Liquid–vapour phase transitions at interfaces: sub-nanosecond investigations by monitoring the ejection of thin liquid films

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Abstract. The phase-transition dynamics of isopropanol (C_3H_8O) films with thicknesses on the order of 100 nm deposited on silicon wafers are investigated. A Nd : YAG nanosecond laser pulse is used to heat the substrate. Due to heat transfer, the fluid adjacent to the interface evaporates and the film on top is ejected as an intact liquid layer. The phase transition and the ejection process are monitored by reflectometry with a temporal resolution of about 200 ps and a spatial sensitivity on the nanometre-scale in the direction perpendicular to the substrate. We demonstrate that this approach allows us to determine the generated pressures, the achievable superheating and the relevant timescales of the process and as a consequence provides insights in the nature of the very early stages of the phase transition.

Contents

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1. Introduction

Phase transitions of liquids in contact with a laser-heated solid surface are of fundamental importance for a variety of applications, such as Steam Laser Cleaning of nano-particles from sensitive surfaces [1, 2], laser desorption mass spectrometry [3] and laser surgery [4, 5]. Furthermore the topic involves many basic physical aspects like nucleation processes, spinodal decomposition, bubble dynamics, etc. A comprehensive up-to-date overview on the subject can be found in [6]. Although different experimental and theoretical studies in the past have addressed various of these aspects [7]–[10], the very first stages of the liquid–vapour transition remain poorly understood. Recently, molecular dynamics simulations have been employed to gain a deeper understanding of the beginning of the evaporation process in bulk liquids [11] and in liquids at a solid surface [12, 13]. The simulations involving a solid substrate predict thin liquid films on the order of 5 nm to be ejected as an intact layer within several 10 ps. Moreover it is shown that the ejection time increases for thicker films. Initial experimental ejection studies confirm this behaviour [14]. The experiments presented here provide a considerably improved temporal resolution and thus constitute an essential step from the understanding of the long-term evolution of the system towards the processes that occur within the first few nanoseconds of the phase transition.

2. Setup

A schematic sketch of our experimental setup is depicted in figure 1. The isopropanol films are deposited on the silicon wafer by condensation from a flow of heated gas, which is saturated with isopropanol vapour. The liquid deposition system is omitted for the sake of clarity. A detailed description can be found in [2].

The condensation process is monitored by measuring the reflected intensity from an attenuated laser diode ($\lambda = 635$ nm, $P_{\text{diode}} = 2\,\mu\text{W}$). During the isopropanol deposition, the intensity features oscillations caused by the interference in the liquid layer. This curve is calibrated by comparison to the theoretical dependence of the reflectivity on the film thickness. A Nd : YAG laser pulse ($\lambda = 532$ nm, full width at half maximum (FWHM) = 7 ns), which is absorbed in the substrate, is used to induce the phase transition. The pulse is detected with a trigger diode and in conjunction with the reflectometer curve the film thickness in the moment of the phase transition can be determined with an accuracy of about 1 nm.

