Potential of an ionic impurity in a large $^4$He cluster

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This paper presents an analysis of the motion of an impurity ion in a nanometre scale $^4$He cluster. Due to induction forces, ions are strongly localized near the centre of the cluster, with a root mean squared thermal displacement of only a few Å. The trapping potential is found to be nearly harmonic, with a frequency of 2.5(1.0) GHz for a positive (negative) ion in a He cluster of radius 5 nm. The anharmonicity is small and positive (energy increases slightly faster than linear with quantum number). It is suggested that by using frequency sweep microwave radiation, it should be possible to drive the ion centre-of-mass motion up to high quantum numbers, allowing the study of the critical velocity as a function of cluster size.

1. Introduction

The last few years have seen dramatic advances in the spectroscopy of atoms and molecules attached to large He clusters [1]. These clusters provide an unique environment for a spectroscopy which combines many of the attractive features of both high resolution gas phase spectroscopy and traditional matrix spectroscopy [2]. These include the ability to obtain rotationally resolved spectra of even very large molecules [3] and the ability to form and stabilize extremely fragile species [4], including high spin states of molecules.

Despite rapid progress, many fundamental questions remain about spectroscopy in this environment. One important topic that has received little attention is the dynamics of the centre-of-mass motion of an impurity in a $^4$He cluster [5]. A recent experiment reported by Grebenev et al. [6] has convincingly demonstrated that these clusters are superfluid. Thus we expect that an impurity, like in bulk superfluid He, should be able to move with little or no friction as long as its velocity stays below a 'critical velocity' which is found to be on the order of 30 ms$^{-1}$ for motion of positive ions in bulk superfluid $^4$He [7, 8]. Doped He clusters provide an attractive system to study the size dependence of superfluid hydrodynamics.

There have been several theoretical studies reported that consider the motion of an electron bound to the surface of He or other dielectric clusters [9–14]. Most of these have only considered the electrostatic potential for the ion outside of the cluster, and solved for the quantum levels of the electron, including determining the minimum size for a cluster to bound an electron. The only exceptions in the open literature known to the authors is the work of Antoniewicz and co-workers [10, 11] that presents the electrostatic potential inside the cluster, but the potential given in that work is in error by a factor of two, and a paper by Northby et al. [15] that presents an approximate potential, similar to that given in section 2 below, but without any derivation. The exact electrostatic expressions have been given in the PhD theses of Ballester [16] and Kim [17].

This paper will present a realistic potential for the motion of an ion in a He cluster, based upon the electrostatic potential produced by the dielectric response of the He to the ion. A similar response is partly responsible for the trapping potential of an ion beneath a He–vapour interface that was exploited by Poitrenaud and Williams [18] to determine the effective mass of positive and negative charge carriers in bulk He. This paper will then propose experiments that can be viewed as the natural extension of this earlier work on bulk He. In addition to allowing the determination of the size dependence of the effective mass of ions, it should also allow for the study of the effective size dependence of the critical velocity of an ion in the cluster.

In a following paper, the motion of a neutral impurity atom or molecule will be considered, and an effective Hamiltonian for its motion, including both long range potential and hydrodynamic contributions, will be derived. The potential localizes the neutral impurity near the centre of the cluster, though much more
weakly than for the case of an ion which has much stronger long range interactions with the He, falling as $r^{-4}$ versus $r^{-6}$. In the case of molecules, there is a coupling of the rotation and the centre-of-mass motion which leads to a broadening mechanism in the rotational or ro-vibrational spectrum.

2. Potential for an ion in a He droplet

A large fraction of the studies of impurities in He clusters have exploited mass spectrometry [19–21]. The migration of the charge in a cluster (which is most likely initially localized on a He atom) will be influenced by the effective potential of such a charge [22]. By electrostatics, the charge will be most stable at the centre of the cluster, furthest from the polarization charge that will develop on the cluster surface, due to the dielectric constant of He. The purpose of this section is to derive an expression for this potential and explore some of its predicted consequences. This potential does not include the energy of solvation of the He around the impurity.

Assume that we have an ion of unit charge, $e$, at a radius $a$ from the centre of the droplet, and pick the coordinate system such that the $z$ axis is along the displacement of the ion from the centre. In order to calculate the energy, we can sum up the ion induced dipole interaction of the ion with the ‘missing’ He that would be ‘outside’ the droplet. This makes the ‘zero’ of energy an ion in an infinite bulk of liquid He, and also avoids the difficulties with the nearby He atoms which are strongly bound to the ion.

