixture of vapour and dry air. Note that due to mass conservation law the mass flux of vapour across the liquid-gas interface in normal direction, should be equal to the mass flux of liquid, perpendicular to the liquid-gas interface (relative to the interface) in the liquid phase:
\[ j_m = \rho_l (\vec{u}_l \cdot \vec{n} - u_\Gamma) = \rho_v (\vec{u}_v \cdot \vec{n} - u_\Gamma) - D_{\text{vapour in air}} \nabla \rho_v \cdot \vec{n}. \] (5.4)

Density of mass flux of dry air, \( j_{m, \text{air}} \), across the liquid-gas interface is assumed to be zero:

\[ j_{m, \text{air}} = \rho_{\text{air}} (\vec{u}_g \cdot \vec{n} - u_\Gamma) - D_{\text{air in vapour}} \nabla \rho_{\text{air}} \cdot \vec{n} = 0, \] (5.5)

where \( \rho_v \) and \( \rho_{\text{air}} \) are densities of vapour and dry air, respectively; \( D \) is the diffusion coefficient; \( \vec{u}_l \) and \( \vec{u}_g \) are velocity vectors of liquid and gas, respectively; \( u_\Gamma \) and \( \vec{n} \) are shown in Fig. 5.1. As the gas (water vapour + dry air) under consideration includes more than one species of molecules, then the mass flux for each species in the air phase consists of two components: convective part, \( \rho_v \vec{u}_v \), and diffusive one, \( D \nabla \rho \). Flux in the pure liquid includes only a convective term, \( \rho_l \vec{u}_l \). Normal fluxes at the liquid-gas interface are considered relative to the liquid-gas interface. The latter results in an additional term: \( -\rho l u_\Gamma \). Let us adopt the following assumption: 

\[ \rho_g = \rho_{\text{air}} + \rho_v = \text{const} \cdot \] The latter assumption means incompressibility of the gaseous phase. This assumption results in

\[ \nabla \rho_{\text{air}} = -\nabla \rho_v. \] (5.6)

The binary diffusion coefficient, \( D_{AB} \), for a binary mixture of ideal gases \( A \) and \( B \) (molecules are represented by hard spheres) in the Chapman-Enskog form [107] is given below (in centimetre-gram-second system of units):

\[ D_{AB} = \frac{3}{32n\sigma_{AB}^2} \left[ \frac{8kT}{\pi} \left( \frac{1}{m_A} + \frac{1}{m_B} \right) \right]^{1/2}, \]

where \( D_{AB} \) is a binary diffusion coefficient (cm\(^2\)/s), \( n \) is the total concentration of both species (molecules/cm\(^3\)), \( T \) is temperature (°K), \( k \) is the Boltzmann constant (ergs/°K), \( m_A \) and \( m_B \) are molecular masses of species (grams), \( \sigma_{AB} = (\sigma_A + \sigma_B)/2 \) is a collision diameter, separation between molecular centres of unlike pairs upon collision (cm).

From the above formula for a binary diffusion coefficient, \( D_{AB} \), one can see that it is symmetric with respect to the species, that is \( D_{AB} = D_{BA} \). Therefore we accept in our model the following equality:
\[ D_{\text{air in vapour}} = D_{\text{vapour in air}} = D. \] (5.7)

After substitution of Eqs. (5.6) and (5.7) into Eqs. (5.4) and (5.5) and simple algebraic manipulations we arrive to an expression for the density of mass flux across the liquid-gas interface, \( j_m \), as a function of molar vapour concentration, \( c \), in gas phase:

\[
j_m = -D\rho_v \cdot \vec{n} = -Dc \cdot \vec{n}, \quad (5.8)
\]

where the following relation has been used: \( \rho_v = cM \), \( M \) is the molar mass of an evaporating substance (water). Eq. (5.8) connects the evaporation flux, \( j_m \), with both the gradient of vapour concentration in the normal direction and the concentration itself. On the other hand, the rate of mass transfer across the liquid-gas interface is given by the Hertz-Knudsen-Langmuir equation [104, 105]:

\[
j_m = \alpha_m \sqrt{MRT} \left( c_{\text{sat}}(T) - c \right), \quad (5.9)
\]

where \( \alpha_m \) is the mass accommodation coefficient (probability that uptake of vapour molecules occurs upon collision of those molecules with the liquid surface); \( R \) is the universal gas constant; \( T \) and \( c \) are the local temperature in °K and molar vapour concentration at the liquid-gas interface, respectively; \( c_{\text{sat}} \) is the molar concentration of saturated vapour, which is taken as a function of local temperature, \( T \), and local curvature, \( K \), of the liquid-gas interface according to Clausius-Clapeyron [97] and Kelvin [93] equations:

\[
\ln \left( \frac{p_{\text{sat},0}}{p_{\text{ref}}} \right) = -\frac{\Lambda}{RT} \left[ \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right] \quad \text{(Clausius-Clapeyron equation)},
\]