The dynamics of the phase transition are monitored by measuring the reflected intensity from an Ar$^+$-cw-laser ($\lambda = 488$ nm, $P_{Ar^+} = 500$ mW) with a temporally highly resolving photo diode (rise time 200 ps). The high power Ar$^+$ probe laser is necessary to achieve a good signal-to-noise ratio in the nanosecond timescale reflectivity signals. In order to avoid undesirable substrate heating by the probe laser, an electro-optical-modulator (EOM) is used to limit the duration of the Ar$^+$-laser illumination to an interval of 750 ns, which is synchronized with the Nd : YAG laser pulse. A temporally highly resolving Nd : YAG pulse trigger diode, which has been synchronized to the reflectometer with a picosecond laser pulse, is used to relate the reflectivity signal to the temporal evolution of the Nd : YAG pulse.
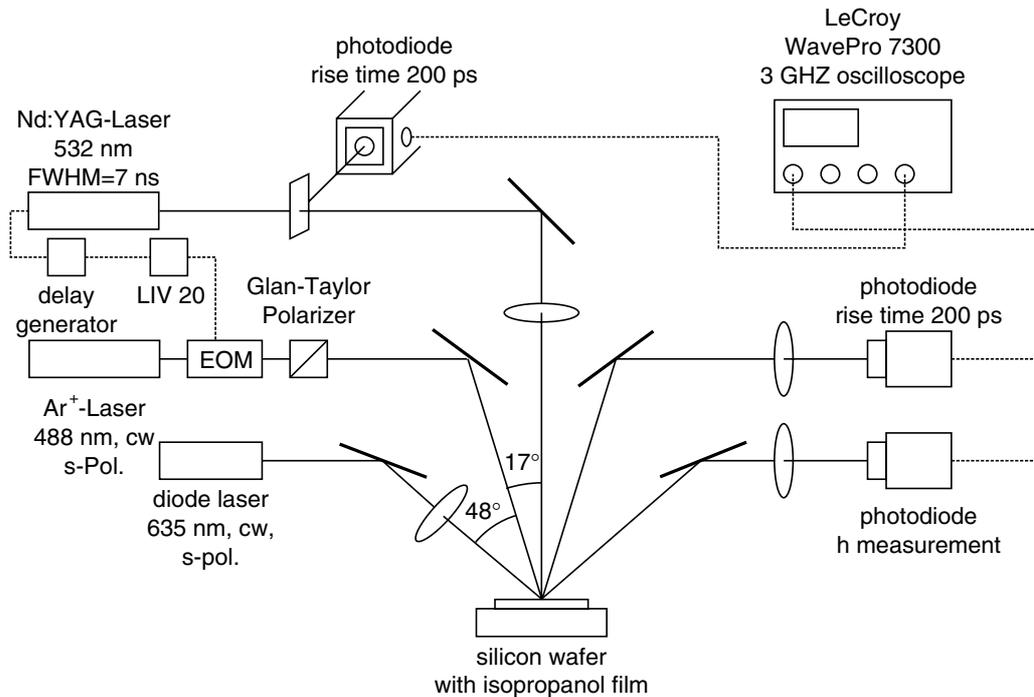
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Figure 1. Schematical drawing of the optical setup. A Nd : YAG laser pulse induces the phase transition. Two reflectometers are used to measure the deposited film thickness in the moment of the phase transition and the dynamics of the transition with sub-nanosecond resolution.

3. Results and discussion

In the following, we present the results of one particular single-laser shot experiment, which is representative for a large number of experimental runs. Figure 2 displays the observed reflectivity signal from the Ar^+-laser. The oscillations on the nanosecond timescale are caused by interference between the substrate surface and the intact liquid layer, which is ejected because of the phase transition. The decrease of the oscillation amplitude over time can be attributed to emerging roughnesses at the film surfaces. In the first part of the signal ($t < 78$ ns), the oscillation period becomes longer and longer until a turning point is reached after which the period decreases again. This observation confirms the results of initial studies on the subject with lower time resolution, in which a KrF excimer laser was used to induce the phase transition [14].

