Evaporating laminar microjets for studies of rapidly evolving structural transformations in supercooled liquids

Robert E. Grisenti, Anton Kalinin, Claudia Goy & Alexander Schottelius

To cite this article: Robert E. Grisenti, Anton Kalinin, Claudia Goy & Alexander Schottelius (2018) Evaporating laminar microjets for studies of rapidly evolving structural transformations in supercooled liquids, Advances in Physics: X, 3:1, 1418183, DOI: 10.1080/23746149.2017.1418183

To link to this article: https://doi.org/10.1080/23746149.2017.1418183

© 2018 The Author(s). Published by Informa UK Limited, trading as Taylor & Francis Group

Published online: 20 Jan 2018.

Article views: 327

View Crossmark data
Evaporating laminar microjets for studies of rapidly evolving structural transformations in supercooled liquids

Robert E. Grisenti\textsuperscript{a,b}, Anton Kalinin\textsuperscript{a,b}, Claudia Goy\textsuperscript{a} and Alexander Schottelius\textsuperscript{a}

\textsuperscript{a}Institut für Kernphysik, J. W. Goethe-Universität, Frankfurt am Main, Germany;\textsuperscript{b}GSI - Helmholtzzentrum für Schwerionenforschung, Darmstadt, Germany

ABSTRACT
The investigation of non-equilibrium phase transformations, such as crystallization, in supercooled liquids – below their melting point but still liquid – is of fundamental importance in condensed matter physics. However, accessing experimentally the details of such fast structural changes proves challenging. Here, we show that microscopic laminar jets in vacuum offer a powerful tool for novel studies of supercooled liquids on previously inaccessible time scales in a class of atomic and molecular model systems that have so far remained inaccessible because of the lack of adequate experimental approaches. The use of liquid jets represents a remarkable opportunity to significantly advance our knowledge of topics that are relevant to interdisciplinary fields such as atmospheric physics and material science.

ARTICLE HISTORY
Received 2 October 2017
Accepted 1 December 2017

KEYWORDS
Liquid jets; supercooled liquids; crystallization; Raman and X-ray scattering

PACS
47.15.Uv % Laminar jets; 64.70.pm % Liquids; 64.60. My % Metastable phases; 64.70.dg % Crystallization of specific substances; 61.05.cf % X-ray scattering (including small-angle scattering); 33.20.Fb % Raman and Rayleigh spectra (including optical scattering)

CONTACT
Robert E. Grisenti grisenti@atom.uni-frankfurt.de

© 2018 The Author(s). Published by Informa UK Limited, trading as Taylor & Francis Group.
This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.
Introduction

It is possible to cool a liquid below its melting point into a metastable region in which the crystal has a lower free energy than the liquid. The fate of a supercooled liquid ultimately depends on the interplay between cooling rate and nucleation time [1]. Usually, a liquid-to-solid first-order phase transition occurs, the dynamics of which is governed by homogeneous crystal nucleation [2, 3] followed by crystal growth [4–6]. If crystallization can be avoided by cooling the liquid at sufficiently high rates, an amorphous solid (a glass) may form [7–9]. A fundamental understanding of the structural changes occurring in supercooled liquids represents an open problem in modern condensed matter physics relevant to a broad range of interdisciplinary research fields. For instance, ice homogeneous nucleation in supercooled water and aqueous solutions [10, 11] is one of the mechanisms responsible for ice cloud formation with a huge impact on the microphysics of earth’s atmosphere [12, 13]. In a different context, rapid solidification processes in supercooled metallic liquids provide the route for the realization of a wide range of materials with different structural, chemical and physical properties [14].

Detailed experimental studies of structural transformations in supercooled liquids are challenging. They have so far been largely based on the use of colloidal suspensions [15–17], as the characteristic time scales in the atomic and molecular counterparts are typically orders of magnitude shorter. In addition, the presence of possible heterogeneous nucleation sites, such as container walls and impurities in the liquid, often prevent achieving temperatures significantly below the melting point. Recent advances in electromagnetic and electrostatic levitation techniques have allowed partly overcoming the above experimental challenges [18–20], but this approach is limited to the study of metallic liquids cooled at moderate rates of ~1 K s⁻¹ with a time resolution of ~0.1 s. In the present review, we describe a concept based on the generation of a microscopic liquid jet in a vacuum environment that allows the study of non-equilibrium structural transformations in a number of unique model systems, from the simplest supercooled quantum and classical liquids to complex liquids such as supercooled water, which were so far inaccessible because of extreme experimental conditions.

