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A critical review of the developments in molecular dynamics simulations to study femtosecond laser ablation

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Abstract

Laser-matter interaction is a complex physical process that has come to the forefront of scientific research, particularly due to the advancements of laser technology and its wide availability in recent decades. Studying ultrashort pulsed lasers directly through the experiments is challenging due to the short time scales involved, which could be of the order of a few picoseconds to femtoseconds. Accurate insight and knowledge about these ultrafast light-matter interactions can potentially provide valuable opportunities to advance ultra-precision manufacturing and offer more control over deterministically processing materials with ultrashort pulsed lasers. In a chronological evaluation of the scientific outputs on this matter, several research trends are noticeable. This review paper outlines the prominent trends over the years to summarise the developmental journey so far in our understanding of this complex process. We review modern developments in ultrashort pulsed laser ablation, especially the contributions of Molecular Dynamics (MD) simulations to the laser technology. We articulated the progress from analytical mathematical techniques employed in the 1990s, which facilitated widespread use of these lasers in applications ranging from medical procedures to material processing and beyond, to the advent of high-performance computing and the current focus on numerical atomistic modelling for improved real-time analysis of single pulse laser ablation. This knowledge is vital to advance the macroscopic understanding of various precision manufacturing processes relying on femtosecond lasers.

Keywords: ultrashort pulsed laser, femtosecond laser, molecular dynamics simulation, laser ablation

1. Introduction

Modern ultra-precision manufacturing capabilities are a legacy of numerous inventions and innovations and the field is continuing to grow by incorporation of tools ranging from diamond to lasers [1]–[3]. Lasers in general have been known as valuable sources of energy since the 19th century and the interaction of various light sources with the matter has been studied ever since. Einstein's explanation of the photoelectric effect via quantised energies that were suggested to be wavelike particles known as photons, travelling in a straight line at the speed of ~0.3 million km/s, became the foundation of our modern theory of the light-matter interactions. As a direct result of this theory, one crucial turning point in the evolution of ultra-precision manufacturing and metrology has been the invention of lasers. Some of the highly desirable properties of lasers in this context are coherence, very narrow frequency or very short pulse/time (near monochromaticity within a very narrow spectral width or pulsed in ultrashort time), highly collimated beams that can be focused to a very small spot and a controllable high-power output. Following the discovery of the fundamental rules of light-matter interactions, a crucial branch of science we call photonics has been established. Reviewing the fundamental understanding of laser-matter interactions indicates that our understanding of the process is mainly based on the observed experimental effects while, so far, little attention has been paid to atomistic simulations as a versatile method of studying this subject which, is vital to improve the material removal process at the atomic level. This review paper aims at exploring the development of the available atomistic simulation options, highlighting possible opportunities and the current limitations.

2. Early-stage development of mathematical modelling

Laser-matter interaction is a complex phenomenon with several variables affecting the outcome of the process. Timescale has become an important factor with the advancement in laser technology and ultrashort pulse generation. Marla et al [4] in their chronological review of the laser ablation modelling, argued that interaction with matter from the outset of laser invention was believed to be single step radiation on the target leading to an instantaneous conversion to heat that proceed to raise its temperature. Mathematical modelling of the process was done by Fourier's heat conduction equation with the addition of laser heat as the source term. The developed parabolic models were accurate for the pulse duration of nanoseconds and referred to as Parabolic One Step (POS) models. However, with the pulses becoming shorter than 100 picoseconds, models start to deviate from experiments, and they no longer accurately represent the process.

In 1993, Qiu et al [5] suggested that the basic assumption of laser heat instantaneously propagating in the material is questionable. They proposed wave type propagation of heat with a finite rate and consequently, the addition of heat transfer rate. This transformed the POS equation into a Hyperbolic One Step (HOS) method. In 1955, almost four decades prior to Qiu et al [5], Kaganov et al [6] predicted that heat energy is absorbed by electrons and there must be a finite energy transfer rate between electrons and the lattice. Two decades later, in 1974, Anisimov et al [7] proposed a phenomenological model to describe how this energy exchange rate affects laser heating of metals. This assumption led to further modifying the equation into a Parabolic Two Step (PTS) model. This model of electron and lattice temperatures in non-equilibrium state is known as two-temperature model these days. It was the governing principle for the materials used for the mirrors of a short pulsed laser, investigated by Qiu et al [8] in another experiment in 1994. Generally, the thermal design of gold-plated mirrors for high power lasers is based on Fourier's heat conduction model where the secondary material with a higher heat diffusivity spreads the heat away from the reflecting surface and reduces the risk of thermal damage. However, in short-pulsed laser machines, this concept becomes irrelevant because at shorter timescales, Fourier's heat conduction model is no longer valid and the absorbed energy cannot reach the bulk material [9]. The proposed solution to this issue was the multi-layer coating of the surface where the lattice of the material in the lower layer, chromium in this case, has a higher electron-lattice transfer rate than gold and would convert most of the absorbed radiation energy by free electrons into lattice energy and away from the reflective surface.

This study was one of the early simulations of short pulsed laser interactions with metals and its outcome was further improvement of the modified Fourier heat conduction equation for this purpose. A Hyperbolic Two Step (HTS) equation was proposed to represent a molecular system of high intensity irradiation energy transfer with a short duration. HTS is the current method for simulating high intensity, femtosecond pulse laser interaction with metals where it collapses into a PTS model if the pulse duration is increased beyond electron relaxation time (longer than 10 picoseconds). HOS applies to lower intensities and in the case of slow heating processes it will simplify to POS. Figure 1 shows the interaction during the heat transfer process with the interrelationship between these models outlined by Marla et al [4] and Qiu et al [8].

