

Structure of positive impurity ions in liquid helium*

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Experimental study by Glaberson and Johnson of impurity-ion mobility in liquid ^4He shows a dependence on core-ion species, contrary to the prediction of the Atkins model. We modify this model to improve its self-consistency and to take account of the electronic properties of the core ion. For the case of an alkaline-earth impurity, we find a structure similar to the electron bubble, owing to the presence of a remaining valence electron on the singly charged positive ion. The alkali ion structure differs only slightly from the Atkins form. Trends in the predicted radii are in qualitative agreement with experiment.

I. INTRODUCTION

The motion of charged particles in liquid helium has been the subject of fruitful study for nearly twenty years.^{1,2} The principal value of this investigation has been to elucidate bulk properties of the superfluid state, the most spectacular example being the discovery of quantized vortex rings by Rayfield and Reif.³

More recently, attention has focused upon details of the structure of the ions.^{4,5} Because the characteristic size of the ion complex is 7 Å for the positive and 15 Å for the negative species, studies of its properties provide information useful for understanding the properties of a Bose fluid varying on a microscopic scale. The acquisition of such information is the principal goal of this study. However, it should be realized that we hope to derive and understand even more general properties, for example the liquid-solid surface tension, which can be studied only through such probes of the fluid.

The study reported here was stimulated by recent experimental results of Glaberson and Johnson⁶ on the mobility of positive ions in liquid ^4He . They found (see Table I) that the mobility depends on the identity of the core ion. For the alkali ions K^+ , Rb^+ , and Cs^+ , the mobility is smaller than that of the He^+ ion and decreases as the atomic number of the core ion increases. On the other hand, for the alkaline earth ions Ca^+ , Sr^+ , and Ba^+ , the reverse trend was observed. These facts cannot be reconciled with the simple theory of Atkins⁹ described in Sec. II, which predicts that the radius is a function only of the ionic charge. The role of the mass was found to be minor by studying the difference between mobility of two isotopes of Ca.

Stimulated by these findings, we have revised the Atkins model to incorporate properties specific

to the core ion. In particular, we have included three new kinds of interaction with the surrounding fluid. These are the direct interaction with the central ion's valence electrons, an interaction associated with the absence or excess of He near the ion, and a van der Waals interaction with the core ion. Glaberson and Johnson⁶ suggested that the last of these might play a role in differentiating between the various species. The second should be considered even if the core ion is He^+ .

The induced dipole interaction proposed by Atkins, $V_A \propto r^{-4}$, between the positive charge and a He atom at r is the dominant determinant at large r of the fluid density $n(r)$. For $r \lesssim 10$ Å, the terms mentioned above become important. Our treatment will employ local thermodynamics for the most part, which assumes slow variation of $n(r)$ on an atomic scale. This deficiency is shared by most treatments of ions and vortices in helium. The

TABLE I. Ion parameters.

Species	R (Å) ^a	δR_{expt} (Å) ^a	C_I (10^{-60} erg cm ⁶) ^b	δR_{theor} (Å) ^d
He^+	7.9			
Na^+			2.8 ^c	0.11
K^+	8.35	0.45	8.7 ^c	0.28
Rb^+	8.4	0.5	10.35	0.32
Cs^+	8.40	0.5	15.60	0.43
Ca^+	7.1	-0.8	22.5	-0.64
Sr^+	6.7	-1.2	22.8	-0.78
Ba^+	6.1	-1.8	29.9	

^a From Ref. 6 at $T=1.18$ K.^b Derived from Eq. (21) unless otherwise noted, with numerical values from Refs. 7 and 8.^c Derived from the calculations of Ref. 19.^d Calculated with $s=0.5$ and the dielectric constant at solidification for the alkalis. Calculated from Fig. 4 with $R_h=4.7$ for Ca^+ and $R_h=4.6$ for Sr^+ , with $R_0=7.9$ Å.

qualitative success we and others achieve implies that our results incorporate the principal features of the real world.