Evaporating microscopic liquid jets

A microscopic jet forms by forcing a pressurized liquid through a micrometre-sized circular aperture (‘nozzle’) [21, 22]. If the flow is laminar, the liquid ejects as a continuous cylindrical filament before it eventually breaks up spontaneously at a certain critical distance downstream of the aperture into a directed stream of spherical droplets (Figure 1(a)). In general, stable laminar liquid flow occurs for low Reynolds’ numbers, \( Re = \nu d / \sigma < 2300 \), where \( \nu \) is the flow velocity, \( \rho \) is the liquid’s density, \( d \) is the nozzle’s diameter, and \( \sigma \) is the surface tension. Jet formation and stability depend also on additional factors, such as the nozzle shape and...
inner-wall smoothness. In this respect, the use of silica glass capillary nozzles presenting a smoothly converging inner channel can greatly reduce cavitation- and wall friction-induced turbulent flow. The jet instability responsible for droplet formation was first described by Rayleigh \cite{23}, whose name it now bears. The Rayleigh instability can be triggered by an externally applied excitation at a frequency close to the intrinsic Rayleigh frequency \cite{21, 22}. In this case, the triggered breakup delivers a highly periodic stream of perfectly uniform droplets, as shown in Figure 1(b), whose diameter can be fine-tuned from below $2d$ to over $2.5d$ by varying the trigger frequency.

When the liquid jet is injected into vacuum, it rapidly cools by surface evaporation \cite{24} until it undergoes a liquid-to-solid phase transition driven by the onset of homogeneous crystal nucleation. The clean, continuously replenishing vacuum-exposed jet surface completely suppresses possible heterogeneous nucleation sites. The formation of droplets in Figure 1(a) and (b) indicates that the jet (in this case water) is still liquid at the Rayleigh breakup point, and freezing will occur further downstream \cite{25, 26}. By contrast, Figure 1(c) shows an example of a cryogenic jet generated by forcing liquid hydrogen at 16 K. Here, the jet freezes well before Rayleigh breakup can take place, causing the formation of a continuous, several millimetres long solid filament \cite{27}. Solid formation in Figure 1(c) can be identified as a slight change in the jet optical features. Rapid jet freezing usually occurs for liquids, such as hydrogen and argon, which are characterized by a high vapour pressure at the triple point, resulting in evaporative cooling rates as high as $10^8 \text{ K s}^{-1}$. A jet of a low-volatility liquid, such as water, cools at a smaller maximum rate of ~$10^6 \text{ K s}^{-1}$ \cite{24}. The kinetics of the jet freezing can be probed \textit{in situ}, e.g. by light-scattering techniques. The most crucial feature here is

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1}
\caption{(a) Ambient temperature liquid water jet ejecting in vacuum from a 3.2-μm-diameter glass capillary orifice. The Rayleigh breakup into droplets is clearly visible in the image. (b) The same water jet triggered at 834.7 kHz to generate a periodic stream of perfectly uniform ≈6.6-μm-diameter water droplets. (c) Liquid hydrogen jet generated from a 5-μm-diameter glass capillary nozzle at a source temperature of 15 K.}
\end{figure}
the correspondence between the distance along the jet propagation direction (e.g. \( z \)) and time according to \( t = z/v \). The linear dimension of the sampled jet volume thus ultimately sets the observation time scale of the experiment, which for typical jet velocities of \( v \approx 100 \text{ m s}^{-1} \) can become as short as 100 ns [27].

The liquid jet’s lifetime \( \tau \) in the supercooled state scales with the inverse of the sampled volume \( V \) according to \( \tau \approx (\Gamma V)^{-1} \), where \( \Gamma \) is rate of homogeneous nucleation [11]. Accordingly, the challenge is to generate jets with a size as small as possible in order to reach the highest possible degree of supercooling. This challenge is not only related to the manufacturing of small apertures with the required accuracy, but also to the ability to reliably filter impurities and clean the overall injection system in order to avoid nozzle clogging. Clogging is the most serious issue that arises in the generation of microscopic liquid jets from sub-10-\( \mu \text{m} \)-diameter orifices [28]. One possible approach to circumvent this difficulty has been demonstrated recently for water jets by Deponte et al. [29], and is based on a liquid injection system that employs a so-called gas dynamic virtual nozzle (GDVN). In a GDVN, the continuous liquid water stream that emerges from a large, primary capillary orifice (with a diameter typically greater than 20 \( \mu \text{m} \)) is dynamically compressed by a pressurized co-flowing gas sheath before passing into vacuum through a secondary aperture. This dynamic compression shrinks the jet diameter, thereby allowing the generation of smaller droplets. In principle, a GDVN shows promise for reaching the sub-1-\( \mu \text{m} \)-droplet size [30], which would allow reaching the extremely deep supercooled regime. One major drawback of this approach is the interaction of the droplets with the co-expanding gas, which may eventually cause droplet collision and coalescence phenomena, resulting in a stream of droplets with a non-uniform size distribution.

**Hydrogen and deuterium: from the simplest quantum molecular fluids to the realization of a quantum binary mixture**

The experimental feasibility of the concept outlined above was recently demonstrated for liquid hydrogen [27, 31]. Because quantum effects dominate its bulk properties [32, 33], hydrogen represents a particularly fascinating model system with respect to the possibility of supercooling it significantly below its melting temperature of 13.8 K. The hydrogen molecule can assume only even or odd values of the rotational quantum number \( J \). At temperatures below 20 K only the \( J = 0 \) or \( J = 1 \) rotational states are populated [32]. The state characterized by \( J = 0 \) is known as para-hydrogen (\( \text{pH}_2 \)), whereas that characterized by \( J = 1 \) is known as ortho-hydrogen (\( \text{oH}_2 \)). Theoretical studies have shown that quantum effects add a further degree of complexity to the behaviour of supercooled liquids, leading to many exotic phenomena [34–37]. In particular, because of the spherical symmetry of the \( J = 0 \) rotational ground state, \( \text{pH}_2 \) was suggested as the next promising candidate, in addition to the helium isotopes, which might exhibit superfluid behaviour [34]. So far, indirect evidence for superfluidity comes only
from spectroscopic studies of tiny pH₂ clusters [38, 39]. With a predicted superfluid transition temperature of ≈3 K [40], the question on the possible existence of superfluid pH₂ is clearly connected to the extent to which bulk liquid pH₂ can be supercooled before crystallization becomes unavoidable [41].