A distance versus time plot for the ejected isopropanol layer is obtained by calibrating the signal in figure 2 with the theoretically determined reflectivity as a function of the distance between the film and the substrate. For the calculation it is assumed that the ejected film maintains its initial thickness and that the refractive index in the interspace between the ejected film and the substrate is 1. Both assumptions constitute good approximations in view of the ejection scenario described in molecular dynamics simulations [12] and considering that only a narrow layer of the total film at the interface is heated above the boiling temperature, as shown by the temperature simulations described later on. The data points in figure 3 are obtained by assigning the corresponding distances and times for the oscillation minima and maxima to each other. In addition the beginning of the trajectory is resolved more precisely, since the acceleration
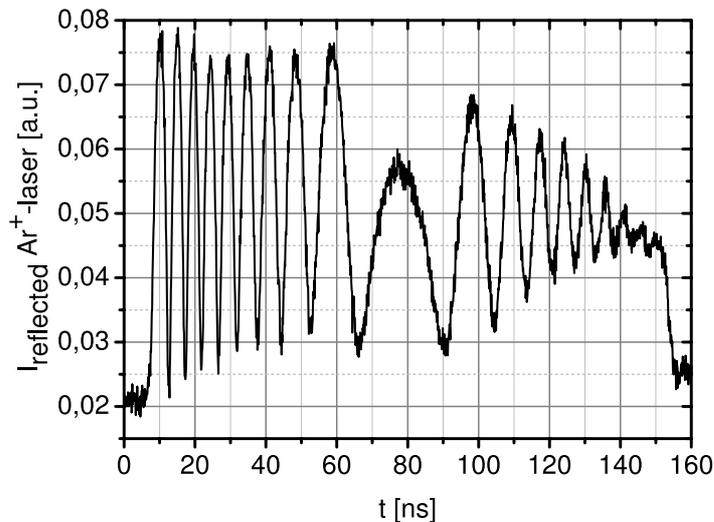
Figure 2. Typical reflectivity signal for the Ar⁺-laser during the ejection of the liquid film. The oscillations are caused by interference between the substrate surface and the ejected liquid layer (incident laser fluence $= 138\,\mathrm{mJ\,cm^{-2}}$, initial film thickness $h = 102\,\mathrm{nm}$). $t = 0\,\mathrm{ns}$ corresponds to the beginning of the Nd : YAG laser pulse.
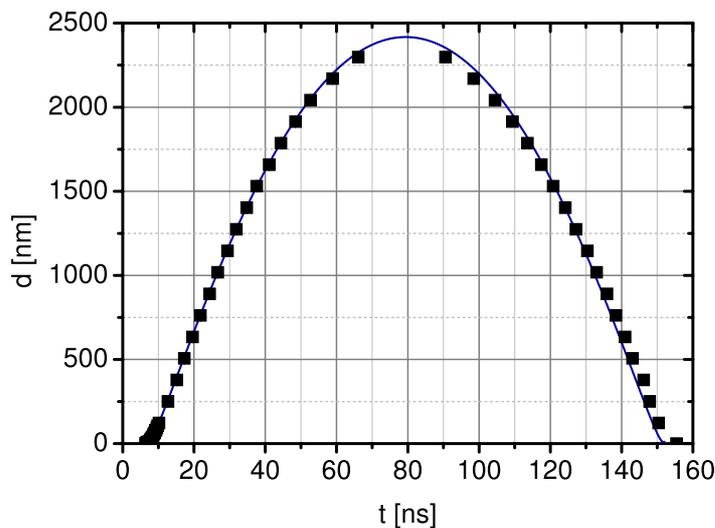

Figure 3. Trajectory of the isopropanol film after the phase transition. The solid line represents a fit to the data points according to the expanding vapour layer model described in the text.

in this part provides the main information about the nature of the phase transition. For this purpose, the amplitude of the theoretically calculated reflectivity versus distance curve is scaled to match the oscillation between the initial level and the first maximum of the measured signal. Afterwards the amplitude of the experimental signal is measured every 200 ps and the corresponding distances from the theoretical curve are attributed.
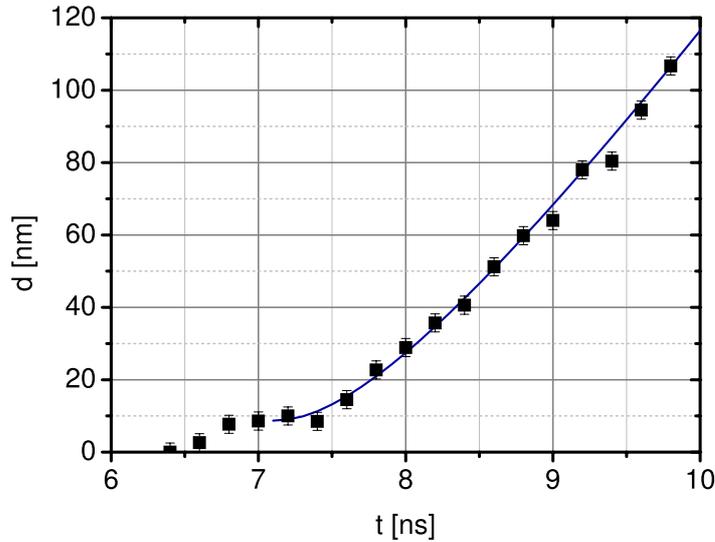
Figure 4. Magnification of the first few nanoseconds of the ejection process in figure 3. The solid line corresponds to the same fit as in figure 3. After the formation of a vapour layer in the first 700 ps (6.4–7.1 ns), the overlying liquid is accelerated away from the substrate for about 8.6 ns until the expansion causes the pressure under the film to drop below the pressure above.