In Sec. II we describe our model and results for the alkali ions. Sec. III discusses the alkaline earth ion case, which requires a somewhat different approach. Section IV offers conclusions from our study and suggests further experiments.

II. ALKALI IONS

We discuss first the approach relevant for treating the alkali ions, since the method differs only in part from that developed by Atkins and used by many workers.^{1,2,9} In the Atkins theory, the ion complex is taken to be a solid He sphere surrounding the positive core ion. This structure arises because of the induced dipole attraction

$$V_A(r) = -\alpha e^2 / 2\epsilon^2 r^4 \quad (1)$$

between the core ion and a He atom at r . The quantity α is the He atomic polarizability, and ϵ is the r -dependent dielectric constant. As r decreases the fluid pressure increases, until at some distance R the solid forms. The equation describing thermodynamic equilibrium within the He (both liquid and solid) is¹⁰

$$\mu = \tilde{\mu}[p(r)] + V(r). \quad (2)$$

Here μ is the chemical potential, which is a constant determined by the pressure p_0 at infinity, and $\tilde{\mu}[p(r)]$ is the chemical potential of a *uniform* system which has the local pressure $p(r)$. All thermodynamic quantities depend on the temperature T , which we take to be a given constant.

Integration of Eq. (2) from infinity to R with the relation $(\partial \tilde{\mu} / \partial p)_T = v$, the atomic volume, yields

$$-\int_{p_0}^{p_1(R)} v_1 dp = V(R). \quad (3)$$

The other condition which R must satisfy is that the pressure be discontinuous across the liquid-solid interface,

$$p_s(R) - p_l(R) = 2\sigma/R, \quad (4)$$

where σ is the liquid-solid surface tension.¹¹ We shall take σ to be independent of R for lack of better information. A nonzero value of σ means that the liquid pressure at the interface $p_l(R)$ exceeds the melting pressure p_m .

Atkins solved Eq. (3) with the potential given in Eq. (1). We suggest here two modifications of his method. First, as noted by Glaberson and Johnson,⁶ the presence of a core ion produces an

additional attractive potential of the van der Waals type,

$$V_I(r) = -C_I r^{-6}, \quad (5)$$

associated with the interaction between fluctuating dipole moments of the core ion and a He atom at r . The quantity C_I should differ from its free space value because of modification of the core ion's electronic structure by its environment, but such a refinement is beyond the scope of the present investigation.

The second revision of the Atkins approach is almost an order of magnitude more important than the first. This consists of including the additional attraction due to the high density solid surrounding the core ion. A He atom at r will experience an attractive force simply because there are more He atoms centered about $\vec{r}' = 0$ than are present in the uniform fluid, and each atom at \vec{r}' interacts with it through a potential energy

$$U(\vec{r} - \vec{r}') = -C |\vec{r} - \vec{r}'|^{-6} \quad (6)$$

if the separation $|\vec{r} - \vec{r}'| \geq 3.5 \text{ \AA}$. We are able to include this effect only in an approximate way because (a) the net potential at \vec{r}' depends on the density $n(r)$, which thus must be calculated self-consistently, and (b) our understanding of the properties of an inhomogeneous bose fluid is incomplete. Recent progress^{5,12,13} in this direction is encouraging, however, and we hope to improve the present treatment in the future.