The behaviour of deeply supercooled pH₂ was investigated by Raman spectroscopy of a liquid jet [27], as shown schematically in Figure 2(a). Figure 2(b) shows Raman spectra of the vibrational $Q_1(0)$ transition recorded as a function of the distance from the orifice. The band at 4151.5 cm⁻¹ is associated with the liquid phase, and its shift to lower wave numbers is a direct manifestation of the cooling.

**Figure 2.** (a) Schematic view of the experimental setup for Raman spectroscopy of liquid pH₂ jets. Raman scattering was excited by a single mode cw Ar⁺ laser beam (green) focused down to a diameter of 14 μm onto the jet (blue). The Raman signal (red) was collected at 90° with respect to both the laser beam and the jet axis, and then focused onto the 20 μm wide entrance slit of a high-resolution grating spectrometer equipped with a nitrogen cooled CCD detector. (b) Selected Raman spectra of the vibrational $Q_1(0)$ transition recorded as a function of the distance from the orifice (vertical scale) between $z = 0.03$ and 2.03 mm. (c) Jet temperature determined from the spectra in (b). The green circles represent the average filament temperature, whereas the red and blue circles show the highest and lowest temperatures, respectively. The solid lines are numerical results based on the Knudsen theory of the cooling process. The dashed line marks the melting point of bulk liquid pH₂. (d) Solid fraction extracted from the spectra in (b). Source: Figure adapted from Ref. [27].
of the \( \text{pH}_2 \) jet. Here, the dependence of the fundamental molecular vibrational stretching band on temperature \([42]\) makes Raman spectroscopy a non-invasive ‘thermometer’ for the experimental determination of the temperature of molecular liquid jets. The asymmetric, broad shape of the Raman band results from the filament’s radial temperature gradient, and the observed narrowing at longer propagation times reflects the temperature equilibration in the filament interior by heat transfer \([27]\). The temperature of the jet obtained from the analysis of the Raman bands is shown in Figure 2(c), where the red and blue circles represent the ‘hottest’ and ‘coldest’ regions in the jet’s inner core and outer surface, respectively, whereas the average liquid temperature is shown as green symbols. The solid lines in Figure 2(c) are numerical calculations of the jet temperature obtained on the basis of the Knudsen kinetic theory of evaporative cooling \([24, 25, 27]\). The good agreement with the experimental data provides conclusive evidence for the achieved deep supercooling of a macroscopic fraction of the liquid \( \text{pH}_2 \) jet. The steep increase in the jet temperature observed for \( z > 0.9 \) mm coincides with the onset of crystallization, as evidenced by the appearance in the Raman spectra of the vibrational line at 4149.6 cm\(^{-1}\) (Figure 2(b)) associated with the solid phase. From the temporal evolution of the solid fraction (Figure 2(d)) it was possible to determine a rate of linear crystal growth of \( \approx 33 \) cm s\(^{-1}\) \([27]\). The crystal growth rate is the fundamental physical quantity governing the kinetics of crystallization \([4]\), and is in general difficult to measure in the deeply supercooled regime with sufficient accuracy \([5, 6]\).