In 1996, Chichkov et al [10] conducted a semi-empirical study investigating the effects of pulse duration from nanoseconds to picoseconds and femtoseconds, focusing on the edge quality of the drilled holes and the burr on the surface after the ablation. For the mathematical modelling, they followed the same principles explained above and chose models based on thermalisation and relaxation times. However, no calculation results were presented in this work to validate the derived formulae. Nonetheless, they experimented with several different metals as well as a thick silicon target while tuning the laser fluence and pulse frequency to achieve identical drilled depths and their observations suggested that in femtosecond material processing, the liquid phase is absent and the heat conduction to the surrounding areas are negligible. They also concluded that the vapor and plasma phases are very rapid while the femtosecond laser pulses produce sharp and well-defined patterns, making them a promising tool for precise material processing. Work in this direction is still evolving and recent research efforts are taking advantage of these analytical approaches [11].

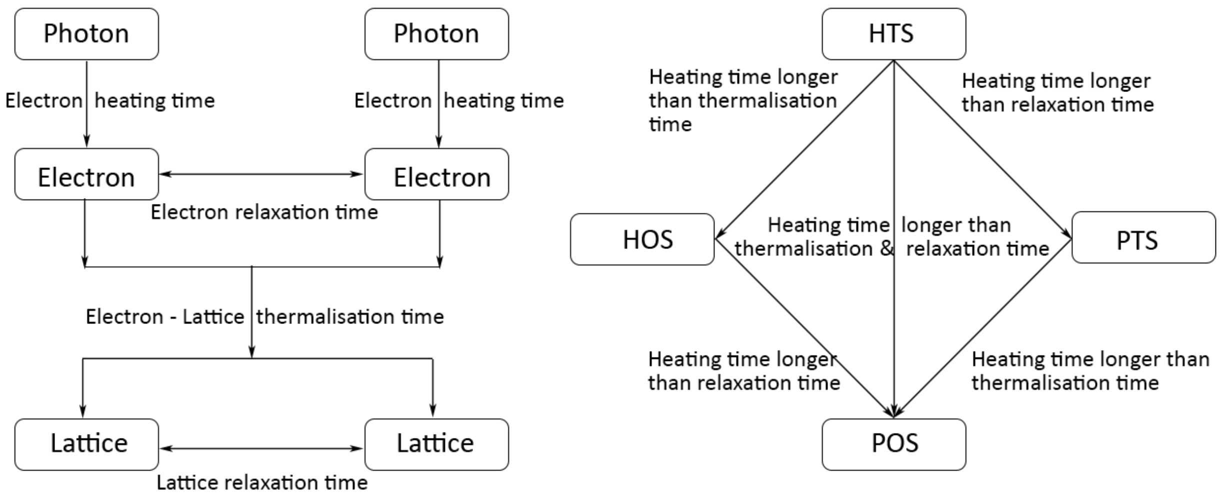

Fig.1. Microscopic interaction during the heat transfer process and the interrelationship between heat transfer models [4][8]. (HTS: Hyperbolic Two Stage, HOS: Hyperbolic One Stage, PTS: Parabolic Two Stage, POS: Parabolic One Stage).

3. Physical mechanisms during ultrashort pulsed laser ablation

In 2001, Ye et al [12] compared picosecond and femtosecond pulsed laser ablation of titanium in vacuum using time-of-flight and emission spectroscopy. They measured the velocities of ions ejecting from the surface during the ablation process and compared their crater depths. Their measurements indicated that the ejecta of 80 femtosecond lasers at λ =800 nm has more kinetic energy than particles ablated by the picosecond pulse at the same repetition rate and wavelength. They argued that this result agrees with molecular dynamics simulation results obtained by Zhigilei et al [13] which concluded that ejecting velocity is linearly proportional to the atoms' initial position in the skin layer of the substrate and can be described by modified Maxwell-Boltzmann distribution to account for the range of stream velocities. Ye et al [7] further suggested that radiation absorption in metals involves bound electrons in addition to free electrons excited by Inverse Bremsstrahlung (IB) absorption. In other words, photoionisation excites bound electrons to the free electron level and multiphoton ionisation is more dominant at relatively higher laser intensities. They also observed that ejection cluster size is proportional to the laser fluence, and the crater made by 1000 pulses of the femtosecond laser is cleaner and smoother than the same number of pulses of picosecond laser which, makes femtosecond lasers more advantageous for ultra-precision machining. This study emphasised that for picosecond and longer laser pulses, the ablation depth is dictated by thermal diffusion whereas, for femtosecond laser pulses, optical penetration depth and electronic heat conduction are the dominating factors.

These studies investigated mechanisms that are important to Pulsed Laser Deposition (PLD) where the ablated nanoparticles can be used for various applications. Ablation rate and cluster size were closely monitored for improving the process and an identified impediment here was the plasma plume formed above the surface that interacts with the incoming laser beam and reduces its effectivity. However, ultra-precision manufacturing is concerned with the ablated surface and the penultimate process for this purpose is known as direct laser writing. Hirayama and Obara [14] conducted a series of ablation experiments on gold, silver, copper and iron surfaces using a Ti:sapphire femtosecond laser. They reported the formation of an amorphous metal layer on the area ablated by a femtosecond laser. They claimed that the residual beam energy that does not contribute to the ablation process, forms a thin layer of melt phase that is abruptly cooled down before recrystallisation. They also referenced a simulation work that seemingly has reported the formation of the melted layer at the ablation spot. However, no further elaboration was made on the contributing factors to this phenomenon and possible remedies if the amorphous metallic layer is an undesirable outcome. These experiments were carried out in air at room temperature.