The method we employ is to calculate the interaction $V_c(r)$ between the atom at r and the *excess* atoms in the solid associated with the higher solid density $n_s > n_l$. For simplicity we assume the solid to be of constant density n_s . The attraction (6) must be modified when r approaches R because of the presence of short range repulsion. We then adopt the following form for this interaction:

$$V_C(r) = \int_0^R (n_s - n_l) U(\vec{r} - \vec{r}') d\vec{r}', \quad r > R + d, \quad (7a)$$

$$V_C(r) = \text{const}, \quad R < r < R + d. \quad (7b)$$

The constant in (7b) is chosen to be the value of (7a) at $r = R + d$. Here $d = 2.56 \text{ \AA}$ is the hard core diameter in the He-He interaction and $C = 1.59 \times 10^{-60} \text{ erg cm}^6$ is the attractive part of the interparticle interaction to be used in (6).¹⁴ The choice (7b) is based on the fact that while atoms within a sphere of radius d about r provide a repulsion, all the others provide (albeit weaker) attraction. Of course this procedure is rather arbitrary, but we are looking only for qualitative trends.

The integral in (7a) can be performed analytically. With $z = \cos \theta$ and $\Delta n = n_s - n_l$,

$$V_C(r) = -\Delta n C 2\pi \int_0^R x^2 dx \int_{-1}^1 [x^2 + r^2 - 2rxz]^{-3} dz$$

$$= -\Delta n C \frac{\pi}{2r} \int_0^R [(r-x)^{-4} - (r+x)^{-4}] x dx,$$

$$r > R + d,$$

$$V_C(r) = -A(r^2 - R^2)^{-3}, \quad r \geq R + d, \quad (8a)$$

$$V_C(r) = -A(2dR + d^2)^{-3}, \quad R \leq r \leq R + d, \quad (8b)$$

$$A = 4\pi C \Delta n R^3 / 3.$$

Note that for $r \gg R$, $V_C(r) = -\Delta n C r^{-6}$, where $\Delta n = \frac{4}{3}\pi R^3 \Delta n$, the number of extra atoms in the solid, as should be the case.

Figure 1 shows $V_C(r)$ calculated with $R = 8 \text{ \AA}$ and $\Delta n = 7.5 \times 10^{21} \text{ cm}^{-3}$, the difference^{14,15} between the solid density at melting and the liquid density at saturated vapor pressure, both for $T = 1.86 \text{ K}$. One sees that $V_C(r)$ is about as large as the electrostrictive potential $|V_A(r)|$, except for $r > 14 \text{ \AA}$. The interaction V_I with the core ion is, in contrast, almost negligible. However, it is just this small term which discriminates between the radii of different alkali ions.

We do not calculate the ion radii directly, which would require use of the bulk liquid equation of

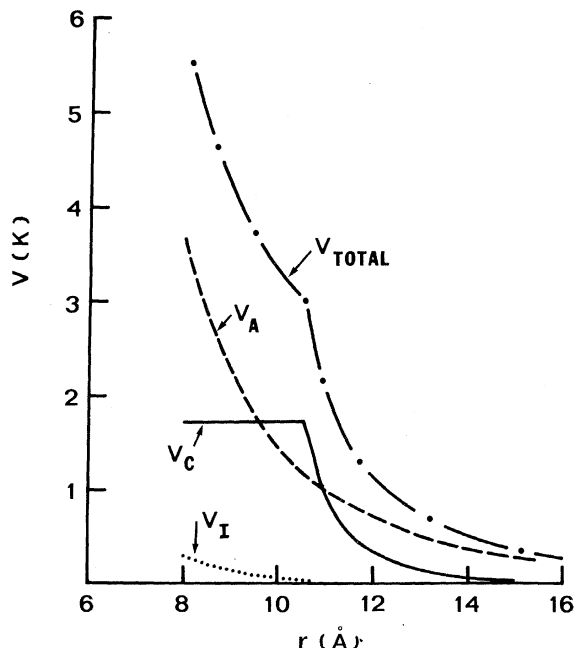


FIG. 1. Various components of the interaction between a He atom and an alkali-ion complex of assumed radius 8 \AA . (a) Dashed line, the induced dipole electrostrictive interaction of Atkins; (b) dotted line, the ion interaction $V_I = -C_I r^{-6}$ for the Rb^+ ion; (c) solid line, the interaction with the excess He atoms in the solid; (d) dash-dot line, the total interaction.

