Molecular Dynamics Simulation of the Leidenfrost Effect

D A Biryukov¹, D N Gerasimov² and E I Yurin²

¹ Joint Institute for High Temperature RAS, Russia, 125412 Moscow, Izhorskaya, 13-22
² National Research University “MPEI”, Russia, 111250 Moscow, Krasnokazarmennaya, 14

YurinEI91@gmail.com

Abstract. Results of the molecular dynamics simulation of the contact between an argon droplet and an overheated copper surface (with the temperature exceeding critical for argon) are presented. The direct contact of argon (supercritical fluid) and the overheated surface is observed in the numerical experiment. Dynamics of the droplet size change is described by a simple equation.

1. Introduction

Liquid cannot touch an overheated surface. This phenomenon is now referred to under the common term the ‘Leidenfrost effect’ [1]. However, one should remember that, in general case, the ‘contactless contact’ can be caused by two different physical features: the wettability and the evaporation of a liquid droplet. The pure Leidenfrost effect occurs when a droplet levitates on a ‘vapor bag’ of molecules evaporated from that droplet, i.e. when any mention of wettability has no sense.

For stationary droplet levitation, the force of gravity must be balanced by the forces caused by evaporation. Commonly, two ways may be considered: a) the balancing force is the reactive force of the evaporation flux, or b) the balancing force is the overpressure under the droplet. From the first point of view, one may formulate the condition for levitation of a droplet of radius \( R \): the evaporated mass flux from the droplet must be \( j \sim \rho \bar{R}g/\nu \), and for the liquid density \( \rho \sim 10^3 \) kg/m\(^3\), for the mean velocity of the evaporated molecules \( \nu \sim 10^5 \) m/s the droplet of radius \( R \sim 10^{-2} \) m can levitate when the mass flux is about \( 10^{-1} \) kg/m\(^2\).s. This is a huge evaporation flux but this value is not impossible, and such a droplet (with radius \( \sim 1 \) mm) should be evaporated completely at this rate at \( t \sim 10 \) s; this value does not look unreal either. The case b) looks more soft and traditional, it demands overpressure \( \Delta \rho \sim \rho \bar{R}g \), i.e. \( \sim 10^2 \) Pa for the example considered, which can be easily achieved due to the evaporation of the droplet.

In some works, the Leidenfrost effect is considered in thermodynamics language (i.e. with the equilibrium thermodynamics description): sometimes, terms like ‘saturation pressure’, ‘binodal’, etc. are used. This way seems questionable because of non-equilibrium conditions of the evaporating droplet; the quasi-equilibrium approach needs special evidences. Another way seems to be more convenient: molecular dynamics simulation allows one to find out many parameters of a non-stationary system directly. Of course, MD simulation has its intrinsic problems too, but – with some reservations – this method is the analog of a direct experiment.

In this work, we present the results of MD simulation of the initial stage of the Leidenfrost effect – the contact of the droplet and the candent surface.
2. Numerical simulation

The process of the contact between an argon droplet and an overheated copper surface is considered.

The method of the molecular dynamics (MMD) simulation is used. Interaction between atoms is described by Lennard-Jones potential

\[
\varphi(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right],
\]

where \( r \) is the distance between the atoms; \( \sigma \) and \( \varepsilon \) are interaction coefficients. Coefficients for interaction between argon and copper atoms were calculated using Lorentz-Berthelot rule [2][3].

Lennard-Jones potential coefficients and masses are presented in the table below for argon [4] and copper [5].

|       | \( \varepsilon/k_B \) (K)* | \( \sigma \) (Å) | \( m \) (kg \( \cdot \) 10\(^{-26} \)) |
|-------|-----------------------------|-----------------|-----------------|
| Ar    | 125.70                      | 3.345           | 6.63354         |
| Cu    | 3 168.8                     | 2.330           | 10.5521         |
| Ar – Cu | 631.125                  | 2.838           | –               |

* \( k_B \) is the Boltzmann constant

Numerical integration is performed using leap-frog method with a step of 10 fs [6]. It should be noted that cut-off radius is not used during the simulation, and calculation speed is increased by using CUDA technology [7].