Later in 2004, Rethfeld et al [15] reiterated that the processes involved in the ultrashort pulsed laser ablation are temporally separated and they can each be studied individually. They concluded that the excitation of the solid occurs during the time that laser is incident on the target. Then subject to the excitation strength, melting takes place in the picosecond regime. Laser properties like intensity and wavelength as well as the material characteristics determine the state of the material after irradiation.

Around the same time, Feng et al [16] used a femtosecond Ti:sapphire laser to drill microholes in a single crystal superalloy with and without plasma-sprayed thermal barrier coating. These microscale holes were utilised for air cooling aero-engines. Failure of these engines can often have a catastrophic impact and the focus of their work was to analyse any possible defects that can result from laser drilling. Their examination by scanning electron microscopy indicated that there was no melting, heat-affected zones, recast layers, or microcracks around the machining area and the only form of damage reported was a laser induced plastically deformed layer of approximately 5 microns when the fluence was around or slightly above the ablation threshold. These experiments were conducted in air at room temperature and their results near the ablation threshold fluence seem to echo the outcome of Hirayama and Obara's [14] study mentioned earlier. The superalloys used in these experiments have an ablation threshold of 203 ± 20 mJ/cm^2 and the laser fluence used was in the range of 0.1 J/cm^2 to 160 J/cm^2. This study concluded that femtosecond micromachining is a promising method for consistent production with minimal damage of high-volume manufacturing microscale features in multi-layered turbine aerofoil and combustor materials.

In 2005, Grojo and Hermann [17] investigated femtosecond laser ablation of titanium, zirconium and hafnium by means of time-of-flight observation and fast imaging. They directly observed the ablated plasma plumes in nanosecond time and discovered that the kinetic energy of the nanoparticles in the plume is independent of the laser fluence. They concluded that the energy absorbed by electrons must be redistributed within the electronic subsystem before reaching the lattice. Based on the characteristics of the plasma plume in their experiments, they suggested that electrostatic effects such as Coulomb explosion or space-charge acceleration can be ruled out from the mechanisms involved in ultrashort pulsed laser ablation because they would lead to an increase in kinetic energy of ablated particles. Another key observation in this work was the relationship between the size of ablated clusters and the atomic mass. They reported that larger clusters were ablated in materials with lighter atoms.

4. Development of molecular dynamics (MD) simulations

Modelling has a long lineage and is a convenient way to understand processes which are not readily amenable to the naked eye or low-cost experimental apparatus. Modelling in recent times has turned into a computational design and prediction tool as well as being an investigative tool [18]. In 1982, Cleveland et al [19] carried out pioneering work on laser-annealing using MD simulations which followed with many other works including that of Yamashita et al [20] in 2006 where examples of ultrashort pulsed laser ablation simulation using MD was presented for the first-time using a two-temperature model. Yamashita et al [20] borrowed the two-temperature model developed in the preceding decades and incorporated it into the conventional molecular dynamics, calling it "modified molecular dynamics" (MMD). In addition to the assumption that the heat transport mechanism is wave-like in nature, they proposed that the electronic heat capacity and conductivity being a function of temperature is one of the important factors to be incorporated in the prediction of laser-matter interactions. Nevertheless, the implementation of these variables as a function of temperature was challenging and they simplified the simulations by assuming them as fixed values. Their simulation results suggested that the heat transport mechanism in materials (aluminium in their case) is dominated by electron heat conduction in the early stage and within a few picoseconds, some temperature variations were observed. They attributed the presence of temperature gradients to the thermal shock wave that propagated until the equilibrium was established and the lattice vibrations dominated the energy transport at longer timescales.

Following the rapid advancement and broader accessibility to faster and more sophisticated computers in the early 2000s, MD simulations became preferable to gain insights into the rapidly unfolding chain of events during the ultrashort pulsed laser interaction with materials. The advantages of MD compared to the finite elements method (FE) are very well documented [21]. Therefore, MD studies attracted a lot of research interest and helped advancing the field to its current state. In 2006, Chen et al [22] introduced the electron drifting velocity and electron kinetic pressure terms to the equation of energy balance in the electronic subsystem to better account for the effects of the electric field. By comparing the phenomenological two-temperature model with the more recently developed semiclassical two-temperature model, through numerical analysis of ablating gold films, they suggested that the thermal response is different in each model and the damage fluence threshold obtained from the semiclassical simulations are more in agreement with the experimental data. This correction to the energy transfer equation is currently adopted by simulation software such as LAMMPS (https://lammps.sandia.gov).

5. Applications of ultrashort pulsed laser ablation

Around 2007, after almost two decades of exploring the physics of the energy transfer in a short timescale, fabrication of functional surfaces with ultrashort pulse lasers and in general, the applications of ultrashort pulsed laser ablation started to be tested for commercial use. Experiments of Tsukamoto et al [23] with a femtosecond laser attempting to fabricate cone-like protrusions on titanium plate to be used in clinical orthopaedics' became the early-stage demonstrators. With an average fluence of 0.75 J/cm^2 (ablation fluence for pure titanium is around 0.1021 J/cm^2

[24]) and varied pulse frequencies, they managed to create periodic microstructures on the surface. They reported that the alignment of the features was parallel to the laser polarisation vector and their size increases by forming bridging structures between adjacent protrusions. It is interesting to note that a paper published by Vorobyev and Guo [25] in the same year, claimed that they performed the first femtosecond laser surface treatment of titanium for biomedical implants. This subtle declaration of rivalry highlights the potential impact of the successful execution of this process. Unlike the previously mentioned work, Vorobyev and Guo [25] kept the laser fluence below the ablation threshold (kept around 0.067 J/cm^2) and created periodic patterns of about 20 nanometres. This method offers some control over the produced periodicity and feature sizes, and it is now known as Laser Induced Periodic Surface Structuring (LIPSS).