state, extrapolated above p_m . Instead, we determine δR , the difference between radii of an alkali ion and a He^+ ion. This is just due to the presence of V_I in Eq. (3); such a term is negligible in the He^+ case because of its very small polarizability. The calculation is easy if $\sigma = 0$, in which case the upper limit in the integral in (3) is the melting pressure. Let R_0 be the radius of a He^+ ion complex, so that from Eq. (3),

$$-\int_{p_0}^{p_m} v_i dp = V_H(R_0), \quad (9)$$

$$V_H(R) \equiv V_A(R) + V_C(R). \quad (10)$$

A similar set of equations holds for the alkali ion of radius $R_0 + \delta R$, except for the addition of V_I to the potential. Since the integral is the same for the two cases, we have

$$V_H(R_0) = V_H(R_0 + \delta R) + V_I(R_0 + \delta R). \quad (11)$$

Then to lowest order in δR , with $V'_H = dV_H/dr$,

$$\delta R \approx -[V_I/(V'_H + V'_I)]_{r=R_0}. \quad (12)$$

We now consider the case $\sigma \neq 0$. Then the He^+ ion and alkali ion, respectively, satisfy

$$-\int_{p_0}^{p_i(R_0)} v_i dp = V_H(R_0), \quad (13)$$

$$-\int_{p_0}^{p_i(R)} v_i dp = V_H(R) + V_I(R). \quad (14)$$

Subtracting (13) from (14) and assuming δR small give

$$V_I(R_0) = v_{ii}[p_i(R_0) - p_i(R)] - \delta R(V'_H + V'_I)_{r=R_0}, \quad (15)$$

where v_{ii} is the liquid volume per atom at the interface pressure $p_i(R_0)$. To determine the pressure difference in brackets, consider the equation for the alkali-ion case obtained from combining (4) with (2) evaluated at the interface for liquid and solid,

$$\bar{\mu}_l(p_i) = \bar{\mu}_s(p_i + 2\sigma/R). \quad (16)$$

Subtract from this an identical equation for the He, where $R = R_0$. The difference yields [using $(\partial \bar{\mu}/\partial p)_T = v$],

$$v_{ii}[p_i(R) - p_i(R_0)] = v_{si}[p_i(R) - p_i(R_0) - (2\sigma/R_0^2)\delta R], \quad (17)$$

$$p_i(R_0) - p_i(R) = 2\sigma n_{ii} \delta R / R_0^2 \Delta n_i. \quad (18)$$

Here $n = 1/v$ and Δn_i is the density discontinuity across the interface. Since R is smaller for He^+ than for an alkali ion, the interfacial pressure discontinuity (4) demands a higher $p_i(R)$ for the He^+ case. This difference in p_i is precisely the

right-hand side of Eq. (18), which we now insert in (15) to obtain

$$\delta R = -V_I[V'_H + V'_I - (2\sigma/R_0^2\Delta n_i)]^{-1}, \quad (19)$$

where all functions on the right-hand side are evaluated at $R=R_0$. Because of the pressure discontinuity (proportional to σ), the radius shift δR is larger than for the case $\sigma=0$ given in (12).

It is of interest to ask whether the possibility exists of Eq. (19) predicting an infinite δR due to a zero of the denominator. We shall show elsewhere¹⁶ that the denominator is proportional to $\Omega''(R_0)$, the second derivative with respect to R of the thermodynamic potential of the system. For stability this must be positive definite, so the suggested singularity does not ordinarily occur. However, if the system is supercooled above the melting pressure p_m , $\Omega''(R_0)$ will vanish eventually at a pressure p_c . This pressure is the absolute stability limit of the system with respect to solidification nucleated by the ion. At p_c , an ion created with radius R_0 will grow to infinite size, as Eq. (19) suggests. For liquid pressures intermediate between p_m and p_c , the system is metastable, but the presence of the ion facilitates the solidification transition.¹⁶