Figure 3 depicts the entire trajectory of the film. The deceleration causing the parabolic trajectory curve and eventually the redeposition of the film occurs, since the pressure between the liquid layer and the substrate drops below the atmospheric pressure after a certain expansion is reached. The initial stage of the trajectory is shown in figure 4. After the phase transition sets in at $t = 6.4$ ns, three stages in the trajectory curve can be distinguished. First a vapour layer of (8.7 ± 1.0) nm thickness is formed between the substrate and the liquid layer within approximately 700 ps. At present this formation process cannot be resolved more precisely and therefore it will not be discussed in more detail. However, the occurrence of a plateau in the trajectory curve between $t = 6.8$ ns and $t = 7.4$ ns indicates that the film is still basically at rest after the formation. Subsequently, the generated pressure causes an acceleration of the liquid layer away from the surface starting at approximately $t = 7.1$ ns. In the third stage ($t > 15.7$ ns, see figure 3), the pressure above the fluid already exceeds the one below and the back acceleration towards the surface starts, which eventually leads to the redeposition of the film.

The solid line in figures 3 and 4 presents a fit to the data points based on an expanding vapour layer model. In the first step of this model, we derive the equation of motion for the liquid layer:

$$\frac{\mathrm{d}^2}{\mathrm{d}t^2}d(t) = \frac{P_0}{\rho \cdot h} \cdot \left(\frac{d_0}{d(t)}\right)^n - \frac{P_{\mathrm{atm}}}{\rho \cdot h}, \tag{1}$$

with P_0 denoting the initial pressure under the film, P_{atm} the atmospheric pressure, d_0 the initial distance of the film from the surface after the vapour formation, ρ the density of isopropanol, h the thickness of the isopropanol film and n the polytropic exponent. The density of isopropanol at $T = 293$ K is used, since almost the entire layer except for the few nanometres at the interface

remains at room temperature, as shown by the temperature calculations described below. For the derivation it is assumed that the gas under the film undergoes a polytropic change and that no relaxation in the direction parallel to the substrate occurs. This is justified, since the size of the Nd : YAG laser spot on the sample is on the order of several millimetres, while the Ar^+-laser spot size is on the order of $100\,\mu$m and centred in the Nd : YAG spot. Therefore velocities significantly above the speed of sound would be required for a relaxation of the vapour in the lateral direction. The pressure above the film is constantly 1 atm, because the liquid layer velocity is on the order of $40\,\mathrm{m\,s^{-1}}$ to $50\,\mathrm{m\,s^{-1}}$ and distinctly smaller than the speed of sound. Therefore no significant compression occurs in this area. The equation of motion is solved numerically with the ordinary differential equation (ode) solver in Scilab [15]. For the initial conditions we use $d(t = 7.1\,\mathrm{ns}) = 8.7\,\mathrm{nm}$ and $v(t = 7.1\,\mathrm{ns}) = 0\,\mathrm{m\,s^{-1}}$. The result is fitted to the measured data points, using the polytropic exponent n and the initial pressure P_0 as fitting parameters. A minimal deviation from the data points is obtained for $n = 1.00$ indicating an isothermal process and for an initial pressure directly after the vapour formation of $P_0 = (4.9 \pm 0.2)\,\mathrm{MPa}$.