Besides providing a unique test bed for phenomenological models of crystal growth \([4, 27]\), the above results on the rapid crystallization of supercooled \( \text{pH}_2 \) set a severe constraint on the possibility of experimentally observing superfluid behaviour in liquid hydrogen. While the achieved lowest temperature of \( \approx 9 \) K (Figure 2(c)) is a remarkable 30\% below the melting point, it is still far away from the predicted superfluid transition temperature \([40]\). Reaching a deeper supercooling would certainly require higher cooling rates than those resulting from the simple evaporation of a liquid jet in vacuum. Evaporative cooling is intrinsically constrained by the exponential drop in vapour pressure of the liquid with a decreasing temperature. One proposal considered forced jet cooling in ambient gas as a promising strategy to overcome this experimental challenge \([43]\). Conduction and convection of thermal energy from the gas to the liquid jet can, in fact, strongly enhance the cooling process. It was shown that by a combination of smaller jet size and appropriate choice of the species and temperature of the ambient gas it would be possible to increase the rate of cooling of a liquid \( \text{pH}_2 \) jet by more than one order of magnitude, in principle sufficiently enough to avoid crystallization and to reach temperatures very close to the expected superfluid transition \([43]\). Future experiments will hopefully show whether such an approach can be successful in achieving a deeper supercooling to eventually allow the long sought observation of superfluidity in bulk liquid \( \text{pH}_2 \).
Mixing pure pH$_2$ with the $J = 0$ ortho-deuterium (oD$_2$) isotope allows moving over the next stage of complexity in the study of supercooled quantum liquids. From a very general point of view, experiments and theory show that supercooled binary liquid mixtures display a much richer behaviour than the single components [44–52]. For instance, mixing two species is a well-established route to increase the glass-forming ability of supercooled liquids [46, 51, 52]. The study of isotopic supercooled pH$_2$-oD$_2$ mixtures can be further motivated by recent simulation results on a model binary liquid, which suggest that quantum effects can stabilize the metastable liquid phase to produce a quantum glass state, whereas the classical analogue would rapidly crystallize [36]. In this sense, recent investigations of supercooled pH$_2$-oD$_2$ binary liquids by the liquid jet technique sketched in Figure 2(a) provided first experimental evidence for the large impact of the system's quantum nature on the crystallization process under highly non-equilibrium conditions [53]. The main experimental results as obtained from solid fraction curves like that shown in Figure 2(d) are summarized in Figure 3, evidencing a striking behaviour. Starting with the pure pH$_2$ system, the crystal growth rate rapidly decreases with an increasing amount of oD$_2$, becoming up to three times smaller in the 50% oD$_2$ mixture, to then increase again for the oD$_2$-enriched mixtures [53]. This observation is surprising because the intermolecular potential is isotope independent [32], with no evidence of a phase separation at equilibrium. Classical phenomenological models of crystal growth [4] also fail to explain the experimental data [53]. We note here that this dependence on composition of the crystal growth rate is in many respects similar to that found in simulations of classical binary mixtures of hard-spheres with different sizes [48]. Path-integral Monte Carlo simulations of supercooled pH$_2$-oD$_2$ mixtures [53] revealed that these similarities are not fortuitous: quantum fluctuations increase the effective radius of the pH$_2$ and oD$_2$ molecules, yet the strength of this effect differs for pH$_2$ and oD$_2$ because of their different masses, resulting in a particle size ratio different.

**Figure 3.** Rates of crystal growth for jets of pH$_2$-oD$_2$ liquid mixtures determined for the pH$_2$ (blue symbols) and oD$_2$ (red symbols) components. The plotted data indicate relative values with respect to the growth rate of 33 cm s$^{-1}$ measured for the pure pH$_2$ jet. Source: Figure adapted from Ref. [53].
Further studies on Raman scattering from liquid jets formed by mixing either pH$_2$ or oD$_2$ with small amounts of the much heavier neon atoms [54] offered a particularly suggestive trend: the extent of the observed slowdown of crystal growth appears to be directly correlated with the ratio of the effective sizes of the impurity and solvent particles. Thus, while these results on supercooled binary quantum mixtures hint at some form of geometric frustration of crystal growth, establishing this correlation at the microscopic level remains a formidable task. Further insights in this regard might come from the study of supercooled classical atomic liquids, which are the subject of the next section.

**Argon & Co.: the archetypical classical model systems**

Classical rare gases, such as argon and krypton, are characterized by weak van der Waals interatomic interactions that can be well described by isotropic Lennard-Jones (LJ) potentials. For this reason, they served over the last decades as the conceptually most simple and fundamental model systems for numerical investigations of crystallization in supercooled liquids [55–60]. These simulations provided a detailed picture of the early stages of crystallization, well illustrating the complexity of the liquid-to-solid phase transition even for such simple systems. For instance, the crystal was found to grow from predominantly face-centred cubic (fcc) critical nuclei with random hexagonal close-packed (hcp) domains [59, 60]. The fcc and hcp structures differ by their stacking patterns of the close-packed triangular layers – ABCABC for fcc, and ABAB for hcp, where A, B and C refer to the three possible positions of the layers on top of each other. Experimentally, rare-gas liquids crystallize into the fcc crystal structure, though small amounts of the metastable hcp polymorph in the bulk at ambient pressure were occasionally observed in rare-gas solids either grown by gas deposition at very low temperatures [61], or frozen from the liquid close to the melting point [62]. The observation of hcp regions likely stems from the very small energy difference between the fcc and hcp states, and only the inclusion of zero-point vibrational effects makes the fcc structure more favourable [63].