The present result (19) for δR offers the promise of presenting a stringent test of any model for the ion complex. This is because Δn_i and V'_H appear in a difference between two terms of the same order of magnitude, so δR is sensitive to their values. Unfortunately we do not know very reliably the coefficients C_I , which enter V , or the liquid-solid surface tension.^{2,11} For this reason we determine δR from (19) assuming various values of both R_0 and the parameter

$$s = (\sigma/\Delta n_i) \times 10^{22} \text{ (erg cm)}^{-1}. \quad (20)$$

A reasonable estimate of 0.5 for s comes from $\sigma \approx 0.1$ erg/cm² obtained by Schwarz^{2,17} and $\Delta n_i \approx 2 \times 10^{21}$ cm⁻³ as the density discontinuity across the melting curve. Figure 2 shows¹⁸ the resulting δR for the K^+ ion. Since the new term V_C , due to the high-density solid, has zero derivative at R_0 , it does not contribute to $V'_H(R_0)$. The value $C_I = 8.7 \times 10^{-60}$ erg cm⁶ was derived by subtraction of the induced dipole term, $-\alpha e^2/2r^4$, from the K^+ -He interaction calculation of Kim and Gordon.¹⁹ Similar curves for any ion can be generated by use of the appropriate C_I value. Unfortunately, these coefficients are not known very accurately. Glaberson and Johnson⁶ suggest the approximation

$$C_I = \frac{3}{2}(II_1/I + I_1)\alpha\alpha_1, \quad (21)$$

in which $I_1(I)$ and $\alpha_1(\alpha)$ are the ionization potential and polarizability of the alkali ion (He atom). An identical expression for the rare-gas-atom inter-

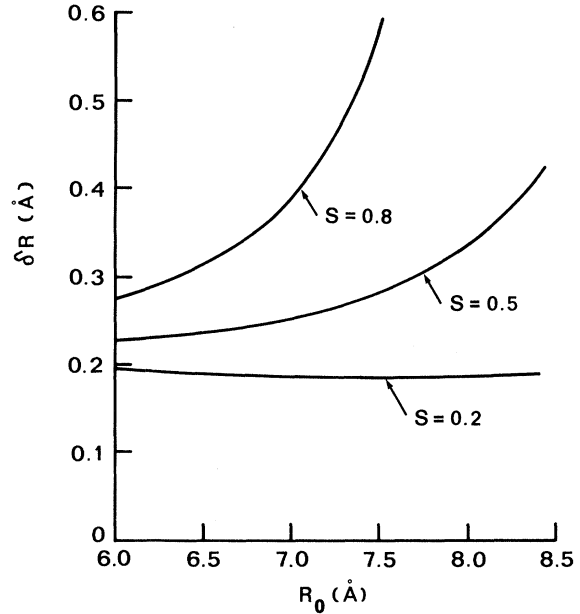


FIG. 2. Difference between radius of K^+ ion complex and that of He^+ (R_0) as a function of R_0 , for various values of the parameter $s = (\sigma/\Delta n_i) \times 10^{22}$.

action coefficient is accurate to within 20%. For K^+ -He, the result is 16% lower than that cited above. A further problem is a comparable uncertainty in the ionic polarizability.

These various uncertainties suggest the intriguing possibility that ion mobility studies can determine the asymptotic interaction coefficient C_I . This assumes that one has a good model of the He^+ ion structure, and we have indicated here that the Atkins model requires revision to be more self-consistent. However, the present scheme shows how R is related to C_I in a perturbative way, so studies with a variety of ions will permit such evaluations of both the model's validity and the C_I values.

With these limitations in mind, we take the estimate $s = 0.5$ mentioned above to calculate alkali ion radii shifts. The results are presented in Table I, in which a comparison is made with data of Glaberson and Johnson at $T = 1.18$ K, for which $R_0 \approx 7.9$ Å. The order of magnitude agrees very well. We would be surprised if the agreement were better because of the dubious values of C_I , and the arbitrariness of the choice for s . Certainly a measurement for Na^+ would be valuable in this context.

