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Formation of Positively Charged Liquid Helium Clusters in Supercritical Helium and their Solidification upon Compression

Hejer Gharbi Tarchouna,^{†,§} Nelly Bonifaci,^{*,†} Frédéric Aitken,^{*,†} Luis Guillermo Mendoza Luna,[‡] and Klaus von Haeften^{*,‡}

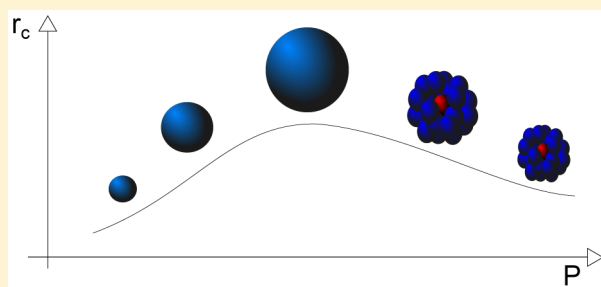
[†]G2ELab-GreEn-ER, Equipe MDE, 21 avenue des Martyrs, CS 90624, 38031 Grenoble Cedex 1, France

[§]Laboratory for Materials, Organization and Properties (LabMOP), Campus Universitaire - El Manar, 2092 Tunis, Tunisia

[‡]Department of Physics and Astronomy, University of Leicester, University Road, Leicester LE1 7RH, United Kingdom

ABSTRACT: Positively charged ions were produced in supercritical helium at temperatures from 6 to 10 K and up to 2 MPa using a corona discharge. Their mobility was measured via current–voltage curves, and the hydrodynamic radius was derived using Stokes law. An initial increase and subsequent decrease of hydrodynamic radius was observed and interpreted in terms of growth, compression and solidification of ion clusters. The mobility was modeled using a van der Waals-type thermodynamic state equation for the ion-in-helium mixed system and a temperature-dependent Millikan-Cunningham factor, describing experimental data both in the Knudsen and the Stokes flow region.

Regions of maximum hydrodynamic radius and large compressibility were interpreted as boiling points. These points were modeled over a large range of pressures and found to match the Frenkel line of pure helium up to 0.7 MPa, reflecting similarity of density fluctuations in pure supercritical helium and gas–liquid phase transitions of ionic helium clusters.



The interaction of solutes with supercritical solvents is relevant to many chemical processes and applications, for example, the decaffeination of coffee using carbon dioxide, dry cleaning, and nanoparticle synthesis.^{1–3} All these processes have in common the formation of a homogeneous phase of clusters comprising molecules of the solute and the supercritical solvent in regions close to the critical temperature of supercritical fluids, T_c . Spectroscopy has provided plenty of evidence for the existence of these clusters,⁴ but for a good understanding of cluster formation it is very important to have direct size information.⁵ Such data is scarce because dissolved clusters cannot be directly addressed to measure their size.⁶ Furthermore, the study of cluster formation in supercritical gases would benefit from simple, model-type solvents such as helium, which—being nonpolar and having few electrons—is appealing to theory. From an experimental point of view, supercritical helium has the advantage that, close to $T_c = 5.1953$ K, it is practically free of impurities, because in this temperature regime all other substances are frozen. A consequence of this feature is that the choice of molecular solutes is restricted.

Positively charged ions have frequently been studied in liquid helium where they can be solvated and where they are known to produce clusters—often referred to as “snowballs”.^{7–11} However, whether clusters exist at low temperatures above T_c is currently an open question. Measurements of positive ion mobility in the supercritical phase could shed light on this issue, but to the best of our knowledge no data is available to date. Many ion production techniques require vacuum and are thus incompatible with high densities in the supercritical phase. An

exception is the corona discharge method, by which ions can be generated in a wide pressure range of the carrier gas, up to several hundred bar. For corona discharges in point-plane geometry, ion mobility can be straightforwardly derived from $I(V)$ curves:¹² the current that flows between tip and plane electrodes has a quadratic dependence on the voltage and is directly proportional to the mobility. Hence, measurement of $I(V)$ curves at different voltages allow one to derive the mobility via the slope of an $\sqrt{I}(V)$ plot.