Nayak et al [26] explored the influence of ambient gases in ultrashort pulsed laser treatment of titanium and silicon. They reported the fabrication of a regular arrangement of sharp nanostructures on cone-shaped microstructures (hierarchical structures) in a vacuum and 100 mbar helium ambient conditions for the first time. Their experiments suggested that during the early irradiation of silicon, the periodicity of the ripples was around the wavelength of the laser beam. Unlike what was observed in titanium treatment, this periodicity gets altered during the pillar formation. Another observation indicated that features were sharper when produced in a vacuum and the height of pillars favoured lower ambient gas pressure. The exact reason for this behaviour remains unknown and the authors concluded that it warrants further investigation. Computer simulations can be a useful tool to gain some insight into these rapid structure formation events. In a keynote paper, Bruzzone et al [27] argued the importance of engineered surfaces, linking the mechanical and optical properties of surfaces to high impact applications, including bioengineering. However, they concluded that the metrology of engineered surfaces is also an important area for supporting the industrial diffusion of new applications. This is one of the reasons that computer simulations that inherently provide accurate metrology insights are of utmost importance to the field of nano structures and engineered surfaces.

In 2008, Lin et al [28] conducted a series of first-principle calculations on eight representative metals, Al, Cu, Ag, Au, Ni, Pt, W and Ti at strong nonequilibrium conditions of varied temperatures between electron and phonon. They investigated the assumptions of linear temperature dependency of the electron heat capacity and constant electron-phonon coupling factor used in calculations to improve the accuracy of computer simulations. Their results indicated that the strength of the electron-phonon coupling varies with temperature fluctuations and not all materials respond the same way to the changes. In Al, Au, Ag, Cu and W, the coupling became stronger when the electron temperature was increased, Ni and Pt showed a decrease in the coupling strength and titanium exhibited nonmonotonic behaviour. It was argued that at high electron temperatures, electrons below Fermi level are excited and their contribution to the electron-phonon energy exchange dictates their addition to the quantitative analysis of this process. However, experimental evidence suggested that in low laser intensities, assuming a constant electron-phonon coupling factor does not have a significant impact on the outcome of two-temperature calculations. Based on these ab-initio calculations, they believed that it is inappropriate to assume that the temperature dependency of electron heat capacity is linear. However, the solution for incorporating these findings in MD simulations was not put forward.

In the following year, 2009, Lewis and Perez [29] presented MD simulation results, illustrating what they believed to be the mechanisms involved in ultrashort pulsed laser ablation of strongly absorbing materials. They summarised the mechanisms as a function of absorbed energy to spallation, phase explosion, fragmentation and vaporisation. The fragmentation mechanism was introduced here as "disintegration of a homogeneous material into clusters under the action of large strain rates". They also identified that spallation is unique to femtosecond pulses and phase explosion does not happen under ultrashort pulses. Based on this classification, a laser beam with varied intensity distribution (gaussian distribution) would initiate a mix of these mechanisms simultaneously depending on the effective amount of energy absorbed in the target or in other words, the local energy density received from the laser pulse. These simulations were performed on a fictitious 2D material with reduced potentials (Lennard-Jones), however, they claimed that essentially, their explanation covers the thermal regime and understanding the non-thermal regime is the challenging objective ahead.

Around the same time, Zhigilei et al [30] studied the effects of varying fluence of ultrashort pulsed lasers on the ablation mechanisms of nickel through atomistic simulations. Based on their work, a steep increase in ablation rate in experimental observations indicated the transition from normal vaporisation to phase explosion. They explained that a rapid energy deposition during a short pulse irradiation leads to a sharp temperature rise and may generate compressive stresses. Then it converts into tensile stresses while interacting with the free surfaces. When tensile stresses become sufficiently large, they caused mechanical fracture in the solid material. The relaxation of these laser induced stresses resulted in the ejection of large solid particles or liquid droplets, which is known as spallation or photomechanical ablation. Interestingly, they claimed that their simulations show an abrupt transition from spallation to phase explosion in contrast to the previously mentioned study. This work suggested that melting, spallation and phase explosion occur simultaneously and they are closely intertwined while their ratio is determined by the laser fluence. They emphasised that the transition from one dominant mechanism to another is taking place abruptly at certain laser fluences. Electron-phonon coupling factor in these calculations were assumed to be constant and authors claimed that most results reported in their study was obtained before the temperature dependency of this variable was known. Nevertheless, they believed that this assumption only affected some quantitative predictions such as values of fluence threshold for melting, spallation etc, and the qualitative physical picture is still valid.

By 2010, molecular dynamics simulations were widely used to model ultrashort pulsed laser ablation. Inogamov et al [31] reported that electron collisions have a minor effect on light absorption in solid aluminium and by employing MD simulations they were able to investigate kinetics of aluminium crystal melting between 0 and 4 picoseconds to explain the behaviour of their probes. Seydoux-Guillaume et al [32] also utilised MD simulations to observe shock wave propagation into the bulk of monazite, studying the formation of defects. They reported that mechanical defects caused by ultrashort pulsed laser irradiation dominat thermal ones. Fang et al [33] also performed series of calculations based on two-temperature model, varying fluence of ultrashort pulsed laser to identify effects of temperature gradient on electronic properties. The authors argued that electronic collision plays a key role in the process, affecting the electronic properties. They concluded that their results are in agreement with experimental data and reiterated that electron heat capacity, thermal conductivity, absorption coefficient and absorptivity depends on temperature and must not be neglected. They incorporated their proposition into the two-temperature model and presented an updated model in their paper.

