Applicability of the Atkins model to the ion behavior in superfluid helium

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Abstract. The properties of ion clusters in superfluid helium are usually treated within the model proposed by Atkins (the snowball model) [1] who was the first to note a large “polaronic” effect associated with the injection of positive ions into liquid helium. The simplicity and clarity of this model where polaronic effects are finally reduced to the development of a spherical solidified helium core (with the estimated radius of $R_a \simeq 7$ Å) around the ion together with the absence of qualitative obstacles to explaining the large effective mass as well as the details of phonon (roton) mobility were very appealing features of the model, and the snowball turned (without any special grounds for it) into a universal picture describing the structure of the ion cluster in helium. However, although a solid sphere around the seed ion can actually exist (to within the details associated with the proximity effect; the sphere radius is comparable to the thickness of the liquid-solid transition layer), it is vitally important to which extent it really governs the scattering mechanisms of various thermal excitations at the cluster. Detailed analysis of available data on the phonon as well as the impurity and Stokes mobilities reveals that the true unifying factor in the discussed picture is a power-law density enhancement in the vicinity of the seed charged particle caused by the polarization forces rather than the radius $R_a$.

1. Introduction
The properties of ion clusters in superfluid helium are usually treated within the model proposed by Atkins (the snowball model) [1] who was the first to note a large “polaronic” effect associated with the injection of positive ions into liquid helium. The simplicity and clarity of this model where polaronic effects are finally reduced to the development of a spherical solidified helium core (with the estimated radius of $R_a \simeq 7$ Å) around the ion together with the absence of qualitative obstacles to explaining the large effective mass as well as the details of phonon (roton) mobility were very appealing features of the model, and the snowball turned (without any special grounds for it) into a universal picture describing the structure of the ion cluster in helium. However, although a solid sphere around the seed ion can actually exist (to within the details associated with the proximity effect; the sphere radius is comparable to the thickness of the liquid-solid transition layer), it is vitally important to which extent it really governs the scattering mechanisms of various thermal excitations at the cluster (it is exactly this role that is assigned to the solid sphere of radius $R_a$ in the Atkins model). Fortunately, it is now possible to obtain a qualitative answer to this question. To that end, it is sufficient to analyze the available mechanisms of the thermal and impurity excitations interaction with the positive ion which govern the observable details of its kinetics (dynamics) in different regimes. One should consider the phonon as well as the impurity and Stokes mobilities where the universality of radius $R_a$ could be revealed.

2. Phonon regime
At low temperatures the phonon mobility of the cluster $\mu_{ph}$ is governed by scattering of the long wavelength phonons at the cation. For such phonons incident onto a hard sphere the scattering
cross-section $\sigma$ is [2]

$$\sigma_{ph}(\omega) = \frac{7\pi}{9} \left( \frac{R_a^2 \omega^2}{s^2} \right)^2$$

(1)

In a more general cluster model (cloud model) which only takes into account the power law density enhancement of the liquid in the vicinity of the charged particle the cross-section $\sigma$ is

$$\sigma_{ph}(\omega) = 4\pi \Lambda^2 \omega^4, \quad \Lambda = \int_0^\infty \left[ \frac{1}{s^2} - \frac{1}{s^2(r)} \right] r^2 dr$$

(2)

where $s$ is the sound velocity in the homogeneous liquid helium, $s(r) \geq s$.

It is obvious that the phonon mobility $\mu_{ph}$ calculated with the cross-sections given by (1) and (2) has the same temperature dependence consistent with the experimental data [3]. Therefore the resulting radius $R_a \approx 7$ Å could be used when discussing the cation mobility in other regimes. However, the Atkins model runs into difficulties also in the phonon domain. The case in point the total effective cation mass $M_{eff}$. Its available estimates [1] which account for the contribution of the crystallized core of radius $R_a$ yield $M_{eff} \approx (70 - 80)m_4$. On the other hand, the direct measurements of this mass [4,5] reveal that $M_{eff} \approx (30 - 32)m_4$. An alternative cloud-model for the calculation of $M_{eff}$ in ideal liquid (see Refs. [6,7]) allows to avoid the hard core contribution and is therefore much closer to the experimental results.

3. Impurity-controlled mobility

While in the phonon part of the mobility problem the concept of $R_a$ can, in principle, be employed, the impurity-governed mobility completely drops out of the framework of the snowball model. Indeed, the hard sphere model yields for the cluster mobility in the impurity excitation gas $\mu \propto T^{-1/2}$:

$$\mu_3 = \frac{3e}{8n_3 R_a^4 \sqrt{2\pi m_3 T}}$$

(3)

In contrast to that, the experiment [8,9] reveals that $\mu_3$ is temperature independent in a wide range of $0.1 < T < 1$ K.

An elegant solution to the $\mu_3$-paradox is obtained if one assumes that the impurity atoms are scattered (just as in the case (2)) by the density enhancement in the ion vicinity rather than by the hard sphere. As already mentioned earlier, the helium atom resides at the center of increased pressure whose distribution can be derived form the condition of the constant chemical potential for He$^4$ atoms:

$$\delta \mu (r) = P(r) v_4 - \frac{\alpha e^2}{2 r^4} = 0, \quad \delta \rho (r) = \left( \frac{\partial \rho}{\partial P} \right) P(r) = \frac{1}{s^2} P(r)$$

(4)

where $P(r)$ is the local pressure around the ion, $v_4$ is the volume of the individual solvent atom and $s$ is the sound velocity, $\alpha_4$ is the polarizability of a single He$^4$ atom. Of course, individual He$^4$ atoms do not feel the ion as the scattering center when moving close to it. The situation is quite different for He$^3$ atoms which whose efficient volume is $v_3 > v_4$. To the extent of this inequality, the energy $V_3(r)$

$$V_3(r) = \kappa^2 / r^4, \quad \kappa^2 = \frac{\alpha_4 e^2}{2r^4} \left( \frac{v_3}{v_4} - 1 \right),$$

(5)

determines the scattering potential for He$^3$ atoms at the charged cluster.