Figure 1. Initial state of the system B.
Computational region is a parallelepiped. Boundary conditions are set to create a flat copper layer (with area $L_x \cdot L_y$, on the edge of the x-y plane) and a single droplet. In figure 1, copper is located near the edge with $z = 0$, on which reflecting boundary conditions are set. The opposite edge is free: an atom moving along the z axis can move away from the copper layer for an indefinitely large distance.

Boundary conditions for edges parallel to the z axis are not common ones, as they should form an infinite plain copper surface (i.e. periodic boundary conditions), but at the same time there should be a single droplet with no influence of the ‘phantoms’ generated by periodic boundary conditions. This problem is solved by combining periodic and free conditions. For copper atoms, periodic conditions are set, and so as for interaction between copper and argon. But for argon atoms, boundary conditions are free. This trick provides an infinite copper plate that interacts with a single droplet.

Temperature of the copper plate is maintained by the velocity rescaling method [8].

At the very first moment of the simulation (after initial state is formed), droplet velocity drift in the $z$-direction is set equal to 10 m/s.

Numerical simulation is performed for two systems: with number of argon atoms equal to 10 000 (system A) and 20 000 (system B). System parameters are shown in table 2.

| Table 2. System parameters |
|----------------------------|
| System | Copper atoms qty | Argon atoms qty | $L_x \cdot L_y$ (nm nm) |
| A      | 7 350            | 10 000          | 13x13                  |
| B      | 11 094           | 20 000          | 16x16                  |

Powered by GPU (Nvidia Tesla P4), the calculation for system A and B is performed with problem time 0.8 ns (time spent on system formation is not included).

2.1. Results extract
For droplet examination, it is necessary to distinguish atoms that belong to the droplet. For this purpose the Amsterdam method is used [9]. The particle refers to liquid if the number of its neighbors in radius $3 \sigma$ is greater than 30 (average number of neighbors in liquid is approximately 80). In the original method, the observed radius is $1.5 \sigma$ and the number of neighbors is 4. In this work, the observed radius is increased in order to ignore small clusters (especially, absorbed atoms on the copper plate).

For selected particles, the following mean values were calculated (see figures 2, 3):
- droplet velocity $V_z$ (mean velocity in z-coordinate);
- mean kinetic energy $\varepsilon$;
- droplet coordinate $Z$ (mass center coordinate).

It should be noted that the term ‘temperature’ as a parameter of equilibrium state makes no sense for such a process, so we will use the term ‘mean energy of chaotic motion’ (MECM) to describe the measure of chaotic kinetic energy.

Mean values for system A are presented in figure 2. The origin corresponds to the moment with minimum droplet coordinate.
Figure 2. System A a) coordinate, velocity and b) MECM evolution.

Velocity curve has a fluctuation at $-0.1$ ns (and so does the MECM curve). This fact corresponds to the collision of the droplet and the copper plate (and then the copper plate and system bound). There is a slight drift of the plate caused by long-distance interatomic forces between argon and copper (as the cut-off radius is not applied). For system B, this drift is eliminated.

Mean values for system B are presented in figure 3.

Figure 3. System B a) coordinate, velocity and b) MECM evolution.

As can be seen, the copper plate drift is eliminated for system B. The results are discussed below.
3. Discussion of the results

The first thing that should be noted from figures 2 and 3 is that the droplet is extremely attracted by the copper plate at the distance less than 7 nm (velocity value grows from 10 m/s to ~ 30 m/s).

It is not expected that hot gas prevents the droplet from direct contact with the overheated plate, as its density is not high enough (free boundary conditions are set for the gas). Moreover, in our previous research the contact was observed for the system where gas was literally compressed by the liquid layer (that was launched towards the overheated surface with initial velocity) [7].

In figure 4, density and MECM maps of the droplet are given at the moment with minimum z-coordinate.