Leitz et al [34] also argued that phase explosion is one of the dominat mechanisms involved in ultrashort pulsed laser ablation. They presented empirical data comparing the results of ablated substrate in micro, nano, pico and femtosecond laser pulse durations. They also stated from the manufacturing point of view that depending on the laser pulse duration, there are tradeoffs between precision and efficiency meaning ablation rate is higher in longer pulses while shorter pulses produce higher resolution illustrated in their results. Figure 2 shows the scanning electron microscopic images that illustrates their conclusion.

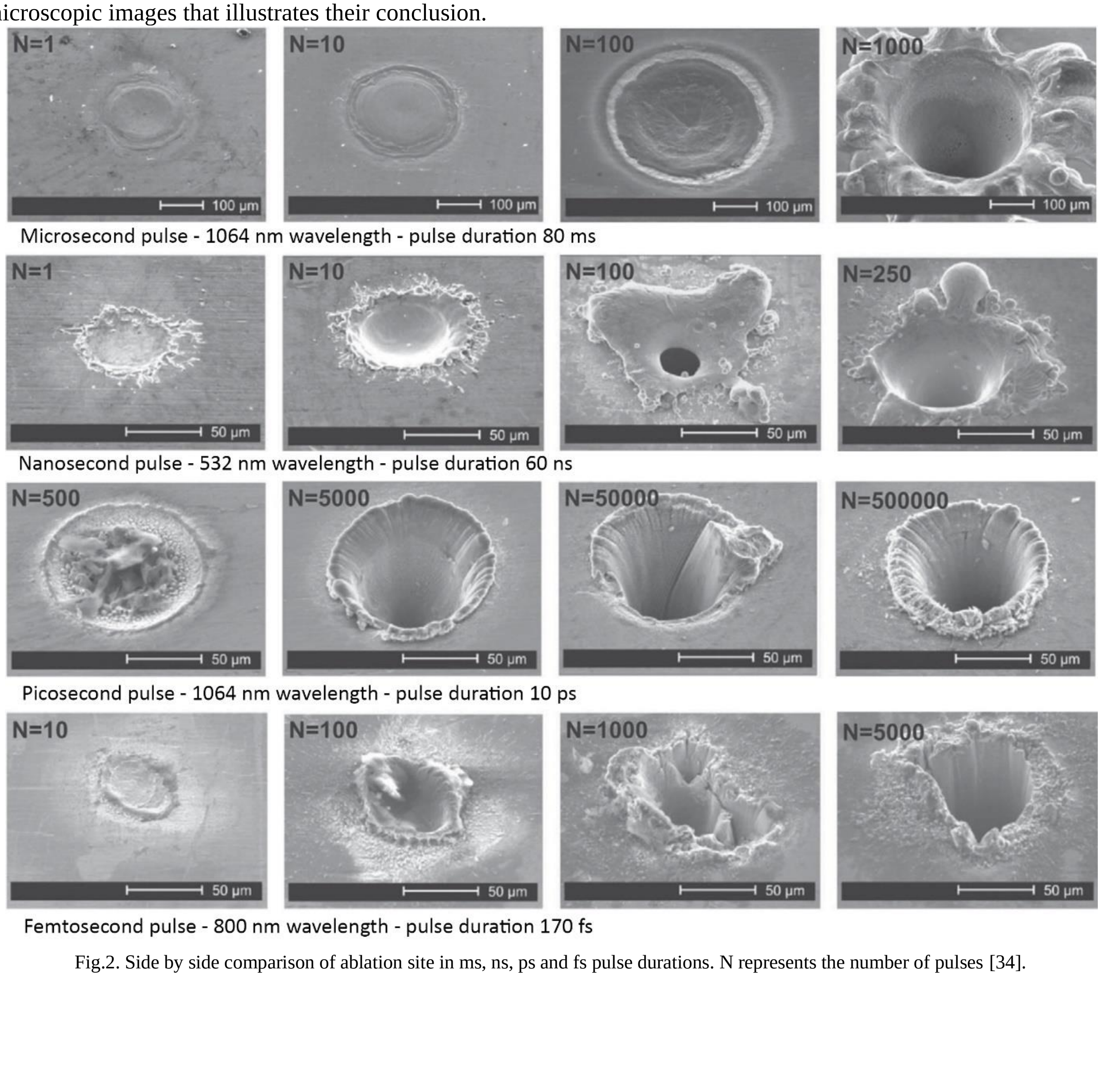

Fig.2. Side by side comparison of ablation site in ms, ns, ps and fs pulse durations. N represents the number of pulses [34].

Building on the continuous endeavours of scientific community to better understand the physics of the ultrashort pulsed laser ablation, more real-life applications of this technology began to emerge around the early 2010s. Improvements in laser generating machines, accurate beam delivery and placement, the production of modern materials used in optics as well as broader accessibility to cheaper laser machines were also important contributing factors. Fadeeva et al [35] successfully fabricated a superhydrophobic surface on titanium to explore bacteriostatic effect of the hierarchical nanostructures they created. They employed a self-structuring technique induced by femtosecond laser (LIPSS) achieving a level of superhydrophobicity. However, the fabricated geometries were not optimised for repelling bacteria and they reported an intermittent repulsion where some species of tested microorganisms managed to colonise the surface. They claimed that mechanically attaching bacteria to the surface could have added to the failure of observing the desired effect. In another research, targeting the ablation of live tissues for clinical surgeries, Nicolodelli et al [36] investigated femtosecond laser ablation of hard tissues, dental and femur samples, to analyse the morphology characteristics of the ablated surface. In order to accurately determine the conditions of the ablation threshold, they were challenged to incorporate the Gaussian distribution of laser intensity into their calculations when the direct derivation from the beam spot size produced inaccurate values. They concluded that the morphology of the resulting cavity after femtosecond pulses is strongly affected by the number of pulses. Even in relatively high fluences, they did not observe a secondary effect of mechanical and thermal damage. They argued that femtosecond lasers are appropriate tools to cut, remove and modify surfaces of human dentin and femur bones with no collateral damage.