After this analysis of the liquid layer trajectory, we now relate the results to calculations of the temperature distribution in the isopropanol film in the following. In this way, we first determine the time during which the system is in the metastable state and the superheating of the liquid. Subsequently, we support the measured result of the initial pressure with an energetic treatment of the phase transition.

The temperature at the surface is numerically simulated using a one-dimensional finite difference heat conductance model. This simulation has proven to be very reliable in different applications; for instance an excellent agreement of the calculated and the experimentally measured laser fluence necessary to induce melting of a silicon surface is found. The heat transfer coefficient (HTC) from the silicon wafer to the isopropanol is determined by running the simulation for several experiments with different laser fluences. A lower limit for the HTC is found due to the requirement that the isopropanol's boiling temperature must be reached for fluences near the threshold necessary for the film ejection. The upper limit is determined by demanding that the temperature in the experiments with the highest fluences remains below the spinodal temperature, which indicates the thermodynamic stability limit for the liquid. According to [16], the spinodal temperature is below $0.9\,T_c = 457\,\mathrm{K}$ over a large pressure range, with T_c denoting the critical temperature. In this manner, the HTC is measured to be $(1.0 \pm 0.2) \times 10^7\,\mathrm{W\,m^{-2}\,K^{-1}}$, in excellent agreement with the result determined in [17].

The calculated temporal temperature evolution during the relevant part of the experiment is shown in figure 5 and the corresponding temporal profile of the Nd : YAG heating pulse is depicted in figure 6. The local temperature distribution in the moment of the phase transition is plotted in figure 7. In the experimental run analysed here the fluence of the Nd : YAG laser ($F = 138\,\mathrm{mJ\,cm^{-2}}$) is considerably above the threshold fluence necessary to induce the ejection for this particular film thickness ($F \approx 40\,\mathrm{mJ\,cm^{-2}}$). Therefore the lift-off in this experiment occurs significantly before the temperature maximum at the surface is reached.

From figures 4 and 5 the time, during which the system is in the metastable regime, can be deduced. The isopropanol at the interface reaches its boiling temperature of $355.5\,\mathrm{K}$ at $t = 5.0\,\mathrm{ns}$. Since the vapour formation starts at $t = 6.4\,\mathrm{ns}$ an estimation for the time duration in the metastable state of $1.4\,\mathrm{ns}$ is obtained. However, since the liquid is still heated, while the system enters the metastable region, this value cannot be identified with an incubation time [18], which refers to the stability of the metastable state at a particular temperature after an instantaneous heating process. It has to be anticipated that the obtained result is dependent on the applied heating rate.
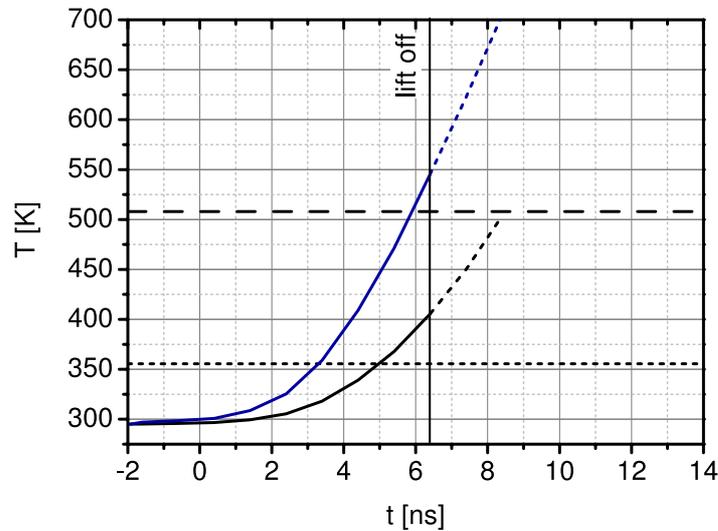
Figure 5. Simulation of the temperature change of the silicon surface (upper curve) and of the isopropanol at the interface (lower curve) as a function of time. The solid curves present the evolution before the phase transition sets in and the dashed curves indicate the further development if no phase transition had occurred. The vertical line at $t = 6.4$ ns indicates the onset of the liquid film ejection. The dotted horizontal line represents the isopropanol's boiling temperature and the dashed horizontal line corresponds to the critical temperature of isopropanol.
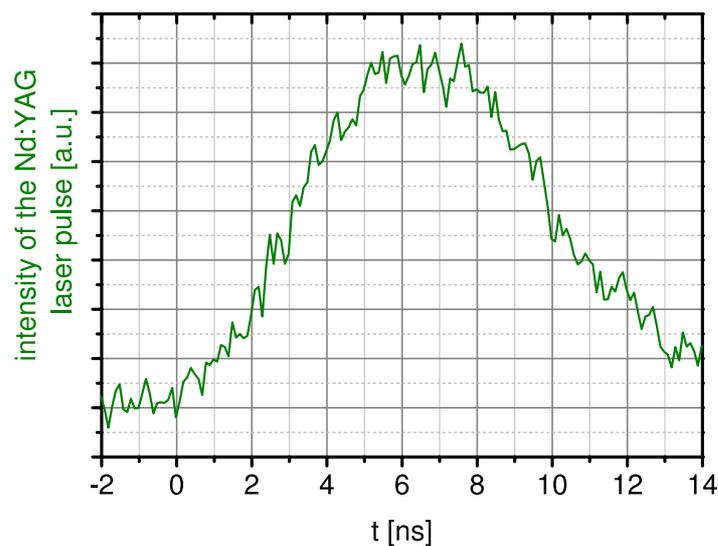