Let $r(\theta)$ be the distance from the ion to the droplet surface at a polar angle $\theta$ measured from the ion. Basic trigonometry gives:

$$R^2 = (a + r \cos(\theta))^2 + r^2 \sin^2(\theta)$$

$$= a^2 + r^2 + 2ar \cos(\theta)$$

from which we can derive:

$$r(\theta) = \sqrt{R^2 - a^2 \sin^2(\theta)} - a \cos(\theta).$$

The field from a charge is given by:

$$E(r) = \frac{e}{4\pi \varepsilon_0 r^2}.$$ 

This leads to an energy difference from the bulk:

$$\Delta E = \int_0^\infty \int_0^\pi \frac{4}{2}(\rho \alpha) E^2(r') 2\pi r'^2 \sin(\theta) \, dr' \, d\theta,$$

where $\rho$ is the number density of He (0.0218 $\text{Å}^{-3}$ [23]) and $\alpha$ is the polarizability of He. Evaluating the integrals (which were done using the Mathcad program [24]), gives the following result:

$$\Delta E = \left(\frac{e^2}{4\pi \varepsilon_0 R}\right) \left(\frac{1}{2\pi} F_0(\alpha/a) R\right),$$

with:

$$F_0(y) = \frac{1}{4} \left(\frac{2}{1 - y^2} + \frac{1}{y} \log \frac{1 + y}{1 - y}\right).$$

$$F_0(y) \approx 1 + \frac{5}{3} y^2 + \frac{11}{3} y^4 + \ldots.$$ 

In this paper, we will consistently use $y$ for the reduced or fractional radius of the impurity ion or molecule. Using the relationships between the polarizability, the electric susceptibility $\chi$, and the relative dielectric constant $\varepsilon$: $\rho \alpha = \varepsilon_0 \varepsilon \chi$, for $\chi \ll 1$, $\varepsilon = \varepsilon_0 - 1$, and $\varepsilon = \varepsilon_0$ [25], we can write this as:

$$\Delta E = \left(\frac{e^2}{4\pi \varepsilon_0 R}\right) \frac{\varepsilon_0 - 1}{2\varepsilon} F_0(\alpha/a).$$

As the ion approaches the surface of the cluster (i.e. $y \rightarrow 1$), the first term in the expression for $F_0(y)$ dominates. It is easily shown that for $\varepsilon \approx 1$ and as $y \rightarrow 1$, the potential becomes the same as the ‘image charge’ potential for an ion approaching a planar He–vacuum interface from the helium side [18]. For liquid He at 3 K, $\varepsilon = 1.05646$ [26]. If we take $R = 5 \text{ nm}$ (which corresponds to $\sim 11$ He atoms), the prefactor in the equation for $\Delta E/\varepsilon_0 = 62 \text{ cm}^{-1}$. If we compare the energy of an ion at the centre of the cluster, $y = 0$, with one near the edge $y = 0.9$, we get a wavenumber difference of $151 \text{ cm}^{-1}$, which is very large compared to $k_B T_c/\hbar c = 0.26 \text{ cm}^{-1}$ for a $^4\text{He}$ cluster at $T_c = 0.38 \text{ K}$. Spectroscopic studies of a number of impurities have demonstrated that He clusters maintain themselves, by evaporation, at a temperature close to this value [3, 27], as had previously been predicted [23]. This potential means that an ion will be strongly pushed towards the centre of the cluster. Once in the centre of the cluster, the thermal motion should produce a Gaussian distribution with a root mean square (RMS) displacement of only 0.5 nm. This can be compared to the size of the ‘snowball’ of frozen He around a positive ion, which is known to have a radius of $\approx 0.6 \text{ nm}$ [28]. Electrons in He form a ‘bubble’ with a radius of $\approx 1.7 \text{ nm}$ [28]. The mechanism and thus time scale for equilibration of an impurity centre-of-mass motion with the internal motion of the He cluster is presently unknown, but most likely involves exchange of energy and angular momentum with quantized surface capillary waves, known as ripplons, as these are the only He cluster modes thermally excited at this temperature [23].