6. Manufacturing techniques utilising ultrashort pulsed laser ablation

The possible impact of ultrashort pulsed laser processing of materials gave rise to a number of creative techniques of utilising its unique capabilities. One such example was the use of nonlinear effect (Kerr self-focusing) of high-power pulses in guiding the laser beam through filamentation. Valenzuela et al [37] compared ablation of steel and titanium with this technique against sharply focused laser pulses. They concluded that using short focal length lenses are superior to filaments if well-defined and precise cut is desired, however, the ability of filaments to ablate materials over a longer distance (10-100 metres) with very minimal beam divergence can be essential for some applications. Another example of creative use of ultrashort pulsed laser properties was developed by Vorobyev and Guo [38] in 2015. With an undisclosed technique they fabricated hierarchical nanostructures on titanium, platinum and brass surfaces exhibiting extraordinary mechanical and optical properties. Figure 3 is a sequence of their demonstration video clip showing superhydrophobicity of one of these surfaces with a tilt angle of 8 degrees. They claimed that these multifunctional surfaces can self-clean as well as exhibiting all the desired functionalities attributed to superhydrophobicity such as anti-corrosion, anti-icing, anti-biofouling etc. Their broadband light absorption capabilities were also enhanced dramatically.

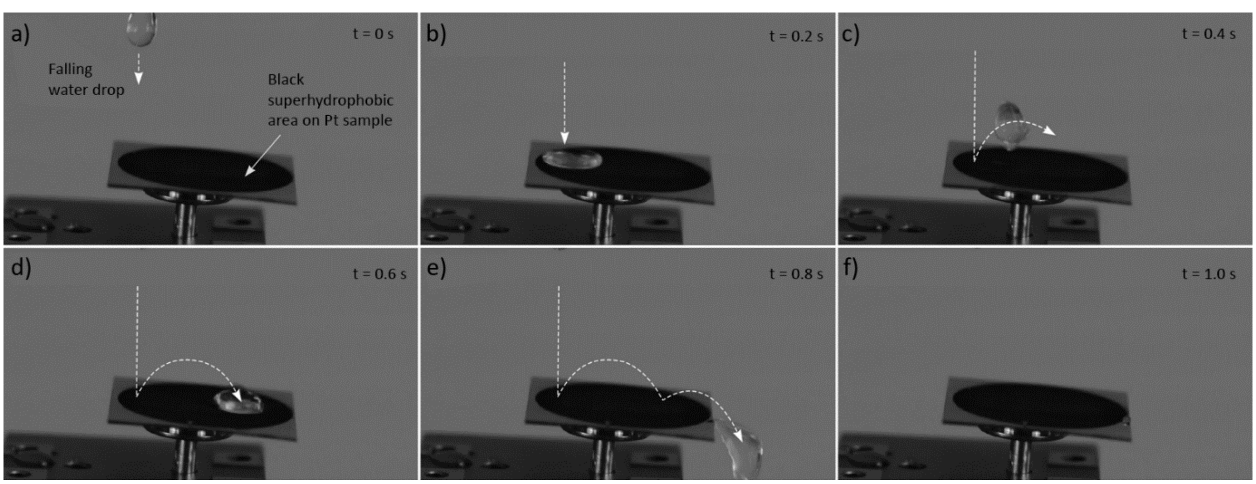

Fig.3. Video clips showing the superhydrophobicity of Pt sample [38].

In recent years, there was also active research in exploring the effects of ablated particles and plasma plume on the surroundings in the immediate aftermath of the ablation, contributing to the growth of knowledge in this matter. Zhang et al [39] studied the propagation of shockwaves resulting from the ablation process. They identified two types of cylindrical waves created by air breakdown (ejection of electrons from the surface and plasma expansion) and phase explosion. In their experiments of ablating aluminium with a femtosecond laser, they recorded the exact formation and propagation time of shockwaves in picoseconds and nanoseconds, concluding that the expansion of the plume is in a cylindrical shape as opposed to previously reported hemispherical geometry.

In another effort to correct and improve the theoretical framework, Rethfeld et al [40] published a review paper in 2017, complementing their work in 2004. They highlighted several issues arising from assumptions made in modelling ultrashort pulsed laser ablation processes. First, they argued that the concept of temperature in nonequilibrium conditions is not accurate because, inherently temperature is restricted to equilibrium energy distribution. Then, they highlighted the possible problem with the use of classical Fourier law. They believed Fourier's law holds true as long as timescales are greater than mean free path of energy carriers (electrons). They also pointed out that lattice parameter changes during the phase transition. Another questionable assumption in their opinion is the equilibrium conditions for electronic subsystem. They claimed that electrons also can exist in nonequilibrium conditions in relation to other electrons and consequently, a number of different electron-phonon coupling factors can exist simultaneously. They also claimed that ultrashort laser beam penetration depth could exceed the expected optical penetration depth due to ballistic movement of electrons, in contrast to Gamaly and Rode's claim [41] that, energy transport by electrons in ultrafast laser pulse ablation processes should not be treated as ballistic. Nevertheless, Rethfeld et al [40] did not provide an indication of the extent of impact these issues have on the outcome of the current simulations.