In this paper we report positive ion mobility in supercritical helium. The ion mobility shows a rapid decrease when the hydrostatic pressure is increased, consistent with growth of clusters. Further increase in hydrostatic pressure reverses this trend and reveals a regime where the clusters are compressed. The compressibility seen in this range is large and incommensurate with a cluster of solid helium. The distinct maxima of the hydrodynamic radius, separating the regions of growth and compression regions for each isotherm, shift to higher pressures for higher temperatures. We attribute these maxima to phase transitions, i.e., points in the P – T plane where the helium atoms condense into liquid clusters surrounding an ion. Increases in pressure beyond these maxima has the effect of compression, and we observe solidification. We model the pressure variation of the hydrodynamic radius in the supercritical phase using thermodynamic state equations for the

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mixed system over a wide range of pressures, spanning the regimes from Knudsen flow to Stokes flow and temperatures from T_c to 11 K. We observe that for all temperatures up to the 7 K isotherm, the position of the maxima in the P – T plane match the Frenkel line¹³ of pure helium, indicating similarity in the boiling of helium ion clusters and the presence of short-lived pure-helium clusters in pure supercritical helium caused by density fluctuations of the fluid.

Figure 1 shows in the upper panel the mobility of positive ions generated in a corona discharge for 6.35, 7, and 10 K

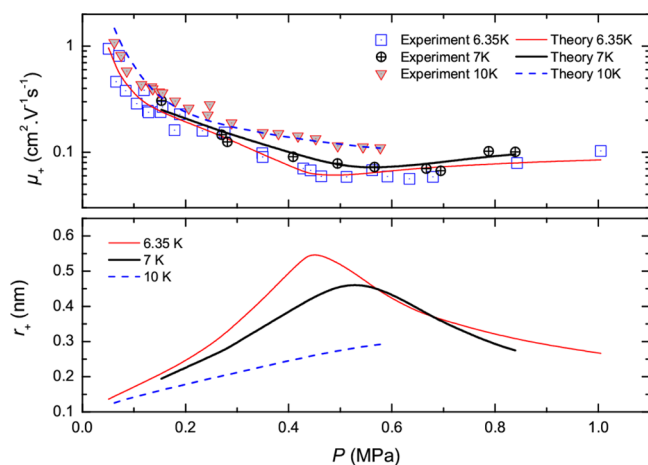


Figure 1. Pressure dependence of the mobility (top graph) and hydrodynamic radius of positively charged ions (bottom graph) in supercritical helium.

carrier gas temperatures as a function of pressure in the range 0.06 to 10 MPa. At the lowest pressure investigated here, the mobility shows a rapid decrease with increasing pressure. This is very different from gases at high temperature or very low pressure where the mobility decreases much more slowly.^{14,15} Further increase in pressure decreases the mobility further up to a characteristic pressure which is temperature-dependent, after which the mobility begins to increase again. In the entire region, the viscosity, η , is monotonically increasing, ranging from 1.6 $\mu\text{Pa}\cdot\text{s}$ to 5 $\mu\text{Pa}\cdot\text{s}$. The hydrodynamic radius, r , related to mobility, μ , via Stokes law $\mu_{\text{Stokes}} = e/6\pi\eta r$ shows an increase, a maximum and an extended region of decrease (lower panel of Figure 1), which can be readily explained by growth of clusters and their subsequent compression. The variation with pressure is markedly different from the liquid phase:¹⁶ an increase of pressure always leads to a reduction in radius, which is attributed to compression of the clusters; this also implies that at the lowest densities needed to establish the liquid phase clusters are already present and do not have to grow.