This treatment of the effective potential for an ionic impurity leaves out the interaction between the induced moments created by the charge. As long as one works in
linear response theory, and one can treat the He as a continuum, then these effects can be included by a classical electrostatic calculation, which are presented in an appendix. Because the relative dielectric constant, \( \varepsilon_r \), is so close to one for liquid He, this more exact treatment is in excellent agreement with the more approximate treatment given above. This supports not only the neglect of three body effects for the present case of an ionic impurity, but also for the neutral impurities to be considered in a later paper.

2.1. Proposed experiments

Let us consider an ion in a He cluster of \( R = 5 \). Taylor expansion of the potential (equation (A9)) around the centre of the cluster gives a harmonic force constant of

\[
F = \left[ \frac{\varepsilon_r^2 (\varepsilon_r - 1)}{4 \varepsilon_0 R} \right] \left[ 1 + \frac{1}{2 \varepsilon_r} \right]^{-1} \frac{1}{R^2} = 6.5 \times 10^{-5} \text{ N,} \quad (9)
\]

If we assume an effective mass of 45 times the mass of \(^4\)He, which was found in bulk He for positive ion mobility [18], we get an effective vibrational frequency \( \nu = 2.3 \text{ GHz} \). The dimensionless length corresponding to this vibration is 1.6 Å. The vibrational transition moment for the \( n = 0 \rightarrow 1 \) transition is \( \mu_{01} = 5.2 \text{ Debye} \). The zero point level corresponds to a RMS velocity of 3.8 m s\(^{-1}\). It will require 90 quanta of vibration to reach a velocity of 30 m s\(^{-1}\), which is near the critical value for the onset of dissipation in bulk superfluid He [7, 8]. Vibration around the centre has a positive anharmonicity with \( x = 6.4 \times 10^{-4} \). This implies that the 89 → 90 vibrational transition will be blue shifted by \( \approx 11\% \). Even for this high level of excitation, the classical turning point for the vibration is \( \approx 1.5 \text{ nm} \), and thus the ion will remain localized close to the centre of the cluster, and thus away from the surface, where the approximations made in this paper are expected to break down.

This suggests the following experiment to measure the cluster size dependence of the critical velocity. For ion motion with a peak classical value below the critical velocity, one expects little damping of the vibrational motion. Thus, excitation of the vibrational transition should have little or no observable effects. However, once the vibrational velocity of the ion exceeds the critical velocity, the motion will become strongly damped and the cluster will continue to absorb energy from a microwave field. This will lead to evaporation of He atoms which can be detected by a mass selected and mass analysed beam. By chirping the microwave frequency, one can exploit the anharmonicity to produce an almost pure number state of the motion, at least before damping becomes important, with the level of excitation determined by the end point of the chirp. It is easily verified that due to the large transition dipole moments, only modest microwave power is required to drive the ion up to high levels of excitation. The motion of positive ions in bulk He is associated with vortex rings, which have the curious property that their velocity is inversely proportional to their energy [7]. The effect of confining the ion in a nanoscale He cluster could dramatically alter the dynamics of ion motion.

Even below the critical velocity, one may expect some coupling between the motion of the ionic impurity and the internal degrees of freedom of the He cluster, particularly the surface ripplons, which are low frequency motions. Using the methods described in the paper that follows this one, on the potential of a neutral impurity in a large He cluster, it is possible to estimate the size of the coupling of the ionic motion to the ripplons. These couplings will be expected to cause perturbations of the frequency of centre-of-mass motion of the ion as a function of excitation level and/or cluster size, as the ion motion and ripplons pass through resonance conditions. It is easily seen that the lowest order in the interaction energy between the ion displacement, \( a \), and a displacement of a ripplon of angular momentum \( L, S(L) \), is proportional to:

\[
H_{\text{ripplon, ion}} \approx \left( \frac{\varepsilon_r^2}{4 \varepsilon_0 R} \right) \frac{\varepsilon_r - 1}{2 \varepsilon_r^2} \left( a / R \right)^4 S(L) \quad (10)
\]

This and higher order coupling terms will allow energy to flow from the ion motion to the ripplons. Energy in the ripplons, in turn, can lead to evaporation and an observable reduction in the size of a mass selected cluster. Such experiments could provide the first measurements of the excitation levels of nanometre scale He clusters.