\[
\ln \left( \frac{p_{\text{sat}}}{p_{\text{sat},0}} \right) = \frac{\gamma KM}{\rho_l RT} \quad \text{(Kelvin equation)},
\]

where \( p_{\text{sat},0} \) and \( p_{\text{sat}} \) are saturated vapour pressures above the flat and curved liquid surfaces, respectively; \( \Lambda \) is the latent heat of vaporization; \( R \) is the universal gas constant; \( p_{\text{ref}} \) and \( T_{\text{ref}} \) are tabulated values of saturated vapour pressure and corresponding temperature; \( \gamma \) is the liquid-gas interfacial tension; \( M \) and \( \rho_l \) are the molecular weight and the mass density of the evaporating liquid; and \( K \) is the
curvature of the liquid-gas interface, determined as $K = (\nabla \cdot \vec{n})_r$, where $\vec{n}$ is the unit vector perpendicular to the liquid-gas interface and pointing into the gaseous phase.

Combining Eqs. (5.8) and (5.9) we obtain a boundary condition for convection-diffusion equation (5.1) at the liquid-gas interface:

$$-\frac{D V c \cdot \vec{n}}{1/M - c/\rho_g} = \alpha_m \sqrt{\frac{MRT}{2\pi}} (c_{sat}(T) - c).$$

Based on the assumption $(\rho_g = \rho_{air} + \rho_v = const)$, the normal velocity of gas at the liquid-gas interface is determined by the condition:

$$\rho_g (\vec{u}_g \cdot \vec{n} - u_r) = j_m. \quad (5.10)$$

In order to choose an appropriate boundary condition for the tangential component of the gas velocity at the liquid-gas interface, let us compare the tangential and the normal components of the gas velocity at that interface.

For simplicity we consider the sessile droplet with contact angle $\theta = \pi/2$. In this case the evaporation flux will be uniformly distributed above the droplet surface, regardless of the regime of evaporation (diffusive or kinetic). Let us assume that the surface density of the molar evaporation flux is equal to some value $j_e$. Then the heat sink will be present at the interface due to the effect of latent heat of vaporization. The intensity of this heat sink is $j_e \Lambda$, where $\Lambda$ is the latent heat of vaporization (in J/mol), for water $\Lambda = 44320 \text{ J/mol}$. In our computer simulations we use a highly heat conductive substrate (copper), therefore we can assume that the temperature at the bottom of the droplet will be equal the ambient temperature $T_e = 293^\circ K$. Neglecting a convective heat transfer within the droplet, and taking into account only conductive one, we can estimate the temperature at the apex of the droplet. To do so we equate the density of the conductive heat flux from the bottom to the top (apex) of the droplet and the intensity of the heat sink at the apex of the droplet (heat flux through the gas is neglected): $k_w \frac{T_{apex} - T_e}{L} = j_e \Lambda$, where
\( k_w = 0.6 \frac{W}{m \cdot K} \) is the thermal conductivity of water. The temperature at the apex of the droplet can be used to estimate the gradient of the temperature on the droplet surface, which is, being multiplied by the modulus of the thermal coefficient of the surface tension \( |\gamma'_T| \), gives the thermal Marangoni stress at the droplet surface:

\[
|\gamma'_T| \frac{T_{\text{spec}} - T_w}{L} = \frac{j_c \Lambda |\gamma'_T|}{k_w}.
\]

This stress should be balanced by the viscous stress in the liquid under the droplet surface (viscous stress in the gas phase is neglected due to comparatively small viscosity of the gas):

\[
\frac{j_c \Lambda |\gamma'_T|}{k_w} = \mu_w \frac{v_r}{L},
\]

where \( v_r \) is the tangential component of the liquid velocity at the droplet surface, and \( \mu_w \) is the dynamic viscosity of water. Liquid velocity on the liquid-solid interface is zero, as the no-slip boundary condition is applied at the liquid-solid interface. Assuming that the maximal possible tangent velocity of the gas phase on the liquid-gas interface equals the tangent velocity of the liquid on that interface, we arrive to the expression for the maximal tangent gas velocity:

\[
v_t = \frac{j_c \Lambda |\gamma'_T|}{k_w \mu_w}.
\]

At the same time the normal velocity of the gas phase is generated by the evaporation process, therefore it is directly related to the surface density of the evaporation rate:

\[
v_n = \frac{j_c M_w}{\rho_g},
\]

where \( M_w \) is the molecular weight of the evaporating substance (in this case water), and \( \rho_g \) is the gas density. Relating the tangent and normal components of the gas velocity, we derive:

\[
\frac{v_t}{v_n} = \frac{\Lambda |\gamma'_T| \rho_g L}{k_w \mu_w M_w} = \frac{44320 \frac{J}{\text{mol}} \cdot 1.7 \cdot 10^{-4} \frac{\text{N}}{\text{m} \cdot \text{K}} \cdot 1.184 \frac{\text{kg}}{\text{m}^3} \cdot L}{0.6 \frac{W}{\text{m} \cdot \text{K}} \cdot 10^{-2} \frac{\text{Pa} \cdot \text{s}}{\text{kg} \cdot \text{mol}}} = \frac{L}{1.21 \cdot 10^{-6} \text{m}}.
\]

It means that tangential component of the gas velocity becomes less than its normal component for droplet sizes, \( L \), less than approximately 1.2 \( \mu \text{m} \).