III. ALKALINE EARTH IONS

The positive alkali ion's outermost electrons fill a shell completely, so for $r \gtrsim 2.5$ Å the interaction with a He atom is attractive.¹⁹ The princi-

pal new factor relevant to the alkaline earth ion case is the presence of a remaining valence electron outside the filled shell. The valence electron's wave function ψ is somewhat more extended in space. This results in a repulsive exchange interaction with a nearby He atom. The situation is reminiscent of the case of electrons^{1,2} and excited-state atoms²⁰ in liquid helium, both of which involve a cavity within the fluid created by the repulsion. A feature unique to the electron "bubble" case is that the quantum kinetic energy associated with localization produces a very large cavity, with radius $R \approx 15 \text{ \AA}$.

We shall now determine the repulsive interaction V_e acting on the He due to this electron, and subsequently the effect of V_e on the radius R of the ion complex. In terms of the electron-atom scattering length a , the interaction for a He atom at r is^{5,21}

$$V_e(r) = (2\pi a\hbar^2/m) |\psi(r)|^2. \quad (22)$$

Values of $V_e(r)$ obtained from a Hartree-Fock calculation²² of ψ for Ca^+ , Mg^+ , and Sr^+ are shown in Fig. 3. The potential V_e is essentially infinite, relative to other energies in the problem, for $r < R_1$, and is negligible somewhat beyond R_1 . To a good approximation we may simply take V_e to be a hard-core interaction with the ion, of "radius" R_1 . An estimate for R_1 from Fig. 3 would be 3.9 \AA for Sr^+ and 3.8 \AA for Ca^+ . The hard core for Mg^+ is much smaller, $R_1 \approx 2 \text{ \AA}$. No wave function is available for Ba^+ .

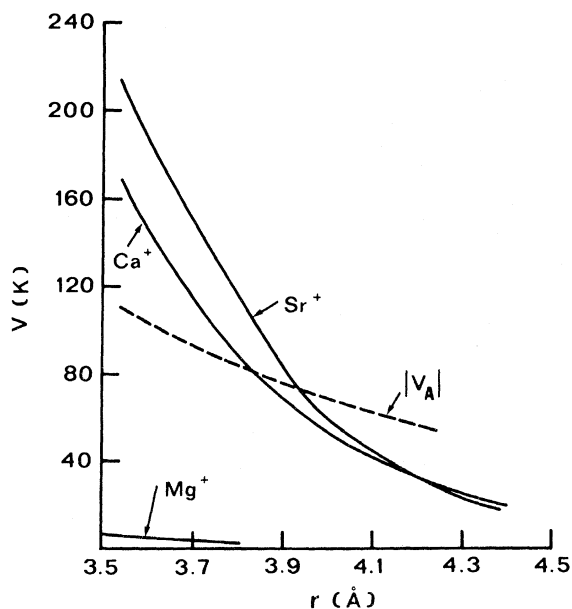


FIG. 3. Repulsive interaction energy V_e due to valence electron of alkaline earth ions, compared with Atkin's interaction V_A .

The local thermodynamic treatment based on Eq. (2) cannot determine correctly the response of the fluid to such a rapidly varying potential as $V_e(r)$. In particular, the vanishing of the fluid wave function at R_1 means that the density is small within a region $R_1 + b$. Liu *et al.*²³ have calculated the density of a hard-sphere Bose fluid near a wall (without an attractive potential) and find that $n < \frac{1}{2}n_0$ within a range $\approx 0.5 \text{ \AA}$. As a model of the present spherical problem, we shall take $n = 0$ for $r < R_h \approx R_1 + 0.5 \text{ \AA}$.