A recent X-ray scattering study employing liquid jets offered the intriguing possibility to investigate the kinetics of crystallization in supercooled rare-gas liquids. In these experiments, performed at the P03 end station of the PETRA III synchrotron [64], X rays scattered from 5-μm-diameter liquid argon and krypton jets (Figure 4(a)) were detected in the wide-angle X-ray scattering (WAXS) geometry covering the 10°–50° 2Θ angular range. The mapping of the time axis onto the distance from the orifice allowed obtaining detailed snapshots of the rapid structural evolution towards the final crystal form proceeding at rates faster than 1 m s$^{-1}$. The broad, isotropic diffraction ring visible in the two-dimensional WAXS pattern of Figure 4(b) uniquely defines the liquid state. At larger distances from the orifice, i.e. with a decreasing temperature, a series of sharp diffraction rings are superimposed on the liquid diffraction ring (Figure 4(c)), until they
become the dominant feature for the fully crystallized filament (Figure 4(d)). The observed diffraction rings actually resemble a virtual X-ray powder diffraction pattern. This is a consequence of the 300 s long acquisition time, during which up to $\sim 10^9$ individual 'samples' crossed the focus of the X-ray beam. The five diffraction rings seen in Figure 4(d) represent the most intense reflections of the fcc crystalline structure, but a more careful analysis reveals additional features. This can be explicitly seen in the radially integrated WAXS patterns shown in Figure 4(e) and (f) for argon and krypton, respectively. The small peaks at $q = 19.1 \text{ nm}^{-1}$ (Figure 4(e)) and $17.8 \text{ nm}^{-1}$ (Figure 4(f)), where $q = 4\pi \sin(\Theta)/\lambda$ represents the change in wavenumber as radiation of wavelength $\lambda$ is scattered, can be identified with the (100) hcp reflection. The observation of macroscopic regions with close-packed structure in both argon and krypton filaments demonstrates that the hcp structure is an essential feature of the kinetic pathway of crystal growth in
supercooled rare-gas liquids, and not merely a transient phase of the early stages of crystallization as it may be expected on the basis of Ostwald’s rule of stages [65].

The above results highlight just one of the insights that can potentially be gained from the investigation of jets of rare-gas liquids. For instance, the nearly ideal miscibility of condensed argon and krypton in the full range of compositions [66, 67], as well as the about 8% difference between the argon and krypton atomic radii make liquid mixtures of these two elements ideal candidates to further investigate the effects of composition and particle size ratio on the crystallization of supercooled binary liquids. A preliminary analysis of recent experimental data on X-ray scattering from liquid jets of mixtures of argon and krypton confirms the trend observed with pH$_2$-oD$_2$ jets (Figure 3), thereby addressing the important question on the general validity of the observed dependence of the crystal growth rate on composition in a binary mixture. We anticipate here that on-going classical molecular dynamics simulations of crystallization of supercooled liquid mixtures of argon and krypton reproduce the main experimental findings. The hope is that such simulations will help elucidate the microscopic mechanism responsible for this striking behaviour.

**Supercooled water: the most anomalous liquid**

Water is an extraordinarily complex liquid whose behaviour is very unusual with respect to that of most other liquids [68]. Probably one of the most well-known anomalous properties of water is the density maximum at 4 °C, a fact that had a huge impact on the evolution and preservation of life on earth. Water’s anomalies include also an increase upon cooling of the magnitude of thermodynamic functions such as the heat capacity and the isothermal compressibility, suggesting that these quantities may diverge in the supercooled liquid region around 228 K [69]. A further peculiar aspect of water is that it can exist in two different amorphous forms – the low- and high-density amorphous ices – with a density difference of about 20% and a first-order phase transition between them [70, 71]. Several scenarios have been proposed to explain the anomalous thermodynamic behaviour of water [72]. One popular interpretation postulates the existence of a hypothetical first order liquid–liquid phase transition between two metastable forms of liquid water [73], a high-density liquid, with a disordered local structure, and a low-density liquid (LDL), with an enhanced tetrahedral local structure [74]. The liquid–liquid transition line eventually terminates at a critical point in the supercooled region, at which the density difference between the two forms of water vanishes and the response functions diverge. While the results of computer simulation studies depend on the chosen molecular model of water [75, 76], rapid ice formation has so far precluded the experimental investigation of supercooled bulk water at temperatures below 235 K [77].

Recently, a liquid jet in vacuum was successfully employed to investigate the structure and crystallization of deeply supercooled water [25, 78–81]. In particular,
Sellberg et al. [25] obtained the scattering structure factor $S(q)$ by probing supercooled water droplets with ultrashort pulses from an X-ray free-electron laser (XFEL). In these experiments, a liquid injection system based on a GDVN [29] was employed to generate single nominal ≈9 and ≈12 μm-diameter water droplets in the estimated 227 to 250 K temperature range [25]. The observed evolution of the shape of $S(q)$ with temperature was considered evidence for a pronounced, yet continuous transition from ambient water to LDL proceeding well into the deeply supercooled region [25]. Further analysis of the experimental data suggested that water’s second critical point, if it exists, must lie below 200 K at high pressure [80], thereby excluding the alternative, singularity-free scenario, in which the critical point should instead occur at negative pressure [72, 77]. Since single-shot X-ray measurements allow distinguishing individual droplets that are either completely liquid or contain ice, it was also possible to determine the ice nucleation rate as a function of the temperature [79]. The precise temperature dependence of the ice nucleation rate is of fundamental importance for a better understanding of cloud formation in the upper layers of earth’s atmosphere, and thus, e.g. for the development of more reliable climate models [13]. Despite their large uncertainties, the reported nucleation rates were significantly smaller than those expected on the basis of extrapolations of results from previous experiments [82]. These deviations were interpreted in terms of a crossover in the behaviour of the temperature dependence of water’s diffusivity from non-Arrhenius to Arrhenius [79].

In an alternative scenario, a crystallization regime in which water freezing is first governed by ice growth would make a reliable determination of the ice nucleation rate questionable [83].