Thus the tangential component of the gas velocity at the liquid-gas interface can be neglected for submicron droplets. For bigger droplets, however, this velocity is not
negligible, and therefore some boundary condition should be posed for the tangential component of the gas velocity.

We have chosen the no-slip boundary condition at the liquid-gas interface, because for macroscopic problems this boundary condition is more natural. One more argument in favour of this boundary condition is the following: due to the transfer of evaporating molecules across the liquid-gas interface (evaporation process), it is most likely that, in average, those vapour molecules will have the same velocity along the liquid-gas interface as the velocity of the liquid along that interface.

Thus, the tangent velocity of gas at the liquid-gas interface is determined by the no-slip condition:

$$\vec{u}_g \cdot \vec{t} = \vec{u}_l \cdot \vec{t}.$$  

Boundary conditions of temperature continuity are applied at all interfaces (liquid-gas, liquid-solid and gas-solid):

$$T_l = T_g, \quad T_l = T_s, \quad T_g = T_s,$$

where subscripts $l$, $g$ and $s$ stand for liquid, gas and solid, respectively. Continuity of the heat flux is applied on solid-liquid and solid-gas interfaces:

$$-k_i (\nabla T) \cdot \vec{n} + k_i (\nabla T) \cdot \vec{n} = 0,$$

$$-k_g (\nabla T) \cdot \vec{n} + k_g (\nabla T) \cdot \vec{n} = 0,$$

where $k$ is the thermal conductivity of the corresponding phase; $\vec{n}$ is the unit vector, perpendicular to a corresponding interface. Note: at all these interfaces the convective heat flux is zero due to no penetration conditions. At the liquid-gas interface heat flux experiences discontinuity caused by the latent heat of vaporization and also there is a convective heat flux through this interface:

$$[\rho c_{pl} T(\vec{u}_l \cdot \vec{n} - u_t) - k_i (\nabla T)_l \cdot \vec{n}] - [\rho c_{pg} T(\vec{u}_g \cdot \vec{n} - u_t) - k_g (\nabla T)_g \cdot \vec{n}] = j \Lambda,$$

where $c_{pl}$ and $c_{pg}$ are specific heat capacities at constant pressure for the liquid and the gas, respectively; $\Lambda$ is the latent heat of vaporization (or enthalpy of vaporization [108], units: $\text{J/mol}$); $\vec{n}$ is the unit vector, normal to the liquid-gas interface, and pointing into the gas phase; $j$ is the surface density of the molar flux of evaporation.
(mol⋅s$^{-1}$⋅m$^{-2}$) at the liquid-gas interface. Using Eqs. (5.2), (5.10), and relation between molar and mass fluxes, $j_m = j_c M$, we derive:

$$\rho_c c_p T (\bar{u}_l \cdot \bar{n} - u_r) - \rho_g c_p T (\bar{u}_g \cdot \bar{n} - u_r) = c_p T j_m - c_p T j_m = j_c M (c_{pl} - c_{pg})$$.

Using the latter expression, Eq. (5.11) transforms into the required boundary condition for the heat flux discontinuity at the liquid-gas interface:

$$-k_l (\nabla T)_l \cdot \bar{n} + k_g (\nabla T)_g \cdot \bar{n} = j_c (\Lambda - M T (c_{pl} - c_{pg}))$$.

At the axis of symmetry ($r = 0$) the following boundary conditions are satisfied:

$$\frac{\partial c}{\partial r} \bigg|_{r=0} = 0, \quad \frac{\partial T}{\partial r} \bigg|_{r=0} = 0, \quad \frac{\partial u_z}{\partial r} \bigg|_{r=0} = 0, \quad u_r \bigg|_{r=0} = 0, \quad \frac{\partial p}{\partial r} \bigg|_{r=0} = 0,$$

where $u_r$ and $u_z$ are radial and vertical components of the velocity vector, and $p$ is the hydrodynamic pressure.

At the outer boundary of the computational domain values of temperature, $T_\infty$, and vapour concentration, $c_\infty$, are imposed. In case when gas convection is taken into account, condition of open boundary (zero normal stress) is imposed at the outer boundary of the gas domain:

$$\mathbf{T} \cdot \bar{n} = 0,$$

where $\mathbf{T}$ is the full stress tensor, and $\bar{n}$ is the unit normal vector. This boundary condition allows the gas both enter and leave the domain.