Suslova and Hassanein [42] also argued that it is inaccurate to assume constant optical properties of material throughout simulations. Inspired by the model of Lin et al [28] which included the electron density of states to account for effects of electrons below the Fermi level in high intensity pulses, they developed a two-temperature code for two-dimensional materials based on the collision theory, called FEMTO-2D. Expecting a more accurate representation of temperature dependency of electronic properties with this new approach, they explored reflectivity and absorptivity of metals as a factor of electronic temperature. They modelled a Gaussian beam profile in their simulation to analyse the behaviour of a simultaneous temperature gradient in materials and their results showed a steady rise in reflectivity of nickel at the beginning of the pulse followed by a sharp decrease, like in other metals they explored. The reason for such trend was unclear and they speculated that it might be a result of rapid change in material plasma frequency compared to effective collision frequency. By simulating a range of laser fluences, they also concluded that the optical penetration depth changes by the temperature fluctuations, however, it does not have a significant effect on the simulations.

In 2018, Žemaitis et al [43] introduced a new model representing the ablation of a rectangular cavity. They investigated multi-pulse ablation. In their work, they incorporated the decrease in ablation threshold and saturation of the ablation depth which were observed with the increase of number of pulses per spot. They also considered Gaussian distribution of laser intensity, helping them mathematically represent the relationship between peak laser fluence in the centre of the beam and the diameter of the created crater. They proposed that the most efficient ablation is achieved when the peak fluence is e^2 times higher than the threshold fluence. Abdelmalek et al [44] also studied ablation of copper using a burst of femtosecond laser pulses. They kept the interval between pulses shorter than electron relaxation time and varied the laser fluence and number of pulses. They suggested that increasing the number pulses enhances the vaporisation rate compared to a single pulse of the same accumulated fluence and therefore, rapid pulses of femtosecond laser irradiation can be utilised to ablate metals more cleanly and more efficiently.

7. Recent developments in ultrashort pulsed laser ablation research

Dong et al [45] analysed effects of moving laser focus in ultrashort multi-pulse laser ablation. The target application for this work was helical drilling of metals and they simulated a laser focus moving downwards with a constant speed. They also reiterated that pulse intervals play an important role in this method suggesting that higher electron and lattice temperatures were achieved with a higher pulse frequency even though the ablation depth is not increased significantly and eventually, it saturates at a maximum value. They also argued that there is an optimum velocity for the downward movement of the laser focus where fast and slow movements respectively cause negative and positive defocusing. They concluded that for their test specimen, copper, the maximum efficiency was achieved while the defocusing was kept under 50 nm. Nevertheless, they acknowledged that ablation depth for copper in their calculations did not agree with previously published values in the literature. In another effort to improve simulations of nonequilibrium systems in 2019, Ullah and Ponga [46] introduced a new approach where they replaced Fourier's heat conduction equation by Fokker-Planck equation to capture local electronic temperature. They claimed that this method can reproduce complex geometries and since it does not require auxiliary mesh, it is easily coupled with classical MD codes. They announced that they integrated their method with LAMMPS code, however, the superiority of their proposal over the current method remains to be reviewed.

Michalek et al [47] investigated ultrafast laser structuring of freeform surfaces in 2020. LIPSS is current popular surface structuring method with laser machines which, has matured enough for some commercial applications. Their study was trying to tackle some of the limitations regarding the freeform surface structuring in order to expand LIPSS applications. LIPSS takes advantage of the Gaussian beam profile to create periodic features by aligning the high and low intensity areas of the beam in a controlled way while scanning the target surface. It is known that laser fluence directly affects ripple depth while beam incident angle and the wavelength impacts periodicity, and the polarisation vector influences feature orientation. However, in scanning a freeform surface, the beam incident angle and focal offset distance are the most prominent factors. With theoretical modelling, they predicted the material response in relation to the laser parameters. By manipulating the process configuration, they proposed an optimum setup that was further validated by experiment. However, simulations suggested that groove formation requires a hydrodynamic effect or pre-existing subwavelength sized ripples in addition to laser beam, as argued by Stratakis et al [48]. In a technical explanation, Bonse et al [49] claimed that electromagnetic scattering plays a major role in LIPSS while there is a debate whether Marangoni or Rayleigh-Taylor instability is dominating when the matter is reorganising itself in the hydrodynamic relaxation stage. Tsibidis et al [50] introduced the crystal orientations and the interpulse delay time to the contributing factors affecting surface pattern formation, arguing that these variables influence the carrier dynamics and the thermal response of the target material.

The overall pattern seen in the literature related to this matter from the early days of developing laser technology can be classified into a few overall trends. Until the early 1990s, the main focus in the scientific community was to create more powerful and shorter pulsed lasers while observing the light-matter interactions in extreme conditions. After reaching femtosecond regime with very high intensity power delivery, the focus was shifted towards better understanding the physics of these interactions to harness their potential, until mid-2000s. It worth noting that majority of the studies were primarily based on experiments with the mathematical modelling used to explain the processes. Around early 2000s, more powerful computers entered the scene, providing an atomistic tool to gain a better insight into these interactions by visualising the proposed theories. From around 2005, with enough growth in the knowledge of its physics and wider access to laser machines and metrology equipment, development of simulating frameworks and applications of ultrashort pulsed laser-matter interaction were accelerated. It is evident from the literature that computer simulations created a large momentum in growing the field and contributed to the identification of useful applications, until around the year 2015. The discovery of some high impact applications of this technology attracted plenty of interest and funds for further research in this area. The sheer volume of scientific publications in recent years is the proof of this statement and as Bonse et al [51] put it "…investigation [of surface structuring with ultrashort pulsed lasers] has developed into a scientific evergreen".