In the experiments by Sellberg et al. [25] the jet temperature calibration was based on the Knudsen kinetic theory. We have shown above (compare Figure 2(c)) that this model provides a reasonable estimate of the temperature of a liquid jet evaporating in vacuum [27]. However, it also strongly relies on the knowledge of a number of relevant experimental parameters, such as the initial droplet diameter in the case of a water jet, which are often very difficult to determine with sufficient accuracy. Given the great extent to which structural changes in water occur for small variations of the temperature in the deeply supercooled region [74], a more reliable estimation of the droplet temperature is mandatory in order to substantiate the interpretation of experimental data obtained in this only hard-to-access regime. Goy et al. [26] recently tackled this problem by obtaining a very accurate and precise measure of the size of very small evaporating water droplets in a triggered jet probed by Raman light scattering. To determine the droplet diameter, they exploited the observation in the Raman spectra of morphology-dependent optical resonances, so-called whispering gallery modes [84], as shown in Figure 5(a). Superimposed on the O–H stretching bands are up to five narrow peaks resulting from a resonant enhancement of the Raman scattering for specific values of the droplet radius-to-wavelength ratio. The resonances are described in the framework of the Mie-Debye light scattering theory [85], which shows that the
observed shift of the resonance peaks (Figure 5(a)) is directly related to a decrease in the droplet diameter with an increasing distance from the nozzle. Accordingly, the droplet diameter could be directly determined from the Raman shifts of the resonance peaks [26]. The obtained values, shown as filled circles in Figure 5(b), then strongly constrained the Knudsen evaporative cooling model calculation, shown as thick solid line in Figure 5(b). From the corresponding temperature curve plotted in Figure 5(c), a lowest liquid droplet temperature of 230.6 ± 0.6 K was thus inferred at about 28.4 mm from the nozzle, the distance at which a small fraction of the about 6-μm-diameter water droplets were still liquid before they froze to ice [26]. These results unambiguously demonstrate that water’s deeply supercooled region can be uniquely probed by employing a micrometre-sized water jet in a vacuum.

Conclusions and perspectives

The goal of the present review was to highlight the enormous potential offered by the use of fast evaporating laminar jets to the study of structural transformations in deeply supercooled liquids. Of course, the spectrum of systems that would greatly benefit from this approach is by far not limited to the few, though unique, examples presented here. For instance, bulk aqueous solutions have been used in the last decades as model systems in a number of studies focused on liquid dynamics and
phase transitions [86]. The addition of small amounts of salt solutes to neat water would allow reaching even lower jet temperatures, with the possibility to provide new hints on the possible existence of a liquid-liquid transition in water [87]. At increasing molecular complexity, it is worth mentioning future investigations of jets of hydrogen-bond liquids such as methanol or other common alcohols. They would offer a novel route to the study of the interplay between crystallization and glass formation in a class of prototypical glass-formers that exhibit peculiar, yet not fully understood timescales for diffusional and orientational motion [88].

Future investigations of liquid jets will also certainly further benefit from the combination with XFELs. Details on the structure and shape of the tiny crystallites that form through thermal fluctuations in the non-equilibrium supercooled liquid remain invariably blurred in diffraction experiments at traditional X-ray synchrotrons (see Figure 4). By contrast, during the very short duration of the X-ray laser pulse the liquid jet (and, consequently, the crystallization kinetics) appears frozen in space (i.e. time), while the high photon flux allows one to obtain a statistically significant diffraction image in one shot. While ultrashort X-ray laser pulses were recently employed to probe liquid water jets [25, 81], their time structure and photon flux, accompanied by the possibility to focus such x-rays down to a nanometre-sized spot, can be further exploited to access the earliest stages of crystal nucleation and growth in a large variety of supercooled atomic and molecular liquids. The XFEL properties would also allow performing experiments based on the use of liquid jets that go beyond simple scattering. For example, the development of novel higher order photon correlation schemes [89, 90] could allow exploring the structural dynamics on previously inaccessible time scales. It would thus be possible to study the evolution of structural short-range order, providing unprecedented insights into the pathways through which a supercooled liquid evolve to the solid state. Such experiments promise to help guide any future refinements of theories of crystal nucleation and growth in supercooled liquids, and thus to substantially contribute to the improvement of our understanding of the crystallization process.

Acknowledgements

We acknowledge financial support from the Bundesmisterium für Bildung und Forschung and the Deutsche Forschungsgemeinschaft. Part of this research was carried out in the Laboratory of Molecular Fluid Dynamics at the Instituto de Estructura de la Materia, CSIC, Madrid, Spain and at the P03 end station of the PETRA III synchrotron, DESY, Hamburg, Germany.

Disclosure statement

No potential conflict of interest was reported by the authors.
Funding

This work was supported by the Bundesmisterium für Bildung und Forschung [project numbers 05K13RF5 and 05K16RF2], and the Deutsche Forschungsgemeinschaft [project number 593962].