We next determine the effect of the "hole" of radius R_h on the density for $r > R_h$. The hole can be treated in the same approximate way as the excess density in the alkali ion case, except that the absence of atoms produces a *repulsion* here. Specifically, the potential at r due to the hole is, by analogy with Eq. (8),

$$V_h(r) = B(r^2 - R_h^2)^{-3}, \quad r \geq R_h + d, \quad (23a)$$

$$V_h(r) = B(2dR_h + d^2)^{-3}, \quad R_h < r \leq R_h + d, \quad (23b)$$

$$B = \frac{4}{3}\pi n_1 C R_h^3. \quad (24)$$

We now want to calculate δR , the radius shift relative to R_0 for He^+ . In the present case, the shift is due²⁴ to two new terms, V_h and V_I . The same procedure used to derive (19) can be applied, yielding

$$\delta R = -(V_h + V_I)[V'_H + V'_I + V'_h - (2\sigma/R_0^2 \Delta n_1)]. \quad (25)$$

Note that the first factor involves a competition between the $V_I (< 0)$, which tends to increase R , and $V_h (> 0)$, which tends to decrease R . Figure 4 shows the results for δR . We observe that even though V_I is larger here than for the alkali case, the hole repulsion dominates this term, so $\delta R < 0$. Because δR depends on whether $R > R_h + d$ [because of Eq. (23)], we have simplified evaluation of δR by neglecting the term V'_h in our calculations. This is not a serious approximation, one finds, but means that the calculated values of $|\delta R|$ are lower limits to the true value (since $V'_h < 0$). With this in mind, one notes the magnitudes of δR shown in Fig. 4. Since our estimate of C_I is about the same for Sr^+ and Ca^+ ($2.25 \times 10^{-59} \text{ erg cm}^6$), the same curves are applicable to either ion. However, the specific value of R_h is different for the two cases. Thus we expect $R_h^{\text{Sr}} \approx 4.7$ and $R_h^{\text{Ca}} \approx 4.6 \text{ \AA}$, from the preceding discussion. We observe from Fig. 4 that the difference between δR for the two species should be of order 2–3 times the difference in R_h . Thus Sr^+ would be expected to be about 1 \AA smaller than He^+ , and Ca^+ should be about 0.7 – 0.8 \AA smaller. This compares very favorably with 1.2 and 0.8 \AA ,

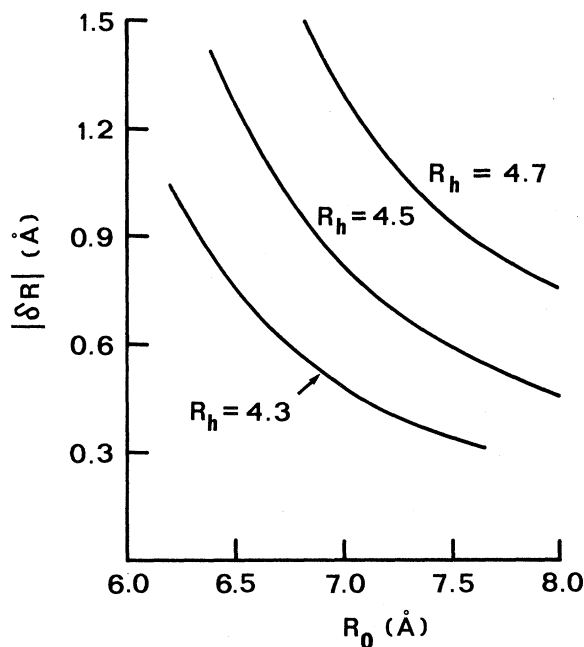


FIG. 4. Lower limit to the absolute value of the difference between an alkaline-earth ion radius and that of He^+ (R_0) for various values of the hole radius R_h (in \AA).

respectively, for $|\delta R|$ found by Glaberson and Johnson at $T = 1.18$ K.