In our computer simulations we assume that contact line is pinned ($L = \text{const}$), and the droplet under consideration retains a spherical-cap shape in the course of evaporation:

$$(z + \delta z)^2 + r^2 = \left(\frac{L}{\sin \theta}\right)^2, \quad \delta z = L \cdot \cos \theta / \sin \theta.$$ 

Then knowing the total mass evaporation flux, $J_m = \int_{\Gamma} j_m \, dA$ ($dA$ is the element of area of the interface $\Gamma$), we can calculate the normal velocity of the liquid-gas interface, $u_r$, at any point of the interface:

$$u_r = \frac{-J_m}{\pi \rho_l L^2} \cdot \frac{z}{(z + \delta z) \cdot n_z + r \cdot n_r} \cdot \frac{1 + \cos \theta}{1 - \cos \theta},$$

where $\rho_l$ and $L$ are the density and curvature of the interface, respectively.
where $\theta$ is the contact angle; $n_r$ and $n_z$ are radial and vertical components of the vector $\vec{n}$, respectively, shown in Fig. 5.1; the origin of cylindrical coordinates $(r, z)$ is supposed to be at the point of intersection of the axis of droplet symmetry and the liquid-solid interface (Fig. 5.1).

5.3. Computer simulations

Computer simulations are performed using commercial software COMSOL Multiphysics. The numerical method used in COMSOL is a finite element method with quadratic Lagrangian elements. The software transforms all equations into their weak form before discretization. The method of Lagrange multipliers is used to apply boundary conditions as constraints.

The computational domain is selected as a circle in $(r, z)$ coordinates of the cylindrical system of coordinates. The centre of this circle located at the origin of coordinates. The radius of the computational domain is 100 times bigger than the radius of the contact line, $L$, which is done to reduce the influence of the outer boundary.

Because of the incompatibility of boundary conditions at the three-phase contact line, numerical artefacts can appear there. Therefore, computational mesh is refined in the vicinity of the three-phase contact line, so that the minimal size of elements is 100 times smaller than $L$. The growth rate for mesh elements is less than 1.1 in the whole computational domain.

5.4. Results and discussion

5.4.1. Isothermal evaporation

The model described here is an extension of the previous one, which was developed for diffusion limited evaporation of water droplets. In distinction to the previous model, the present one takes into account additional phenomena: Stefan flow in gas, effect of curvature of the droplet’s surface on saturated vapour pressure (Kelvin’s equation), and kinetic effects (also known as Knudsen effects). A numerical model allows switching individual phenomena on/off in order to understand their
contribution to the overall process of heat and mass transfer in the course of evaporation.

The value of mass accommodation coefficient $\alpha_m$ is taken as 0.5, which is the average experimentally measured value of $\alpha_m$ for water according to Ref. [104].

When Kelvin’s and kinetic effects are switched off, then the model represents the case of diffusion limited evaporation. This allows us to validate the present model against the previously developed model for diffusion limited evaporation, which in turn was validated against available experimental data. Computer simulations showed that there is agreement with the previous results (see Fig. 5.2).

![Graph](image)

Fig. 5.2: Dependence of the droplet’s molar evaporation flux, $J_{c,i}$, on the droplet size, $L$, for isothermal model of evaporation. Parameters used: $\alpha_m = 0.5$; $\theta = 90^\circ$; relative air humidity is 70%. Note: results for $L < 10^{-7}$ m do not have physical meaning, as additional surface forces must be included into the model. These points are shown to demonstrate the trends of curves.
In Fig. 5.2 the total molar fluxes of droplet’s evaporation, $J_{c,i}$, are presented for various isothermal cases (index $i$ stands for the "isothermal"). The flux was computed according to the presented above model, in which the Stefan flow, heat transfer and the thermal Marangoni convection were omitted. Fig. 5.2 shows that kinetic effects change the slope of curves (see triangles and circles) for submicron droplets ($L < 10^{-6}$ m) only. The influence of curvature of the droplet’s surface (Kelvin’s equation) becomes significant only for droplet sizes less than $10^{-7}$ m. However, at such low sizes the surface forces action (disjoining/conjoining pressure) has to be taken into account (not included in the present model).

Note once more that the presented model is valid only for droplet size bigger than the radius of surface forces action, which is around $10^{-7}$ m = 0.1 μm. That is, the data in Fig. 5.2 for the droplet size smaller than $10^{-7}$ m are presented only to show the trend. Fig. 5.2 shows that if the radius of the droplet base is bigger than $10^{-7}$ m then (i) deviation of the saturated vapour pressure caused by the droplet curvature (Kelvin’s equation) can be neglected, (ii) a deviation from the pure diffusion model of evaporation can be neglected for the droplet size bigger than $10^{-6}$ m, (iii) this deviation becomes noticeable only if the droplet size is less than $10^{-6}$ m. This deviation is caused by an increasing influence of the kinetic effects at the liquid-gas interface (Hertz-Knudsen-Langmuir equation), and this theory should be applied together with the diffusion equation of vapour in the air if the droplet size is less than $10^{-6}$ m.

The latter conclusions show that a consideration of evaporation of microdroplets, completely covered by the surface forces action (that is less than $10^{-7}$ m), should take into account both deviation of the saturated vapour pressure caused by the droplet curvature and the kinetic effects.

