A thermodynamic model to predict the formation, sizes and mobilities of electron clusters and positively charged ('snowball') clusters in all fluid phases of helium

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Van der Waals-type thermodynamic state equations are developed for description of mobilities of electron and ion impurities in supercritical, normal liquid and superfluid helium. The state equations allow to calculate an effective size of the impurities, i.e. the 'hydrodynamic' radius. The mobilities derived from the impurity sizes and the known dynamic viscosities match experimental data with unsurpassed accuracy. This model can be extended to low densities where Knudsen numbers are greater than one by reformulating the Millikan-Cunningham factor to account for size changes. With the ability to predict hydrodynamic radii in different thermodynamic regimes and over large pressure and temperature ranges we are able to simulate growth of clusters formed by the attractive interaction between impurities and solvent atoms or molecules. In the supercritical regime of helium we observe distinct regimes of growth and subsequent compression with further increasing pressure. The compressibility derived from the change of hydrodynamic radius with pressure allowed us to identify a liquid-like phase for positively-charged 'snowball' clusters in normal liquid and supercritical helium for lower pressures. For higher pressures, the 'snowballs' solidify.

Electrons and positive ions are microscopic probes frequently used to explore transport, diffusion and quantum properties of liquid helium. Electrons introduced into liquid helium localise and build clusters with ground state helium atoms due to attraction. Inside these electron-helium clusters there are large cavities with radii up to 20 Å (at 4.2 K and 1 bar), depending on the pressure. The formation of the void results from the repulsive interaction between ground state helium atoms and electrons at short range caused by the Pauli principle and the much longer ranged van der Waals-like attraction. Positive ions in liquid helium behave the opposite way. At short range, electrostrictive forces between the positive charge and the surrounding polarised helium atoms dominate and attract the helium atoms towards the positive centre. As a consequence a dense shell of helium is built, which is why the term 'Atkins-snowball' is often used.

Information of the size and structure of the electron and ion clusters in helium is difficult to obtain in a direct fashion. Thanks to the charged nature of electrons and ions, the measurement of their mobility is relatively straightforward when using electric fields. The mobility is related to a hydrodynamic radius, *r,* via the well known Stokes law for spherical objects flowing within a fluid of viscosity, η ,

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$$\mu_{Stokes} = \frac{e}{6\pi r \eta} \tag{1}$$

While the deduction of the radius requires no other knowledge than the viscosity of the fluid, η , a number of restrictions nevertheless apply. In particular at low densities where the Knudsen number is greater than one the more general Millikan-Cunningham equation must be used instead of eq. (1),

$$\mu_{MC} = \mu_{Stokes}(1+\varphi) \tag{2}$$

where μ_{MC} is the Millikan-Cunningham mobility and φ the Millikan-Cunningham factor.
Finding a coherent description of ion and electron mobility in different density regions, especially the crossover from gas kinetic to Stokes flow is a challenge. An implicit challenge is that ion and electron clusters in helium are expected to change their structure depending on the density.
We develop thermostatic state equations for electrons and He ions in helium and employ the free volume model to derive the hydrodynamic radius. In general terms, the free volume model relates the size of foreign objects, i.e. solute molecules within a fluid to the size occupied by a free volume unit cell, (*V*-*b*)/*N*, using as the first approximation a simple power law between the two. The state equations of *P*, *V* and *T* include two parameters which are calibrated using experimentally determined mobilities using one isotherm in the normal liquid phase, and one in the supercritical or the gaseous phase.

An example of this approach can be seen in Figure 1. The experimentally determined mobility of electrons is shown over a large range of temperatures and pressures. Both, the hydrodynamic radius and the mobility are nicely reproduced using the thermodynamic state equation approach [1]. Particularly, for sufficiently low temperatures in the supercritical phase one can observe a condensation region of the electron clusters and a compression region. Positively charged ions in supercritical helium behave in a very similar manner (not shown).

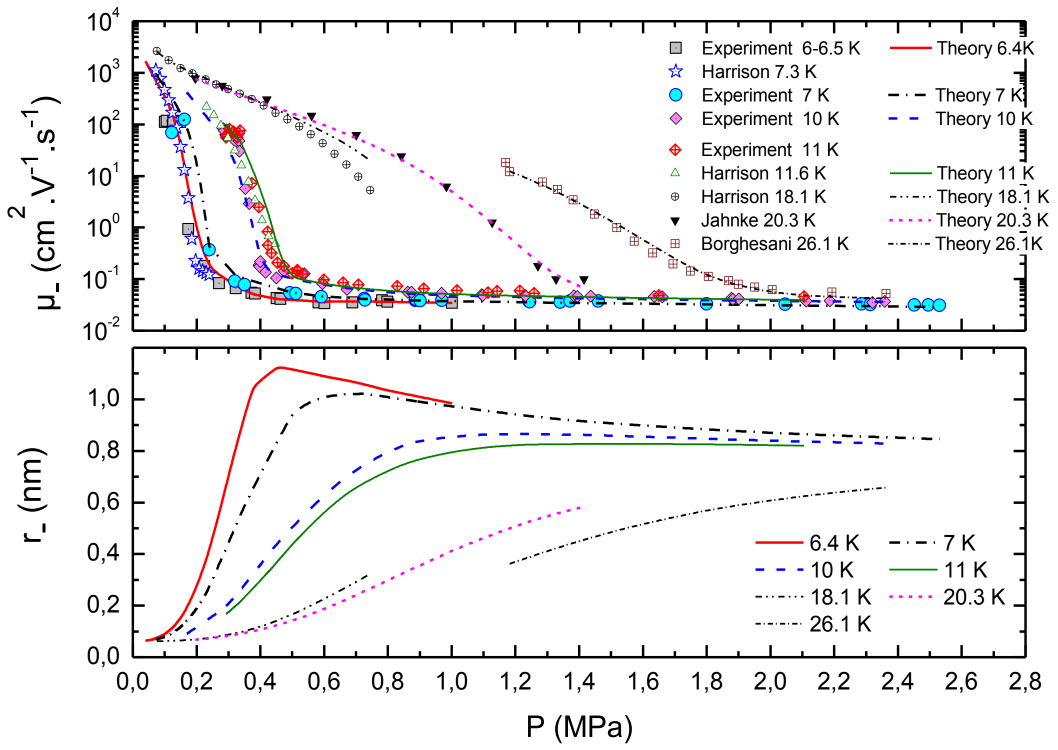

Figure 1: Electron mobility and hydrodynamic radius in the supercritical region of helium. Experimental data of mobilities are taken from Harrison *et al*. (1973), Jahnke *at al*. (1971), Borghesani *et al*. (2002) and ourselves.

[1] F. AITKEN, Z.-L. LI, N. BONIFACI, A. DENAT and K. von HAEFTEN, Electron mobility in liquid and supercritical helium measured using corona discharges: a new semi-empirical model for cavity formation, Phys. Chem. Chem. Phys., Vol. 13(2), pp. 719-724, 2011.