Another potential experiment is to examine the resonances of electrons in He clusters. Such solvated electrons are metastable, and the electrons will eventually be expelled from the cluster [29]. Kim et al. [30] have observed spontaneous and infrared induced electron detachments from large He clusters several milliseconds after formation. The stability of such charged clusters to electric fields demonstrates that the electrons are in bubble states of the He cluster, not attached as surface states [31]. Excitation of the centre-of-mass motion of these ‘bubble states’ should result in a dramatic increase in the rate of electron evaporation from the cluster. The potential for the negatively charged bubble should be the same as for a positive ion, as long as the centre of the bubble is further from the surface than its radius, \( \approx 1.7 \text{ nm} \). The primary difference of the bubble compared to the positive ion is that the effective mass is \( \approx 243 \) times the mass of \(^4\)He [32], which means that for a 5 nm cluster, the harmonic vibrational frequency is
$\approx 1 \text{GHz}$. Since the harmonic vibrational frequency is proportional to the inverse square root of the cluster radius, it should be possible to neutralize selectively all clusters below a certain size by sweeping the microwave field from a certain frequency to higher values. By using microwave double resonance experiments, it should be possible to determine the homogeneous width of the resonance, and thus any drag that the electron bubble inside the cluster may experience.

3. Summary

This paper has developed the potential that governs the motion of an ion inside a nanometre scale He cluster. This motion is determined by long range electrostatic interactions, and thus can be calculated without having to deal with the much more difficult problem of the energetics of solvation of the ion in liquid He. It is found that despite the small dielectric constant of He, the potential is very effective at driving the impurity ion into the centre of the cluster. In thermal equilibrium, RMS displacements of only a few Å are expected.

After ionization by electron impact, the He ion undergoes a ‘random walk’ due to charge exchange with other He atoms until it becomes localized as a He$_2^+$ core which is then solvated [33]. The electrostatic potential derived here will strongly bias this ‘random walk’, given the low temperatures of the clusters [22]. Such a bias could be expected to effect the dynamics following ionization, including the probability of charge exchange with an impurity, which will also likely be localized near the centre of the cluster.

The trapping potential of an ion is found to be highly harmonic, with a frequency in the low microwave region, and having very large transition dipole moments. Experiments are suggested that would exploit these resonances, and the ability to drive the ion up to high quantum states by an adiabatically sweep microwave pulse.

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Appendix

Exact electrostatic treatment for an ion in a He cluster

In this appendix, the classical electrostatic energy that determines the motion of an ion inside a He cluster will be derived, modelling the He cluster as a dielectric sphere. Given the errors in the previous open literature, it is important that the expressions given below be justified. Further, comparison of the exact and approximate energy expression given by equation (8) is important since it allows for an estimate to be made of the approximations used in the companion paper for the energy of neutral impurities in He, where a treatment including many body effects is not practical.

Outside of the cluster, we must satisfy Laplace’s equation and we must only have terms which go to zero at infinity. Thus:

$$V_o(r, \theta) = \sum_{n=0}^{\infty} B_n r^{-(n+1)} P_n(\cos \theta). \quad (A\ 1)$$

Inside the cluster, we have a field due to a point charge (screened by the dielectric) plus fields due to surface charges. The field of the latter must also satisfy Laplace’s equation, but with positive powers:

$$V_i(r, \theta) = \frac{e}{4\pi \epsilon_0 |r-a|} + \sum_{n=0}^{\infty} A_n r^n P_n(\cos \theta) \quad (A\ 2)$$

to determine the angular dependence of the first term, we use the expansion:

$$\frac{1}{|r-a|} = \sum_{n=0}^{\infty} \frac{r^n}{r^n < a} P_n(\cos \theta), \quad (A\ 3)$$

where $r_c = \min (r, a)$ and $r_s = \max (r, a)$. We will be primarily interested in the potential for $r \geq a$

$$V_i(r \geq a, \theta) = \sum_{n=0}^{\infty} \left[ \frac{e}{4\pi \epsilon_0} \left( \frac{a}{r} \right)^n + A_n r^n \right] P_n(\cos \theta). \quad (A\ 4)$$

We can determine $A_n$ and $B_n$ by satisfying the boundary conditions $V_o(R, \theta) = V_i(R, \theta)$ and $\epsilon_r E_{o,r} = \epsilon E_{i,r}$. For these equations to hold for all $\theta$, the respective coefficients of each $P_n$ must be equal. This leads to the following expressions:

$$A_n = \left( \frac{e}{4\pi \epsilon_0} \right) \frac{\epsilon_r - 1}{\epsilon_r} R^{-(2n+1)} \left( \frac{n+1}{n+1+n\epsilon_r} \right) a^n, \quad (A\ 5)$$

$$B_n = \left( \frac{e}{4\pi \epsilon_0} \right) \left[ \frac{(2n+1)\epsilon_r}{n+1+n\epsilon_r} \right] a^n. \quad (A\ 6)$$