References

[1] A. Cavagna, Phys. Rep. 476 (2009) p.51.
[2] S. Jungblut and C. Dellago, Eur. Phys. J. E 39 (2016) p.77.
[3] G.C. Sosso, J. Chen, S.J. Cox, M. Fitzner, P. Pedevilla, A. Zen and A. Michaelides, Chem. Rev. 116 (2016) p.7078.
[4] K.A. Jackson, Inter. Sci. 10 (2002) p.159.
[5] J. Orava and A.L. Greer, J. Chem. Phys. 140 (2014) p.214504.
[6] J. Orava, A.L. Greer and J. Non-Cryst. Solids 451 (2016) p.94.
[7] P.G. Debenedetti and F.H. Stillinger, Nature 410 (2001) p.259.
[8] M.D. Ediger and P. Harrowell, J. Chem. Phys. 137 (2012) p.080901.
[9] C.P. Royall and S.R. Williams, Phys. Rep. 560 (2015) p.1.
[10] J.B. Murray, S.L. Broadley, T.W. Wilson, S.J. Bull, R.H. Wills, H.K. Christenson and E.J. Murray, Phys. Chem. Chem. Phys. 12 (2010) p.10380.
[11] B. Riechers, F. Wittbracht, A. Hütten and T. Koop, Phys. Chem. Chem. Phys. 15 (2013) p.5873.
[12] D. Rosenfeld and W.L. Woodley, Nature 405 (2000) p.440.
[13] B.J. Murray, D. O’Sullivan, J.D. Atkinson and M.E. Webb, Chem. Soc. Rev. 41 (2012) p.6519.
[14] F. Spaepen, Science 235 (1987) p.1010.
[15] U. Gasser, J. Phys.: Condens. Matter 21 (2009) p.203101.
[16] T. Palberg, J. Phys.: Condens. Matter 26 (2014) p.333101.
[17] J. Russo and H. Tanaka, MRS Bull. 41 (2016) p.369.
[18] R. Willneckers, D.M. Herlach and B. Feuerbacher, Phys. Rev. Lett. 62 (1989) p.2702.
[19] K.F. Kelton, G.W. Lee, A.K. Gangopadhyay, R.W. Hyers, T.J. Rathz, J.R. Rogers, M.B. Robinson and D.S. Robinson, Phys. Rev. Lett. 90 (2003) p.195504.
[20] D.M. Herlach and P.K. Galenko, Mater. Sci. Eng. A 449 (2007) p.34.
[21] J. Eggers, Rev. Mod. Phys. 69 (1997) p.865.
[22] J. Eggers and E. Villermaux, Rep. Prog. Phys. 71 (2008) p.036601.
[23] Lord Rayleigh, Nature 44 (1891) p.249.
[24] M. Faubel, S. Schlemmer and J.P. Tocnnies, Z. Phys. D 10 (1988) p.269.
[25] J.A. Sellberg, C. Huang, T.A. McQueen, N.D. Loh, H. Laksmono, D. Schlesinger, R.G. Sierra, D. Nordlund, C.Y. Hampton, D. Starodub, D.P. DePonte, M. Beve, C. Chen, A.V. Martin, A. Barty, K.T. Wikfeldt, T.M. Weiss, C. Caronna, J. Feldkamp, L.B. Skinner, M.M. Seibert, M. Messerschmidt, G.J. Williams, S. Boutet, L.G.M. Pettersson, M.J. Bogan and A. Nilsson, Nature 510 (2014) p.381.
[26] C. Goy, M.A.C. Potenza, S. Dedera, M. Tomut, E. Guillerm, A. Kalinin, K.-O. Voss, A. Schottelius, N. Petridis, A. Prosvetov, G. Tejeda, J.M. Fernández, C. Trautmann, F. Caupin, U. Glaumacher and R.E. Grisenti, Phys. Rev. Lett. 120 (2018) p.015501.
[27] M. Kühnel, J.M. Fernández, G. Tejeda, A. Kalinin, S. Montero and R.E. Grisenti, Phys. Rev. Lett. 106 (2011) p.245301.
[28] U. Weierstall, R.B. Doak, J.C.H. Spence, D. Starodub, D. Shapiro, P. Kennedy, J. Warner, G.G. Hembree, P. Fromme and H.N. Chapman, Exp. Fluids 44 (2008) p.675.
[29] D.P. DePonte, U. Weierstall, K. Schmidt, J. Warner, D. Starodub, J.C.H. Spence and R.B. Doak, J. Phys. D 41 (2008) p.195505.
[30] D.P. DePonte, R.B. Doak, M. Hunter, Z. Liu, U. Weierstall and J.C.H. Spence, Micron 40 (2009) p.507.
[31] J.M. Fernández, M. Kühnel, G. Tejeda, A. Kalinin, R.E. Grisenti, S. Montero and A.I.P. Conf, Proc. 1501 (2012) p.1296.
[32] I.F. Silvera, Rev. Mod. Phys. 52 (1980) p.393.
[33] V.L. Ginzburg and A.A. Sobyanin, JETP Lett. 15 (1972) p.242.
[34] E. Rabani and D.R. Reichman, Annu. Rev. Phys. Chem. 56 (2005) p.157.
[35] T.E. Markland, J.A. Morrone, B.J. Berne, K. Miyazaki, E. Rabani and D.R. Reichman, Nature Phys. 7 (2011) p.134.