According to the model of diffusion limited evaporation, the evaporation flux, $J_{c,i}$, must be linearly proportional to the droplet size, $L$, that is $J_{c,i} \sim L$. The latter is in agreement with data presented in Fig. 5.2 for droplets bigger than $10^{-6}$ m. However,
for a pure kinetic model of evaporation (no vapour diffusion, uniform vapour pressure in the gas) flux $J_{c,i}$ is supposed to be proportional to the area of the droplet’s surface, that is in the case of pinned droplets (constant contact area) $J_{c,i} \sim L^2$ should be satisfied. To check the validity of the latter models at various droplet sizes let us assume that the dependency of the evaporation flux on the droplet radius has the following form $J_{c,i} = A(\theta)L^n$, where $n$ is the exponent to be extracted from our model and $A$ is a function of the contact angle, $\theta$. In general it is necessary to calculate the partial derivative

$$n = \frac{\partial (\ln J_{c,i})}{\partial (\ln L)}.$$  \hspace{1cm} (5.12)

in order to compute the exponent $n$ using the present model. However, in the case of pinned droplet the only varying parameter for each individual curve in Fig. 5.2 was the contact line radius, $L$. Hence, the partial derivatives in Eq. (5.12) can be replaced

![Graph showing exponent $n$ for the isothermal model of evaporation.](image)

Fig. 5.3: Exponent $n$ for the dependence $J_{c,i} = A(\theta)L^n$ for the isothermal model of evaporation. Parameters used: $\alpha_m = 0.5$; $\theta = 90^\circ$; relative air humidity is 70%. Note: results for $L < 10^{-7}$ m do not have physical meaning, as surface forces action must be included into the model here. These points are shown to demonstrate the trends of curves.
by ordinary derivatives, and in this way \( n \) was calculated using data presented in Fig. 5.2. The calculated values of \( n \) are presented in Fig. 5.3.

One can see from Fig. 5.3 that the exponent \( n \), as expected, is equal to 1 for a pure diffusive isothermal model of evaporation within the whole studied range of \( L \) values (diamonds in Fig. 5.3). In case when kinetics effects and Kelvin’s equation are both taken into account in addition to the pure diffusion, Fig. 5.3 shows that the diffusion model of evaporation dominates for droplets with the size bigger than \( 10^{-5} \text{m} \), that is for droplets bigger than \( 10 \mu \text{m} \).

Taking into account only kinetic effects, additional to the diffusion, without Kelvin’s equation (triangles in Fig. 5.3) results in a smooth transition from the linear dependence \( J_{\text{ev}} \sim L \), that is \( n = 1 \) (diffusive model) to the quadratic one \( J_{\text{ev}} \sim L^2 \), that is \( n = 2 \) (kinetic model) as the size of the droplet decreases down to \( L = 10^{-7} \text{m} \) (see Fig. 5.3). The latter shows that \( J_{\text{ev}} \) is tending to be proportional to \( L^2 \) as the size of the droplet decreases, which means that evaporation flux becomes proportional to the area of the liquid-gas interface. Influence of the curvature (Kelvin’s equation) on the saturated vapour pressure results in a substantially lower exponent \( n \) as compared with the kinetic theory (Fig. 5.3). However, the latter happens only for a droplet completely in the range of surface forces action, that is, less than \( 10^{-7} \text{m} \) [65]. Below this limit, the droplet does not have a spherical cap shape any more, even on the droplet’s top (microdroplets according to Ref. [65]). Evaporation process in the latter case should be substantially different from the considered above. Thus the range of sizes less than \( 10^{-7} \text{m} \) is not covered by the presented theory.

### 5.4.2. Influence of thermal effects

Computer simulations were also performed including both Kelvin’s equation and kinetic effects in the case when thermal effects were taken into account. The latter was made to show the influence of the latent heat of vaporization, Marangoni convection and Stefan flow on the evaporation process. Droplet’s evaporation rates,
$J_c$, were normalized using those, $J_{c,i}$ (circles in Fig. 5.2), from the isothermal model. Results are presented in Fig. 5.4.

Fig. 5.4 shows that latent heat of vaporization reduces the evaporation flux as compared to the isothermal case (that is $J_c/J_{c,i} < 1$) in all cases considered. The reason is a temperature decrease at the droplet’s surface due to heat consumption during the evaporation process. This reduces the value of the saturated vapour pressure at the droplet’s surface and, subsequently, reduces the rate of vapour diffusion into the ambient gas. The relative reduction of the evaporation rate (caused by the latent heat of vaporization) reaches the maximum for droplets with $L \sim 10^{-5}$ m. The latter size according to Figs. 5.2 and 5.3 is in the range of diffusion limited evaporation.