Ijaola et al [52] recently reviewed the methods of fabricating functional biosurfaces, focusing on the effects of ambient conditions in surfaces treated by laser. They highlighted a wettability transition from superhydrophilic to superhydrophobic after exposing the surface to air and organic contaminants. They concluded that the presence of carbon on a treated surface of titanium increased its hydrophobicity. Mukharamova et al [53] used experimental techniques (IR pump – Xray probing) to study the influence of periodic plasma produced by femtosecond laser on the process, known as skin effect, and the consequence of propagating shockwaves on surface structures. They found that shockwave propagation is faster in periodic structures. These shockwaves, however, destroyed the periodic formation of structures for a short time before transforming into non-destructive acoustic waves. Skin effect is also a known effect that interacts with the incoming laser beam, reducing its effectiveness. However, there is no proposed solution in the literature so far, for removing the plasma plume from the vicinity of the beam spot zone to improve the efficiency of the process. Inogamov et al [54] recently revisited the heat propagation in material, suggesting that heat is transferred with a supersonic velocity from the skin layer (the optical penetration depth) into the bulk. In their simulations they investigated the effects of water as the ambient medium. They explained the dependency of the expansion of a heated target in ablation process confined by a dense water medium and compared it to the identical process in vacuum. Their simulation results showed that the maximum pressure exists in the medium-target interface, longer than the duration which the maximum laser intensity is present.

Mazhukin et al [55] suggested that a strong electric field is created at the incident spot area following the ultrafast irradiation due to electronic pressure of collectivised electrons near the surface. They claimed that the main deviation between double electric layer (metal surface) approach and the drift-diffusion calculations lies between the interface of electron pressure gradient and the electric field in each technique. They argued that electron pressure is the main reason behind phase explosion in nonequilibrium regime as opposed to phase change in equilibrium condition. They used arbitrary non-stationary coordinate system instead of the common Euler and Lagrangian method, believing that it is useful to calculate discontinuous solutions like shockwaves. In a recent study, Bucă et al [56] introduced a new apprach to simulations claiming that it is computationaly more cost-effective than the currently employed version. The common approach to simulate femtosecond laser matter interactions is to use quantum theories describing the energy absorption followed by solving the heat equations with classical Fourier's heat equation. In this paper, authors explored an opposite approach, treating the initial interaction classically and solving the heat equation with quantic operators (Cattaneo-Vernote equation). Their simulations were performed by tweaking coupling factor and relaxation time and they concluded that lower coupling factor and/or higher electron relaxation time results in a higher electron temperature due to slower heat transfer to the lattice. They simulated the ablation of a golden surface and their results does not violate any previously believed facts, however, the possible advantages/disadvantages and specific applications of their model remains to be reviewed.

With constantly evolving simulation frameworks, researchers are taking advantage of MD simulations to verify or complete previous theories and assumptions. Xie et al [57] simulated ablation of a copper film and investigated the role of pulse duration in the process, verifying that lattice temperature affects electron-phonon coupling factor. They observed that pulses of 100 fs, 200 fs and 500 fs respectively, disintegrate the target surface, melt and vibrate it and only vibrate the surface. Wang et al [58] also employed MD simulations to study ablation of titanium film with pulses of 100 fs, 300 fs and 500 fs, concluding that spallation occurs more quickly when the pulse length is shortened. Their results also suggested that electron-lattice coupling time is affected by the pulse length while the equilibrium temperature remains the same. As a result, for shorter pulses, more energy was absorbed by the electrons at the bottom of the titanium film. Pan et al [59] used MD simulations to verify the change in absorptivity of molybdenum disulfide as a function of the laser fluence in their experiments. Zhang et al [60] used this tool to study femtosecond laser ablation of nickel-aluminium alloy for drilling the air cooling holes on turbine blades. Their modelling of a Gaussian beam profile revealed that (for their chosen fluence) phase explosion was only occurring at the centre of the spot with the highest intensity and a mix of photomechanical spallation and melting was happening in other regions.

In some of the recent experimental studies, Furukawa et al [61] explored double pulse ablation (DP), focusing on priming the material response after the first irradiation (seed pulse) to improve the ablation rate. Ablation rate is known to be directly related to the laser fluence and this work is exploring the increased absorption rather than the accumulated heat of multiple pulses. However, they detected "ablation suppression" around 100 picosecond delay time between pulses and claimed that it was a transient phenomenon occurring around that time only. They compared titanium with platinum because the electron cooling time is an order of magnitude greater for platinum than for titanium. In theory, the ablation suppression in platinum should be observed at a later time than in titanium due to the delay in diffusivity, which was not the case in this study. This work indicated that the seed pulse changes the surface properties beyond just increasing its temperature and the surface reflectivity is increased for the period that ablation is suppressed. Stratakis et al [48] evaluated the surface texturing techniques including LIPSS, double pulse irradiation, multi-beam interference patterning and more. They suggested that high precision surface manufacturing with optimal control over the shape, size and distribution of the structures can be achievable by direct laser writing.

8. Conclusion

Ultra-precision manufacturing and material processing and manipulation of materials with nanoscale precision requires a high degree of control over the laser ablation process. By achieving more deterministic results that is financially justifiable, this technology can become accessible to wider manufacturing capabilities which, in turn, will accelerate the innovation in this field leading to new inventions and creation of more high impact applications. As concluded by many other researchers discussed in this paper, the biggest impediment to the transition of direct laser writing from science laboratories to the manufacturing sites is the undesired resolidification of materials in the beam affected zone (also known as thermal damage) and it requires further research. This effect is projected when the ideal required resolution is in nanoscale. Better understanding of the mechanisms involved in ultrashort pulsed laser-matter interactions would equip scientists to push the boundaries and provide a better insight into this process. MD simulations is a promising tool for further investigating the complex process of ultrashort pulsed laser ablation and many other processes while this tool itself is evolving and improving rapidly. MD simulations of ultrafast energy transfer in materials induced by an external source is a less developed aspect of the current available software and as argued in this paper, it plays a crucial role in the advancement of the ultrashort pulsed laser ablation technology and consequently, a more deterministic ultra-precision manufacturing.

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