Figure 6. Temporal profile of the Nd : YAG laser pulse heating the substrate.

Regarding the superheating of the isopropanol, the calculated temperature evolution in figure 5 implies that the phase transition at the interface sets in at a temperature of 405 ± 16 K. This is about 80% of the critical temperature of isopropanol ($T_c = 508$ K) [19] and 50.5 K above the boiling temperature under normal conditions (355.5 K).
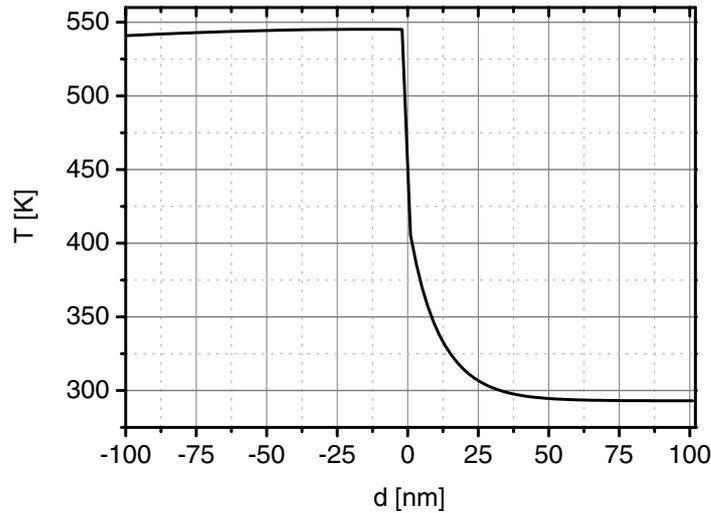
Figure 7. Simulation of the temperature distribution in the moment when the phase transition sets in ($t = 6.4$ ns). Negative values of d correspond to the silicon substrate and positive values to the deposited isopropanol film. The temperature jump at the interface is due to the finite HTC.