From the details of calculations [8,10] we shall cite here an estimate for the minimal distance at which the incident impurity can approach the ion in the head-on collision

$$r_{min}^4 \sim \kappa^2 / T$$

(6)
For temperatures $T \leq 1K$ the quantity $r_{\text{min}} \geq 10^{-7}$ cm, i.e. the inequality $r_{\text{min}} > R_a$, switching off the Atkins’ kernel from the scattering process indeed takes place.

The impurity-related cation mobility $\mu_3$ with the quasiclassical scattering $\sigma_3(q) \propto q^{-1}$ at the potential (5) is [8,9]

$$\mu_3 = \frac{e}{5.32 \kappa_3 \sqrt{m_3}}. \quad (7)$$

It proves to be independent of $T$ in a wide temperature range and agrees with the observed [8,10] behaviour $\mu_3(T)$ without any fitting parameters.

The experimental data on mobility $\mu_3$ in solutions with dominating He$^3$ atoms are also consistent with the suggested picture of the cation interaction with impurity excitations. In that case the density enhancement zone around the charge is formed by liquid He$^3$ while the role of impurities is played by individual He$^4$ atoms. As a result, the effective interaction (5) transforms to

$$V_4(r) = \kappa_2^2/r^4, \quad \kappa_2^2 = \frac{\alpha_3 e^2}{2r^4} \left( \frac{v_4}{v_3} - 1 \right), \quad \frac{v_4}{v_3} < 1 \quad (8)$$

In other words, this interaction changes its sign. Hence in dilute He$^4$–He$^3$ solutions the cations become centers of condensation of He$^3$ atoms. In the vicinity of the phase separation boundary of that solution the local condensation which is sensitive to the proximity to the separation boundary results in a sharp growth of the cation radius (a drop of mobility) as mentioned in Ref. [11]. The Atkins model does not contain this effect.

### 4. Stokes regime

Several pro et contra concerning the manifestation of “phase” effects in the motion of cations in cryogenic liquids.

When studying the Stokes mobility of cations in the vicinity of $T \sim 2$ K, the Atkins radius should be sensitive to a steep growth of the solidification pressure following from the He$^4$ phase diagram near $T \simeq 2$ K. However, nothing of that kind is actually observed (see Ref. [12]).

One more example indicating the absence of any noticeable correlation between the possible formation of a solid core and the finite value of the radius of a charged cluster moving in a normal liquid. Charged particles in normal electrolytes are well known to demonstrate the so-called Stokes mobility, i.e. the mobility due to the friction force given by the Stokes formula

$$F_s \simeq 6\pi R_s \eta V_D \quad (12)$$

where $V_D$ is the ion drift velocity, $R_s$ is the Stokes radius, $\eta$ is the liquid viscosity, and the value of $const \sim 6\pi$ is controlled by the liquid adhesion to the ion surface. Experimental data reveal that dilute electrolytes follow the so-called Walden-Pisarzhevskii rule [13]

$$\sigma \eta = const, \quad (13)$$

relating the conductivity $\sigma$ due to the particular sort of ions and the solution viscosity $\eta$. The correlation (13) obviously favours the Stokes origin of the friction force stabilizing the ion motion. Therefore, Eq. (12) can be used to determine the radii $R_s$ of the corresponding ions. All these radii prove to be mesoscopic, i.e. substantially exceeding Bohr radius: $R_s \gg a_b$. Thus, for positive ions in normal liquid helium $R_+ \sim 5 - 6 \AA$ [1,12]; the oxygen ion in liquid xenon and krypton has the size of the order of $R_0 \sim 6 \AA$ [14]. Here are some Stokes radii $R_s$ (in Å) for ions in water [13]: Li$^+$ — 2.37; Na$^+$ — 1.83; Be$^{2+}$ — 4.08; Mg$^{2+}$ — 3.46; Ca$^{2+}$ — 3.09, etc. The polaronic effect is obvious. No snowball can even be discussed here since in normal electrolytes the situation, as a rule, is far from the phase diagram boundaries.

And only in the vicinity of the phase separation in the He$^3$–He$^4$ mixture where positive ions become the nuclei of an emerging phase do spherical cluster develop whose radius is sensitive to
the proximity to the phase separation [11]. This picture corresponds to Atkins ideology, but it is related to the phase separation details rather than to helium solidification.

Thus, an overall conclusion that is taking shape is rather against the Atkins model. It was found that there exists a whole series of effective radii each of which corresponds to a particular mechanism of the cluster interaction with the medium. In some of the indicated cases the effective radius either do not arise at all (mobility in the He$^3$–He$^4$ solutions) or behaves in an exotic way (effective associated mass of the charged cluster). The true unifying factor in the discussed picture is a power-law density enhancement in the vicinity of the seed charged particle caused by the polarization forces rather than the radius $R_a$.

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