As was demonstrated earlier, the influence of the latent heat of vaporization on (non-isothermal) evaporation rate, $J(L)$, normalized with the corresponding isothermal one, $J_{\pi/2}(L,T_\infty)$, in case of pure diffusive model of evaporation (see Fig. 2.13) does not depend on the droplet size: $J(L)/J_{\pi/2}(L,T_\infty) = const$. But in case when kinetic effects are “switched on”, the evaporation rate (circles and triangles in Fig. 5.2) for submicron droplets becomes much smaller than corresponding evaporation rate in case of a pure diffusive model (diamonds in Fig. 5.2). Thus, due to this reduction of the evaporation rate, the latent heat of vaporization produces much smaller thermal effect (see Eq. (5.11)), as compared to the pure diffusive model. This can be clearly seen in the Fig 5.4 (squares): the ratio $J_c/J_{c,i}$ is not constant anymore, and in kinetic regime of evaporation (when droplet size tends to zero) tends to one: $\lim_{L \to 0} J_c/J_{c,i} = 1$, which means disappearance of the effect of the latent heat of vaporization.

Taking into account kinetic effects, Kelvin’s equation, latent heat of vaporization, and thermal Marangoni convection (for water droplets) affects droplets of size $L > 10^{-5}$ m (triangles in Fig. 5.4). In this case evaporation rate, $J_c$, is lower than that for isothermal model ($J_c < J_{c,i}$) and higher than that if the latent heat included but without Marangoni convection (squares in Fig. 5.4).
Fig. 5.4: Influence of latent heat of vaporization, Marangoni convection, and Stefan flow on the evaporation rate in the case when kinetic effects and Kelvin's equation are included into the model. $J_c$ and $J_{ci}$ are total molar flux of evaporation and the one in the isothermal case, respectively.

For water droplets of size $L < 10^{-5}$ m the influence of Marangoni convection is negligible and evaporation rate, $J_c$, coincides with the one for a model which includes only latent heat of vaporization (squares in Fig. 5.4).

The effect of Stefan flow in surrounding gas (switching on the convective heat and mass transfer in the gaseous phase in addition to the conductive/diffusive one) slightly changes the evaporation rate in the present model (circles in Fig. 5.4) and makes it lower due to an appearance of an outward convective heat flux in the gas above the droplet. This reduces the heat flux from the ambient environment to the droplet’s surface through the gas phase. Thus temperature of the droplet’s surface becomes slightly lower, which reduces the evaporation rate. In our particular case this effect appeared to be much weaker than the effects of latent heat of vaporization. Stefan flow effect is also weaker than the effect of thermal Marangoni
convection for $L > 10^{-4}$ m, but a bit stronger for $L < 10^{-4}$ m. However, in any case the influence of the Stefan flow is small and can be neglected.

It is interesting to notice that the influence of the thermal effects on the kinetics of evaporation is less than 5% (according to Fig. 5.4).

In our calculations we used copper as a solid support, that is, of a relatively high thermal conductivity. The latter conclusion is not valid in the case of lower thermal conductivity of the solid support. Thus, additional computer simulations show that the influence of thermal effects is more pronounced for Teflon substrate: the flux is reduced by 19% on Teflon as opposed to 5% on copper (see Fig. 5.5).

Fig. 5.5: Computer simulations: influence of a substrate material (heat conductivity of the substrate) on the evaporation rate of the droplet. $J_c$ is the total molar flux of evaporation, when model comprises Kelvin’s equation, kinetic effects, effect of latent heat of vaporization and thermal Marangoni convection. $J_{c,i}$ is the total molar flux of evaporation in isothermal case, when effects of droplet cooling and subsequently thermal Marangoni convection are switched off.
5.4.3. Influence of the contact angle

In the previous section pinned droplets with a fixed contact angle equal to 90° were used. Below we consider the dependence of evaporation rate on contact angle only for the isothermal model (no heat fluxes) and without Stefan flow effect because as it was shown above it can be neglected. This dependence for non-isothermal diffusion limited evaporation was already studied in section 2.4.4. Here we extend this study by considering the influence of the contact angle on the evaporation rate for submicron droplets.

As it was mentioned above, for an isothermal, pure kinetic regime of evaporation (no Kelvin’s equation) the droplet’s evaporation rate, \( J_{c,i} \), should be proportional to the area, \( S \), of the liquid-gas interface, \( J_{c,i} \sim S \). For a spherical cap shape of the droplet: \( S = 2\pi L^2 (1 - \cos \theta)/\sin^2 \theta \). Thus \( J_{c,i} \sim (1 - \cos \theta)/\sin^2 \theta \), or

\[
J_{c,i} / J_{c,i} (\theta = 90^\circ) = (1 - \cos \theta)/\sin^2 \theta
\]  

(5.13)

![Graph showing the dependence of normalized evaporation rate on contact angle, \( \theta \), according to diffusive (Eq. 5.14) and kinetic (Eq. 5.13) models. Markers represent calculated values according to the present isothermal model of evaporation (Kelvin’s equation and kinetic effects are “switched on”). Note, scalings \( J_{c,i} (\theta = 90^\circ) \) are taken from Fig. 5.2 (circles) and are different for all plots and equal to the corresponding evaporation rate at 90°.]