![Figure 4](image_url)

**Figure 4.** a) MECM and b) density map of droplet section (system B)

Figure 4 shows that there is an interlayer between the liquid droplet and the overheated copper surface. However, it is not gas, but a supercritical fluid (its MECM and density are higher than critical parameters for argon – ~150 K and ~13.4 kmol/m³, respectively) that, of course, has no phase-transition surface with the liquid core of the droplet.

It is clear that the smaller droplet (system A, see figure 2) has a higher MECM maximum and this droplet bounces away with a higher velocity. The velocity of the larger droplet (system B, see figure 3) tends to zero and the droplet disappears while evaporating near the copper surface.

3.1. Dynamics of evaporation

This section is dedicated to dynamics of droplet evaporation.

Due to evaporation, the mass of the liquid droplet changes as

$$\frac{dm}{dt} = -jF,$$  

(2)

which gives us (for a spherical droplet and for the mass flux of the evaporation taken as a function of MECM in form of \(j = A\varepsilon^n\)) the following:

$$\frac{dR}{dt} = -\frac{A\varepsilon^n}{\rho}.$$  

(3)

The time dependence \(\varepsilon(t)\) is very complicated, but we know that this value increases when the droplet touches the heated surface, and decreases after the contact. To obtain a simple analytical estimation, we adopt a simple function \(\varepsilon(t) = \varepsilon_0 \exp(-Bt^2)\) (thereby the time origin corresponds to the maximum value of MECM and we neglect the initial temperature of the droplet, assuming that this value is insufficient for significant evaporation), so the droplet radius depends on time as
\[
\frac{R(t)}{R_0} = 1 - \frac{R_0 - R_{\text{min}}}{2R_0} \left[ 1 + \text{erf} \left( \frac{t}{\tau} \right) \right],
\]

where \( R_0 \) and \( R_{\text{min}} \) are initial and minimal radius, respectively; time \( \tau \) has the meaning of a time scale for liquid-surface contact. With (4), one may obtain the droplet mass from expression \( m(t) = \rho \cdot 4\pi \cdot R(t)^3 / 3 \). Function (4) is presented in figure 5 for \( R_{\text{min}} = 0 \) (complete evaporation).

For a more detailed analysis, we will take into account some special nuances. Below we will also use thermodynamic description for some parameters and will focus on the droplet’s size variation. Let’s assume that the droplet has spherical shape, with radius \( R \). Then, density \( n_i \) (number of atoms in m³) of the droplet is determined as

\[
n_i = \frac{N}{4/3 \cdot \pi \cdot R^3},
\]

where \( N \) is the number of atoms in the droplet.

Using this equation we obtain the expression for the surface area of the droplet

\[
F = 4 \cdot \pi \cdot R^2 = \left( 36 \cdot \pi \cdot n_i^{-2} \right)^{1/3} N^{2/3}.
\]

The rate of the atom number variation in the droplet can be described using the evaporation flux with the evaporation coefficient \( \beta \) for the droplet with surface area \( F \):

\[
\dot{N} = -\beta \cdot C_s \cdot \left( \frac{k_B}{2 \cdot \pi \cdot m} \right)^{1/2} \left( 36 \cdot \pi \cdot n_i^3 \right)^{1/3} N^{2/3} \sqrt{\varepsilon_i},
\]

where \( n_i \) is the density of vapor in the saturation state; \( C_s \) is a shape factor; \( \varepsilon_i = C_v \cdot \varepsilon \) is the effective MECM (temperature) of the droplet surface, where \( \varepsilon \) is the average droplet MECM and \( C_v \) – the energy factor. Equation (7) is obtained assuming that the kinetics of evaporation of the droplet can be described with the surface ‘temperature’ \( \varepsilon_i \) obtained from the MECM of the droplet; this approach can be correct, at least, for sufficiently small droplets.

The evaporation coefficient is taken equal to 0.8 [10], and saturation properties (liquid and vapor densities) are calculated using standard equations [11]. The shape factor is a coefficient that takes droplet deformation into account. Also, parameter \( \varepsilon_i \) is the MECM at the surface, different from the average MECM of the droplet \( \varepsilon \) (taken from MMD simulation).