From figure 7, it is found that 7 nm of the isopropanol film are superheated in the moment when the phase transition sets in. From the local temperature distribution the deposited thermal energy in this superheated region, which exceeds the amount required to reach the boiling temperature, can be calculated. It is assumed that the liquid becomes thermally decoupled from the substrate as soon as vapour starts to be formed at the interface. This simplification is justified considering that the HTC between a solid and a gas is generally several orders of magnitude smaller than between a solid and a liquid. In addition, the heat conductance of the gas layer is significantly smaller than the heat conductance of isopropanol in the liquid phase. Consequently, the energy available for the phase transition per area can be calculated as follows:

$$\frac{E_{PhaseTrans}}{A} = c_p \cdot \rho \cdot h_{SuperHeat} \cdot \Delta T, \tag{2}$$

with c_P, ρ, $h_{SuperHeat}$ and ΔT denoting the mass specific heat capacity at constant pressure, the density of isopropanol, the thickness of the superheated layer, and the temperature difference with respect to the boiling point averaged over the superheated region. Although the material properties of isopropanol used in this formula are temperature dependent, the values at the boiling point can be used as reasonable approximations for this energetic analysis. In this way, a value of $E_{PhaseTrans}/A = (0.46 \pm 0.19)\,\mathrm{J\,m^{-2}}$ is found. Considering the latent heat of $6.63 \cdot 10^5\,\mathrm{J\,kg^{-1}}$ for isopropanol at the boiling temperature and its molar mass, this corresponds to $(1.2 \pm 0.5) \cdot 10^{-5}\,\mathrm{mol\,m^{-2}}$. Using the ideal gas law for a gas temperature of 355.5 K, the following relationship for the pressure P and the thickness of the generated gas layer d is derived:

$$P \cdot d = (3.5 \pm 1.5) \cdot 10^{-2}\,\mathrm{Pa \cdot m}. \tag{3}$$

Applying the initial gas layer thickness determined from figure 4, a pressure of (4.0 ± 1.8) MPa is expected based on energetic estimations at the beginning of the lift-off. Due to the large error bars and the fact that the pressure dependence of the boiling temperature is neglected, this result just provides a relatively rough appraisal of the situation. Nevertheless it confirms the order of magnitude of the initial pressure $P_0 = (4.9 \pm 0.2)$ MPa determined from the fit to the data points.

So far our observations have exclusively examined the behaviour for one specific initial film thickness and one particular incident laser fluence. The insights from these results can be extended by identifying the important parameters, which influence the phase transition, and exploring their consequences. As a first step in this direction, the effect of different initial film thicknesses have been investigated. For this purpose, we have measured the ejection velocities in several experiments with a comparable effective laser fluence $F_{\text{eff}} = F \cdot [1 - R(h)]$, with R denoting the reflectivity of the sample with the isopropanol film for the Nd : YAG pulse. By determining the average velocity between $d = 100$ nm and $d = 200$ nm, it is ensured that the measurement is accomplished in a part of the trajectory in which the velocity is approximately constant. The ejection velocity is found to decrease with increasing liquid layer thickness, from a value of (50.9 ± 1.5) m s^{-1} for $h = 97$ nm to (40.1 ± 2.3) m s^{-1} at $h = 227$ nm. The change in the velocity is too small to be explained by a simple momentum or energy conservation law. This might be a first evidence that the nanoscopic properties of the phase transition at the interface are influenced by the liquid layer thickness, e.g. in terms of changing the runtimes of acoustic waves generated by the laser illumination and reflected by the liquid layer surface.

4. Summary

In conclusion, we have presented an approach to study the dynamics of phase transitions in thin liquid films at a rapidly heated surface, by observing the ejection of the films due to the phase transition. To our knowledge, at present this paper constitutes the most sensitive experiment in terms of temporal and spatial resolution on the subject. Admittedly, hitherto the detailed mechanisms of the initial vapour layer formation remain obscure. Future experiments using picosecond and femtosecond laser pulses in combination with an even higher spatial resolution might be capable to resolve this process. However, at present our experiment already offers the possibility to determine the superheating of the liquid, an estimation of the timescale of the phase-transition process and the generated pressure. Even though the dimensions and timescales in corresponding molecular dynamics simulations are currently about one order of magnitude smaller, a connection of those results with our experiments provides extensive possibilities to work out a detailed understanding of the phase-transition process at the interface. Further experiments, such as observations of the heating rate dependence of the process and investigations of the dependence on the substrate structure, offer the possibility to identify all the relevant parameters influencing the phase transition.

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