We can now calculate the electrostatic energy by using the expression given in equation (4.83) of Jackson [25]:

$$W = \frac{1}{2} \int \rho(x) V(x) d^3x, \quad (A\ 7)$$

where $\rho(x) = e\delta(x-a)$ is the free charge density. Since our reference energy is that of a point charge in an infinite dielectric, we must subtract off the monopole term in the potential. This gives:
Substituting in the above equation for \( A_n \) we get:

\[
W = \frac{e}{2} \left[ \varepsilon^2 (\varepsilon - 1) \right] \frac{1}{4\pi R} \sum_{n=0}^{\infty} \frac{1}{n + 1 + n\varepsilon} \left( \frac{a}{R} \right)^{2n}.
\]  

(A 8)

This potential is exactly one half that previously reported by Antoniewicz and co-workers [10, 11]. These authors reference a classic text [34] for their expression, but unfortunately, the present authors could not locate a copy of this book.

In the limit that \( \varepsilon \to 1 \), equation (A 9) agrees exactly with the Taylor expansion of the expression given above (equation (5)) for the energy obtained by ‘adding up’ the ion-induced dipole energy contributions. Since this earlier expression correctly gives the correct planar ‘image charge’ potential as \( y \to 1 \), it cannot be in error by a factor of two, and thus the error must lie with the expression given by Antoniewicz et al. The PhD thesis of Ballester [16] gives the correct power series expression without the factor of two error. The correct expression was also given in the PhD thesis of Kim [17], who corrected some other minor errors in Ballester’s expressions.

For the case of He clusters, if the final sum is dropped in equation (A 9), the resulting approximation is in error by at most a few percent over the range \( 0 < y < 0.9 \). In this same range of \( y \), equation (8) agrees with equation (A 9) even better, with an error of less than \( 1\% \). Thus the fractional error of the approximate treatment that neglects many body effects is considerably smaller than might have been predicted \( \text{a priori} \), \( \approx (\varepsilon - 1) \).

The power series expansion for \( W \) (equation (A 9)) is computationally useful for small \( y \) values (say \( \leq 0.5 \)), but convergence slows dramatically as \( y \to 1 \), since the real solution diverges in that limit. By reference to the form of the correct solution in the limit of \( \varepsilon \approx 1 \) (equation (5)), it is possible to subtract out the power series of the divergent parts of the solution. The resulting expression is:

\[
W = \frac{1}{2} \left[ \varepsilon^2 (\varepsilon - 1) \right] \frac{1}{4\pi R} \left[ \frac{1 + \varepsilon_y}{1 - y^2} + \varepsilon_y \ln \left( \frac{1 + y}{1 - y} \right) \right] + \varepsilon_y (\varepsilon - 1) \sum_{n=0}^{\infty} \frac{1}{(2n + 1)(n + 1 + n\varepsilon_y)} y^{2n}.
\]  

(A 10)

In this form, the fact that \( W \) goes exactly into equation (5) in the limit \( \varepsilon \to 1 \) is transparent. Further, the last sum is convergent, even at \( y = 1 \), although the convergence is slow there. However, in the region of slow convergence, the sum makes a negligible contribution to the total energy. Further, if the sum is truncated at the \( n = N - 1 \) term, the remainder of the sum can be approximated by an integral:

\[
\sum_{n=N}^{\infty} \frac{1}{(2n + 1)(n + 1 + n\varepsilon_y)} y^{2n} 
\]

\[
\approx \int_{N+1/2}^{\infty} \frac{2^{n-1}}{n^2} \, dn',
\]

(A 11)

\[
= \frac{1}{2(1 + \varepsilon_y)} \int_{N+1/2}^{\infty} \frac{2^{n-1}}{n^2} \, dn' 
\]

\[
= \frac{\ln |y|}{y(1 + \varepsilon_y)^2} \Gamma(-1, (2N + 1) |\ln y|),
\]

(A 12)

where \( \Gamma(a,x) \) is the incomplete Gamma function.

Ballester [16] suggests using the method known as Aitkin’s \( \delta^2 \) process [35] to speed up convergence of the series. Kim [17] derived a similar closed form expression for the interaction energy by a different method.

References

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