The large variation of hydrodynamic radius with pressure shown in Figure 1 also illustrates that the ion clusters are very soft and rather more gas–liquid-like than solid, at least in the cluster surface region.¹⁹ Figure 2 shows the isothermal compressibility, β , defined as $\beta = -1/V (\partial V/\partial P)_T$ for the three isotherms of Figure 1. In the region of 0.5 to 0.7 MPa β reaches values up to $6 \times 10^{-7} \text{ Pa}^{-1}$. Horizontal lines mark the lowest compressibility reported in the liquid phase as well as the highest compressibility reported for the solid phase of pure helium. These values can be regarded as benchmarks to assess to what extent snowball clusters appear liquid- or solid-like. This comparison shows that clusters grown at 6.35 and 7 K are liquid-like up to pressures around 0.8 MPa, whereas clusters

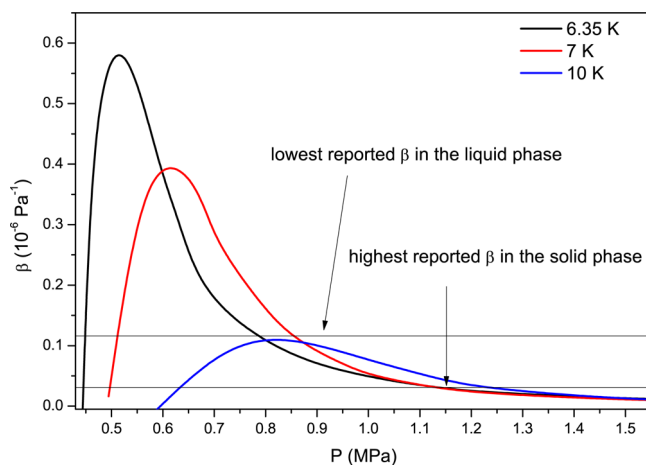


Figure 2. Pressure dependence of the compressibility, β , of ion clusters in supercritical helium for three different isotherms. The lowest reported β in the liquid phase, corresponding to $1.16 \times 10^{-7} \text{ Pa}^{-1}$, and the highest reported for the solid phase, corresponding to $3.1 \times 10^{-8} \text{ Pa}^{-1}$,^{17,18} have been marked to distinguish regions where the clusters are likely to be solid or liquid-like.

grown at 10 K can be either solid or liquid. For pressures larger than 1.2 MPa, the clusters should be always solid.

The fact that the maxima separate regions of growth and compression suggests that, between these regions, the clusters are in a state of condensation/boiling. This is reflected in the large change of the overall cluster radius, decreasing from its maximum value of 0.55 nm at 0.45 MPa to 0.25 nm at 1 MPa on the 6.35 K isotherm, and indicating a large change in bond length. The liquid-like state of the clusters should also facilitate the exchange of solute and solvent because they are of the same substance and surface atoms are indistinguishable from those in the fluid. This has been suggested by Lewerenz and Slavicek.²⁰

To obtain further insight we have modeled the ion mobility and hydrodynamic radius. The free volume model links the size of a foreign object introduced in a fluid to the volume that is not occupied by the fluid molecules.^{21–23} Changes of this “free” volume are correlated to the volume changes of the mixed fluid, which can be expressed in an equation of state. Like any equation of state that reproduces experimentally determined thermodynamic variables P , V , or T for a given known pair of variables is valid, a state equation that produces a correct volume occupied by the foreign object has to be valid as well. The procedure employed here follows our earlier work on electrons in helium^{24,25} and ions in normal liquid helium^{26,27} and will be comprehensively treated for all phases of helium in a forthcoming publication.

Briefly, we find a good match with experimental data when using a van der Waals-type state equation, which relates the free volume, V_f to temperature, T , pressure, P , and internal pressure Π as follows:

$$\frac{V_0}{V_f} = 7 \frac{P + \Pi}{T} \quad (1)$$

In the equation V_0 has been introduced to conserve units, P is given in bar, and T is in Kelvin. The prefactor on the right side has the unit K/bar.