Fig. 5.6: Dependence of normalized evaporation rate on contact angle, \( \theta \), according to diffusive (Eq. 5.14) and kinetic (Eq. 5.13) models. Markers represent calculated values according to the present isothermal model of evaporation (Kelvin’s equation and kinetic effects are “switched on”). Note, scalings \( J_{c,i} (\theta = 90^\circ) \) are taken from Fig. 5.2 (circles) and are different for all plots and equal to the corresponding evaporation rate at 90°.
On the other hand for a pure diffusive isothermal regime of evaporation this
dependence is obtained by Picknett and Bexon [70]:

\[
J_{c,i}/J_{c,s}(\theta = \pi/2) = \begin{cases}
0.6366 \cdot \theta + 0.09591 \cdot \theta^2 - 0.06144 \cdot \theta^3 / \sin \theta, & \theta < \pi/18 \\
0.00008957 + 0.6333 \cdot \theta + 0.0116 \cdot \theta^2 / \sin \theta, & \theta > \pi/18 \\
-0.08878 \cdot \theta^3 + 0.01033 \cdot \theta^4 &
\end{cases}
\] (5.14)

where \( \theta \) is in radians.

In Fig. 5.6 we present the dependence of droplet's evaporation rate on contact angle
for two above mentioned models (Eqs. (5.13) and (5.14)) as well as for our present
isothermal model which includes vapour diffusion, kinetic effects, and Kelvin’s
equation. For comparison we selected 2 droplet sizes only: \( L = 10^{-7} \) m and \( 10^{-6} \) m.

Present model for droplet size \( L = 10^{-6} \) m gives a dependence on the contact angle
close to that for the diffusive model of evaporation. However, in case of \( L = 10^{-7} \) m
the latter dependence is getting close to the kinetic model of evaporation. Note, in
Fig. 5.6 dependences on the contact angle are presented, but not the absolute
values of the evaporation rate. Important that in Fig. 5.6 scaling values of \( J_{c,i}(\theta = 90^\circ) \)
are different for all curves and equal to the corresponding evaporation rate at \( 90^\circ \).
That is why all the curves go through the point \((90^\circ; 1)\).

5.5. Conclusions

Computer simulations of evaporation of small sessile droplets of water are
performed. Present model combines diffusive and kinetic models of evaporation. The
effects of latent heat of vaporization, thermal Marangoni convection and Stefan flow
in the surrounding gas were investigated for a particular system: water droplet on a
heat conductive substrate (copper) in air at standard fixed conditions. Results of
modelling allow estimating the characteristic droplet sizes when each of the
mentioned above phenomena become important or can be neglected.

The presented model is valid only for droplet size bigger than the radius of surface
forces action, which is around \( 10^{-7} \) m = 0.1 \( \mu \)m. That is, the data in Fig. 5.2 for the
droplet size smaller than \( 10^{-7} \) m are presented only to show the trend. Fig. 5.2 shows
that if the radius of the droplet base bigger than $10^{-7} \text{ m}$ then (i) deviation of the saturated vapour pressure caused by the droplet curvature (Kelvin’s equation) can be neglected, (ii) a deviation from the pure diffusion model of evaporation can be neglected for the droplet size bigger than $10^{-6} \text{ m}$, (iii) this deviation becomes noticeable only if the droplet size is less than $10^{-6} \text{ m}$. This deviation is cause by an increasing influence of the kinetic effects at the liquid-gas interface (Hertz-Knudsen-Langmuir equation) and this theory should be applied together with the diffusion equation of vapour in the air if the droplet size is less than $10^{-6} \text{ m}$.

The latter conclusions show that a consideration of evaporation of microdroplets, completely covered by the surface forces action (that is less than $10^{-7} \text{ m}$), should include both deviation of the saturated vapour pressure caused by the droplet curvature and the kinetic effects.

The latent heat of vaporization results in a temperature decrease at the surface of the droplet. Due to that, the evaporation rate is reduced. This effect is more pronounced in the case of diffusion limited evaporation ($L > 10^{-5} \text{ m}$), when vapour pressure at the droplet's surface is close to saturation. The effect of Marangoni convection in water droplets is negligible for droplets of size $L < 10^{-5} \text{ m}$. For the system considered above, Stefan flow effect appeared to be weaker than the effect of thermal Marangoni convection for $L > 10^{-4} \text{ m}$, but stronger for $L < 10^{-4} \text{ m}$. However, in all cases its influence is small and can be neglected. According to Fig. 5.4 the influence of latent heat of vaporization on the kinetics of evaporation in case of copper substrate is less than 5%. In case of Teflon substrate it is less than 19%.

The presented model can be applied for evaporation of any other pure simple liquids not water only.

6. Conclusions

Under a number of reasonable approximations the evaporation of small enough sessile droplets has been investigated in a self-consistent way by considering the
interconnected problem of vapour transfer; heat transfer in solid substrate, liquid and surrounding air; and thermal Marangoni convection inside the liquid droplet.