Even apart from uncertainty in the experimental values in R , this successful comparison with the theory should not be taken as a verification of the model in any but its qualitative features. This becomes apparent from Fig. 5, in which only the full curve has been calculated; the dashed curve is schematic. The upper curve has been calculated without the hole repulsion term V_h . The solid appears when $\rho \geq \rho_m = 0.18$ g/cc, the liquid density at solidification (the precise value of R depending on σ). The lower full curve includes V_h ; note that the compression is smaller than in the former case for $r \geq 6$ \AA . We have indicated that the density must fall to zero at about 4.7 \AA . We can hardly expect a solid to form in the narrow interpolation region (4.7–6 \AA) of width about equal to the hard-core radius $\frac{1}{2}d$ of a He atom. Thus the alkaline-earth ion is rather like the electron bubble, except that the density exceeds the asymptotic density over a rather extended region.

In summary, we have noted that the alkaline earth ion's valence electron produces a hard-core potential at $R_1 \sim 3.9$ \AA , which produces a low He density for $r \lesssim 4.7$ \AA . The absence of He from this region leads to an effective repulsion for $r > 4.7$ \AA , so the density does not become high enough to produce a solid shell. The radius R_h

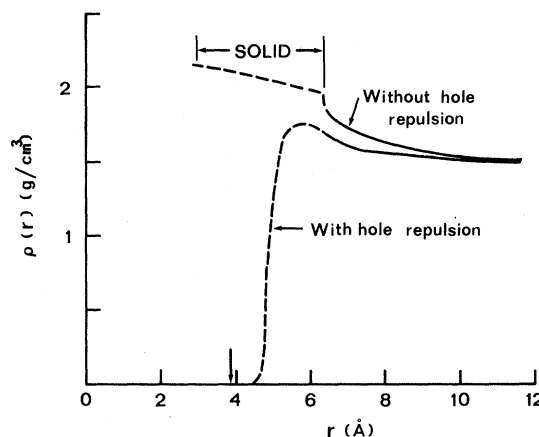


FIG. 5. Qualitative depiction of role of effective repulsion in alkaline earth ion complex. The solid parts of the curves have been calculated with (without) this term. The dashed curves are suggestive extrapolation. The arrow notes the position of the hard-core potential due to the Sr^+ ion's valence electron.

is somewhat smaller in the Ca^+ case, so this effect is not so pronounced as for Sr^+ ; thus the density becomes *larger* in the region $r \geq 5$ \AA in the former case. This appears experimentally as a larger R for Ca^+ than for Sr^+ .

These effects are negligible for Mg^+ because the hole is extremely small. Mg^+ would represent a good test of the present model of ion structure.

IV. CONCLUSIONS

We have proposed that a number of refinements of the Atkins model are appropriate. Even for the He^+ case, the term V_c associated with the attraction due to the high-density solid should be included in a first order self-consistent theory. For the ions, one must include as well the dispersion interaction between the ion and the He atoms. Finally, the alkaline earth ions require an analysis of the hard-core interaction with the He atoms. The latter produces a large cavity of radius 4–5 \AA surrounded by compressed, but not solidified, He.

Unfortunately, our treatment has employed relatively crude approximations, especially for the alkaline earth case. Nevertheless we have achieved qualitative agreement with the results obtained experimentally by Glaberson and Johnson. We believe that this problem represents a challenge to the theory of inhomogeneous bose fluids, and hope to return to it with a more sophisticated approach in the future.

We should like to suggest that experimental study of impurity ions can be of considerable value. The ion potential represents a perturbation, and the measured shift in quantities such as the

mobility and effective mass can be compared with theory to test the latter. Especially valuable would be use of the prediction of Sec. II, that the radius shift δR is a direct measure of the asymptotic ion-He interaction. A particularly interesting experiment would be an effective-mass measurement via the technique of resonance absorption of ions bound near the liquid-vapor interface.^{25,26}

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