[36] S. Grebenev, B. Sartakov, J.P. Toennies and A.F. Vilesov, Science 289 (2000) p.1532.
[37] H.J. Maris, G.M. Seidel and T.E. Huber, J. Low Temp. Phys. 51 (1983) p.471.
[38] O.N. Osychenko, R. Rota and J. Boronat, Phys. Rev. B 85 (2012) p.224513.
[39] P. Schwerdtfeger, N. Gaston, R.P. Krawczyk, R. Tonner and G.E. Moyano, Phys. Rev. B 73 (2006) p.064112.
[40] A. Buffet, A. Rothkirch, R. Döhrmann, V. Körstgens, M.M. Abul Kashem, J. Perlich, G. Herzog, M. Schwartzkopf, R. Gehrke, P. Müller-Buschbaum and S.V. Roth, J. Synchrotron Rad. 19 (2012) p.647.
[65] W. Ostwald and Z. Phys, Chem. 22 (1897) p.289.
[66] R. Heastie, Nature 176 (1955) p.748.
[67] S.F. Barreiros, J.C.G. Calado, P. Clancy, M. Nunes da Ponte and W.B. Streett, J. Chem. Phys. 86 (1982) p.1722.
[68] P.G. Debenedetti, J. Phys.: Condens. Matter 15 (2003) p.R1669.
[69] R.J. Speedy and C.A. Angell, J. Chem. Phys. 65 (1976) p.851.
[70] C.A. Angell, Science 319 (2008) p.582.
[71] K. Amann-Winkel, R. Böhmer, F. Fujara, C. Gainaru, B. Geil and T. Lörrting, Rev. Mod. Phys. 88 (2016) p.011002.
[72] P. Gallo, K. Amann-Winkel, C.A. Angell, M.A. Anisimov, F. Caupin, C. Chakravarty, E. Lascaris, T. Loerting, A.Z. Panagiotopoulos, J. Russo, J.A. Sellberg, H.E. Stanley, H. Tanaka, C. Vega, L. Xu and L.G.M. Pettersson, Chem. Rev. 116 (2016) p.7463.
[73] P.H. Poole, F.G. Sciortino, U. Essmann and H.E. Stanley, Nature 360 (1992) p.324.
[74] A. Nilsson and G.M. Pettersson, Nat. Commun. 6 (2015) p.8998.
[75] E. Moore and V. Molinero, Nature 479 (2011) p.506.
[76] J.C. Palmer, F. Martelli, Y. Liu, R. Car, A.Z. Panagiotopoulos and P.G. Debenedetti, Nature 510 (2014) p.385.
[77] F. Caupin and J. Non-Cryst, Solids 407 (2015) p.441.
[78] J.A. Sellberg, T.A. McQueen, H. Laksmono, S. Schreck, M. Beye, D.P. DePonte, B. Kennedy, D. Nordlund, R.G. Sierra, D. Schlesinger, T. Tokushima, I. Zhovtobriukh, S. Eckert, V.H. Segtnan, H. Ogasawara, K. Kubicek, S. Teichert, U. Bergmann, G.L. Dakovski, W.F. Schlotter, Y. Harada, M.J. Bogan, P. Wernet, A. Föhlisch, L.G.M. Pettersson and A. Nilsson, J. Chem. Phys. 142 (2015) p.044505.
[79] H. Laksmono, T.A. McQueen, J.A. Sellberg, N.D. Loh, C. Huang, D. Schlesinger, R.G. Sierra, C.Y. Hampton, D. Nordlund, M. Beye, A.V. Martin, A. Barty, M.M. Seibert, M. Messerschmidt, G.J. Williams, S. Boutet, K. Amann-Winkel, T. Loerting, L.G.M. Pettersson, M.J. Bogan and A. Nilsson, J. Phys. Chem. Lett. 6 (2015) p.2826.
[80] H. Pathak, J.C. Palmer, D. Schlesinger, K.T. Wikfeldt, J.A. Sellberg, L.G.M. Pettersson and A. Nilsson, J. Chem. Phys. 145 (2016) p.134507.
[81] A. Nilsson, S. Schreck, F. Perakis and L.G.M. Pettersson, Adv. Phys. X 1 (2016) p.226.
[82] T. Koop and B.J. Murray, J. Chem. Phys. 145 (2016) p.211915.
[83] J.R. Espinosa, C. Navarro, E. Sanz, C. Valeriani and C. Vega, J. Chem. Phys. 145 (2016) p.211922.
[84] R. Symes, R.M. Sayer and J.P. Reid, Phys. Chem. Chem. Phys. 6 (2004) p.474.
[85] P. Chýlek, J.T. Kiehl and M.K.W. Ko, Phys. Rev. A 18 (1978) p.2229.
[86] A.C. Angell, Chem. Rev. 102 (2002) p.2627.
[87] K.-I. Murata and H. Tanaka, Nat. Comm. 4 (2013) p.2844.
[88] A.C. Angell and J. Non-Cryst, Solids 131 (1991) p.13.
[89] M. Altarelli, R.P. Kurta and I.A. Vartanyants, Phys. Rev. B 82 (2010) p.104207.
[90] F. Lehmkühler, B. Fischer, L. Müller, B. Ruta and G. Grübel, J. Appl. Cryst. 49 (2016) p.2046.