For the internal pressure, which represents attractive interaction, we find the best match when using the classical van der Waals term:

$$\Pi(\rho, T) = \alpha \rho^2 \quad (2)$$

where $\alpha = 0.00796 \text{ bar}/(\text{kg}/\text{m}^3)^2$ is a constant. Positive ion clusters in normal liquid helium are also characterized by good proportionality between Π and ρ^2 in their state equation, but small corrections are needed to account for accurate modeling of the mobility close to the superfluid–normal liquid and liquid–solid phase transitions.²⁷ This behavior of positive ion clusters in normal liquid and supercritical helium is different from that found for electrons in low-temperature helium gas,²⁴ normal liquid helium, and supercritical helium.²⁵ There, the corrections are larger and attributed to a less well-defined interface between electron clusters and solvent-helium, as is the case for positive ion clusters.

It is reasonable to consider an incompressible part a of the ion radius, r , for which we find the following correlation function with the free volume:

$$r - a = a \frac{\sqrt{\frac{V_0}{V_f}}}{1 + 18 \sqrt{\frac{V_0}{V_f}} \exp\left(-\kappa(T)/\sqrt{\frac{V_0}{V_f}}\right)} \quad (3)$$

where $a = 0.074 \text{ nm}$. The length a represents the cluster radius in the limit of zero pressure and can be interpreted as the size of the “naked” ion. $\kappa(T)$ decreases exponentially with temperature:

$$\kappa(T) = 2.09789 \times 8\pi^2 \exp\left(-\frac{9T}{20T_{\lambda,\max}}\right) \times \left[1 + \exp\left[-0.8\left(\frac{T}{T_{\lambda,\max}} - 1.29483\right)^2\right]\right] \quad (4)$$

$T_{\lambda,\max}$ is the highest temperature on the superfluid phase transition line.

Equations 1, 2, and 3 together represent the equation of state of the mixed system in supercritical helium.

The hydrodynamic radius r of eq 3 is entered in the Stokes equation for ion mobility. For low densities, where Knudsen numbers are greater than 1, a Millikan–Cunningham factor, ϕ , of the measured mobility, $\mu_{\text{MC}} = \mu_{\text{Stokes}}(1 + \phi)$, has to be introduced. We have investigated the mobility of electrons in the supercritical and superfluid phase of helium and discovered that an extension of the classical Millikan–Cunningham factor to include temperature dependence would lead to significant improvement. By adopting a similar approach, we were able to model the transition from Knudsen to Stokes flow:

$$\phi = \frac{2\rho_c}{3\rho} \exp\left[-\left(\frac{\chi(T)}{Kn}\right)^{3/4}\right] \exp\left(-\frac{T_c}{T}\right) \quad (5)$$

with

$$\chi(T) = 8 \times 8.788875 \left(\frac{T_c}{T}\right)^{0.3} \quad (6)$$

and the critical density, ρ_c , the critical temperature, T_c , and Knudsen number $Kn = l/r$; l being the mean free path, and r the characteristic length, which here is the radius of the foreign particle.

The calculated mobilities are shown as solid and dashed lines in the upper panel of Figure 1. In the entire pressure and

temperature range under investigation, they match well with the experimentally derived mobilities (symbols in Figure 1) showing the validity of the chosen equation of state.

Using the formalism described above, we have simulated the pressure dependence of hydrodynamic radii for isotherms up to 11 K. All isotherms show the same trend as Figure 1. With increasing temperature, the maxima lie at higher pressures and the maximum hydrodynamic radius decreases, indicating that with increasing temperature the maximum size of the clusters becomes progressively smaller.