It is found that the vapour diffusion is the main mechanism, which determines the linear proportionality of the total evaporation rate, $J$, to the droplet perimeter, $L$, for millimetre size droplets. We found out that evaporation occurs not only at the perimeter of the droplet, indeed it can be uniformly distributed over the whole area of the droplet surface, so that $J \sim L^2 j$, where $j$ is the surface density of the evaporation flux at the droplet’s surface. The proportionality $J \sim L$ is explained by the inverse proportionality of the local evaporation rate to the droplet’s size, $j \sim 1/L$, which is dictated by the vapour diffusion. Thus $J \sim L^2 j \sim L$, which is proved by our computer simulations to be true, as far as the diffusive model of evaporation is applicable.

The latent heat of vaporization does not change the qualitative dependence of the total vapour flux, $J$, on the droplet size, $L$.

The presence of the thermal Marangoni convection inside of the droplet makes all dependences non-linear. Consequently, the proportionality $J \sim L$ is affected by the thermal Marangoni convection inside of the droplets.

The important outcome of presented computer simulations is the fact, that using the average temperature of the droplet surface can simplify the mathematical model of the non-isothermal problem of evaporating sessile droplet. The influence of latent heat of vaporization and thermal conductivities of all three phases on the average temperature of the droplet surface is estimated and approximated with analytical functions. Accordingly, the variation of the surface temperature is an important element influencing the evaporation rate.

The deduced expressions of the instantaneous fluxes are applied for self-consistent calculations of the time evolution of the evaporation processes of sessile droplets in case of contact angle hysteresis. The theory proposed is in good qualitative and quantitative agreement with experimental data for pure liquids and surfactant
solutions with surfactant concentration above the Critical Aggregation/Micelle Concentration.

The situation is more complex for the evaporation stage (S), which occurs for surfactant concentration range $0 < C < C_{ACC}$, when the liquid-air and liquid-solid interfacial tensions would change as the evaporation progress due to the increase of concentration. The theoretical model for the evaporation stage (S) requires future studies of the kinetics of adsorption of surfactant molecules on interfaces (liquid-gas, liquid-solid, gas-solid), as well as the influence of the adsorption concentration (surface excess) on the value of a receding contact angle.

Computer simulations with combined diffusive and kinetic models of evaporation are performed for a wide range of droplet sizes. The effects of latent heat of vaporization, thermal Marangoni convection, Stefan flow in the surrounding gas, and kinetic effects are investigated for a particular system: water droplet on a heat conductive substrate (copper) in air at standard fixed conditions. Results of modelling allow estimating the characteristic droplet sizes when each of the mentioned above phenomena becomes important or can be neglected.

Results show that if the radius of the droplet base is bigger than $10^{-7}$ m, then (i) deviation of the saturated vapour pressure caused by the droplet curvature (Kelvin’s equation) can be neglected, (ii) a deviation from the pure diffusion model of evaporation can be neglected for the droplet size bigger than $10^{-6}$ m, (iii) this deviation becomes noticeable only if the droplet size is less than $10^{-6}$ m. This deviation is cause by an increasing influence of the kinetic effects at the liquid-gas interface (Hertz-Knudsen-Langmuir equation) and this theory should be applied together with the diffusion equation of vapour in the air if the droplet size is less than $10^{-6}$ m.

The latter conclusions show that a consideration of evaporation of microdroplets, completely covered by the surface forces action (that is less than $10^{-7}$ m), should include both deviation of the saturated vapour pressure caused by the droplet curvature and the kinetic effects.
The effect of latent heat of vaporization is more pronounced in the case of diffusion limited evaporation \((L > 10^{-5} \text{ m})\), when vapour pressure at the droplet’s surface is close to saturation. The effect of Marangoni convection in water droplets is negligible for droplets of size \(L < 10^{-5} \text{ m}\). In all cases the influence of Stefan flow is small and can be neglected.

The models, presented in this work, can be applied for evaporation of any other pure simple liquids not water only.

### 7. Future work

The future work on this research project will be focused on computer simulations of processes of simultaneous spreading and evaporation of sessile liquid droplets over smooth solid surfaces. The aim is to understand the role of Derjaguin’s (disjoining/conjoining) pressure in the process of evaporation and spreading.

Particularly it is necessary to perform computer simulations of unsteady process of evaporation of sessile droplets with moving boundaries. Those simulations will allow the modelling of kinetic processes of simultaneous spreading and evaporation. In the vicinity of three-phase contact line the action of disjoining pressure should be taken into account in order to overcome the singularity problems. For small enough droplets (less than 1 micron) and at the three-phase contact line of very thin droplets the local evaporation rate can be very high. In such cases the kinetic model of evaporation will be used, coupled with the diffusive one.

The evaporation of surfactant solutions with concentration less than Critical Aggregation/Micelle Concentration will be additionally studied. Studies on adsorption kinetics of surfactant molecules and its influence on the value of receding contact angle are required in order to build an accurate mathematical model of the evaporation process.
References


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