As for \( C_s \) and \( C_v \) factors, firstly, they lie between 0 and 1; secondly, these coefficients should be equal to 1 at the distance far from the copper plate (i.e. in the equilibrium state).

Differential equation (7) can be easily solved for \( \varepsilon_i = \text{const} \). However, taking into account the MECM dependence in figures 2 and 3, we solve this equation numerically. The system should also include an energy conservation equation, but we will not consider it here: as it was stated above, the parameter \( \varepsilon_i \) will be taken from the MD simulation. Equation (7) will be solved numerically (using the Euler method). Expressions for \( C_s \) and \( C_v \) factors are discussed below.

3.1.1. Shape and energy factors. In order to take into account both \( C_s \) and \( C_v \) factors we will use a simple assumption. The shape of the droplet is not spherical when it collides with the copper plate. The moment of collision can be determined using radius and mass centre coordinate: spherical segment with height \( R - Z \) is cut off by the copper plate (see figure 6a).
1 – liquid volume;
2 – supercritical fluid volume;
3 – mean MECM from MMD;
4 – predicted MECM of liquid droplet part

**Figure 6.** The shape factor and the energy factor: a) explanation and b) influence

We assume that this ‘non-fitting’ segment (a spherical segment below the plate line) is a supercritical fluid, and the other ‘fitting’ part is a liquid volume of the droplet. Evaporation occurs through the liquid volume surface (marked 1 in figure 6a). Consequently, the shape factor is the ratio of the surface 1 to the surface of the sphere.

To calculate the kinetic energy (in kelvin), we take the mean energy of chaotic motion for the droplet as

$$\varepsilon V = \varepsilon_1 V_1 + \varepsilon_2 V_2,$$

where $V$ is the sphere (droplet) volume, $V_1$ is the volume of a part of the droplet where the medium can be considered as a liquid, $V_2$ is the supercritical fluid volume and $\varepsilon$, $\varepsilon_1$, $\varepsilon_2$ are corresponding MECM.

Fluid MECM $\varepsilon_2$ is to be determined. As it lies in the range between the copper plate temperature (300 K) and $\varepsilon_1$, we set it as equal to $0.5 \cdot (300 + \varepsilon_1)$.

The coefficients obtained above are used in the numerical integration of equation (7). As mentioned above, parameters of integration are taken from the MMD simulation (droplet MECM and coordinate). The initial number of atoms in the droplet is 9 182 and 18 218 for systems A and B, respectively.

**Figure 7.** Relative change of the number of atoms in the droplet for systems A and B
3.1.2. Comparison. In system A (see the figure 2b), the droplet’s MECM exceeds the critical temperature of argon (~150 K). Since we separated the droplet using surface and energy factors (see 3.1.1), it should decrease the droplet’s ‘liquid part’ and cut the maximum (and it does – see figure 6b). The comparison of the calculation and MMD results is given in figure 7 (note that the number of atoms in the droplet is divided by the initial number of atoms).

Figure 7 shows that dynamics is well described with a quite simple equation and voluntary approximation of the factors. The result for system B looks better. We associate this with the fact that there was a plate drift in system A, and also system A is smaller, so non-equilibrium in it is stronger.

Obviously, the left part of curves (before the collision), with shape and energy factor equal to 1, agrees well with the MMD simulation results.

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Conclusion
In the MMD simulation, the process of contact between the argon droplet and the overheated copper surface is observed for a nanoscale droplet (with radius ~7 nm) with initial speed of only 10 m/s. As the result of the contact, the size of the droplet decreases more than twice. During the contact, mean evaporation mass flux was ~10^3 kg/m^2s; in such conditions, the reactive force of evaporated molecules must be considered. After the contact, during the levitation phase, this flux must be much lower; however, we cannot state that this flux becomes negligible at that conditions.

A simple model for describing this process that uses parameters from the MD simulation found a good agreement with the numerical experiment. As we see, the combination of thermodynamics and kinetics provides appropriate results. It is possible to improve the model in many ways, of course: adding the energy conservation equation, adopting a model for droplet motion and deformation, etc.

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