In Figure 3 we have plotted the position $(r_+)_{\max}$ of maximum cluster radius in the P – T diagram together with the Frenkel

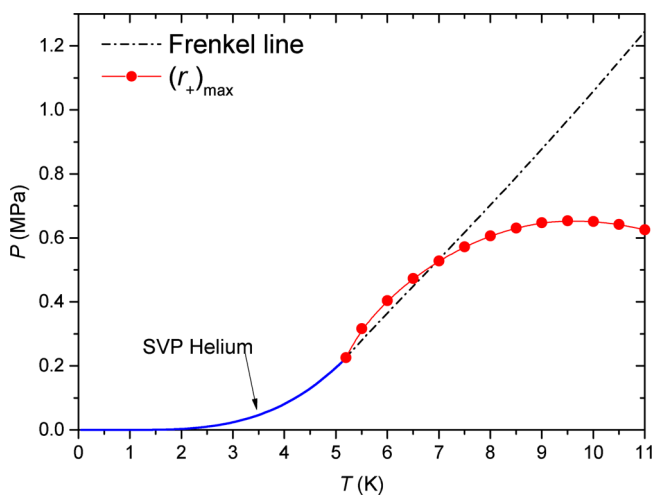


Figure 3. Saturated vapor pressure curve of pure helium (solid blue line), Frenkel line (dash-dot), and positions where the hydrodynamic radius of positive ion clusters, $(r_+)_{\max}$, become maximum (red circles). See text.

line, which connects points where increased light scattering is observed and where the isochoric heat capacity, c_v , and the isobaric heat capacity, c_p , of pure helium have a maximum along isobars. Maxima of c_v and c_p are indicative of phase transitions, and are usually observed on the vapor pressure curve. Although, by definition, no first-order phase transition exists in the supercritical phase, maxima of c_v and c_p are still observed beyond T_c . The Frenkel line, connecting these points, was found to be a continuation of the vapor pressure curve beyond the critical temperature and can be attributed to strong density fluctuations of the helium.¹³

Figure 3 shows that for temperatures between 5 and 7 K the position $(r_+)_{\max}$ of maximum cluster radius is close to the Frenkel line, reflecting the similar nature of the gas–liquid transition of helium ion clusters and density fluctuations in pure helium. At temperatures higher than 7 K the lines diverge, showing that the mixed system has different properties than the pure fluid system. These differences should not be unexpected given that the ion clusters in this region are very small, effectively exhibiting an increasingly higher ion concentration.

In conclusion, we have measured the mobility of positive ions in supercritical helium and derived the hydrodynamic radius. The variation of hydrodynamic radius with pressure shows regions of increase and decrease separated by a distinct maximum, interpreted in terms of condensation, growth and compression of positively charged clusters. Modeling of the mobility using a temperature-dependent Millikan–Cunningham factor provided good agreement with experimental data

over large pressure ranges, covering both the Knudsen and the Stokes flow regimes. Large compressibility typical for gas–liquid-like systems was found on all isotherms at low and moderate pressures. At higher pressures the compressibility was smaller, indicating the clusters were solid.

In addressing the apparent lack of size data of free clusters which are in thermal equilibrium within a supercritical gas, our results directly show how these clusters grow and how they change their thermodynamic phase. Our results are promising for the investigation of other ion clusters in helium, including anions²⁸ as well in other nonpolar supercritical gases.

EXPERIMENTAL METHOD

The experimental method has been described in detail in previous publications,^{25,29–32} and we give here only a brief summary. A discharge cell in point-plane geometry was mounted on a liquid helium bath cryostat and filled with helium gas of purity level 99.9999% (research grade) by passing the gas through liquid nitrogen-cooled, activated charcoal filters to remove impurities to the highest possible level. For point-plane geometry, the current is unipolar space charge-limited and concentrated along the tip axis,^{33,34} for both gases and liquids. In dense fluids and above a threshold voltage, the current depends quadratically on the voltage between tip and plane:

$$I = C_t \mu \epsilon \frac{(V - V_0)^2}{d} \quad (7)$$

where I represents the current, $C_t = 2$ is a constant (see ref 12), μ the mobility, ϵ is the dielectric constant of the medium ($\epsilon_0 \epsilon_r$), V is the voltage, V_0 is the threshold voltage, and d is the electrode separation.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: nelly.bonifaci@grenoble.cnrs.fr

*E-mail: frederic.aiken@grenoble.cnrs.fr

*E-mail: kvh6@le.ac.uk

Notes

The authors declare no competing financial interest.

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