that the electron is ahead of the proton on leaving the foil by $\sim\frac{1}{2}a_0$. Uncertainties in absolute initial phase become relatively unimportant when differences in phase $\Delta\varphi$ from different target gases are compared. We find, for example, that $\varphi_{O_2} - \varphi_{Ar} = -0.1 \pm 0.3$ rad, meaning that within errors the phase angles φ in the form $A\cos(\omega t - \varphi)e^{-\Gamma t}$ are very nearly equal for these two very different target gases. As a function of beam energy, $\varphi_{He} - \varphi_{Ar} = -0.4 \pm 0.2$, 0.0 ± 0.2, and 0.5 ± 0.4 at 110, 190, and 290 keV respectively, exhibiting a velocity dependence of φ so weak as to be nearly within the 1σ (1 standard deviation) statistical fitting errors quoted in this range of beam energies. Within these errors, φ has also been shown to be nearly independent of target gas. It is quite possible these dependences will be stronger at lower, more adiabatic collision velocities.

The present method thus provides an effective tool for sorting out intrinsically solid-state surface effects on atoms excited in foils *vis-à-vis* gases. Additionally, theories of ion-atom charge transfer may be tested by examining the relative phases of opposite-parity capture amplitudes.

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Charged Droplets in Cryogenic ^{4}He Vapor

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We have measured the mobility of positive ions in ^{4}He vapor for temperatures between 1.3 and 2.0 K and for saturation ratios between 0.1 and 1.0. We present a model which relates the size of a charged droplet to its mobility and find good quantitative agreement with our data when we calculate the size of the droplet which forms about the ion with classical macroscopic thermodynamic arguments. The radius thus obtained ranges from 7 to 9 Å.

When a positive ion is formed in a vapor the polarization force on the surrounding atoms induces a pressure gradient about the charge. At some distance R, the increased pressure will equal the vapor pressure over a curved surface of that radius and thus a droplet of radius R should form. An equation relating the size of the droplet to the saturation ratio (p/p_{sat}) and temperature was first obtained by Thompson[1] by applying arguments from macroscopic thermodynamics on a microscopic scale.[2,3] When the vapor is ideal and the liquid dielectric constant is nearly unity, the (modified) Thompson equation may be written

$$kT\ln(p/p_{sat}) = 2\sigma/n_l R - \alpha e^2/2R^4, \qquad (1)$$

where σ and n_l are the bulk values of surface tension and liquid density, and α is the atomic polarizability. There are at least two reasons why it is important to try to verify this prediction directly. The first is that similar arguments are central to classical nucleation theory but in that case their confirmation must be quite indirect.[2-5] The second is that if such microscopic droplets are shown to exist they will present a valuable opportunity to study the effect of finite size on the thermodynamic properties of a fluid. Helium vapor provides an excellent system in which to study droplet formation because its small surface tension at low pressures favors a large effect. In addition, there is already some tentative evidence from ac mobility measurements[6] that drops form in the saturated vapor at 4.2 K. We also note the productive analogy with the Atkins model of positive ion structure in liquid helium.[7,8]

In order to determine whether the predicted droplets do in fact form, we have chosen to study the low-field mobility of positive ions in ^{4}He at low pressures and temperatures.[9] Under these conditions the vapor may be considered ideal[10] to that Eq. (1) should hold. In addition, if the density is small only binary collisions are important in determining the mobility, μ. In this case it can be shown[11] quite generally that if the interaction between the ion and a vapor atom is independent of the vapor density, n, at constant temperature the reduced mobility $\mu_r \equiv (n/n_{\rm ref})\mu$ will be constant ($n_{\rm ref} \equiv 2.69 \times 10^{19}$ cm^{-3}). On the other hand, if μ_r is observed to depend on density it will provide strong qualitative evidence of a growing droplet.

We have measured the mobility by a pulsed, time-of-flight method, the details of which will be given elsewhere. Ions are produced in the vapor by a tritium β source, and are electrically gated into a 10-cm uniform-field region. The transit time is measured as a function of both electric-field and pulse amplitude to ensure that we are in the low-field region and that space-charge fields are negligible. The resolution of our mobility measurements is ±1%; the estimated absolute accuracy of ±4% arises from uncertainty in the effective length of the drift region. The cell pressure, p, and the vapor pressure of the surrounding liquid helium bath, $p_{\rm sat}$, are measured with a capacitance manometer to an accuracy of 1%.

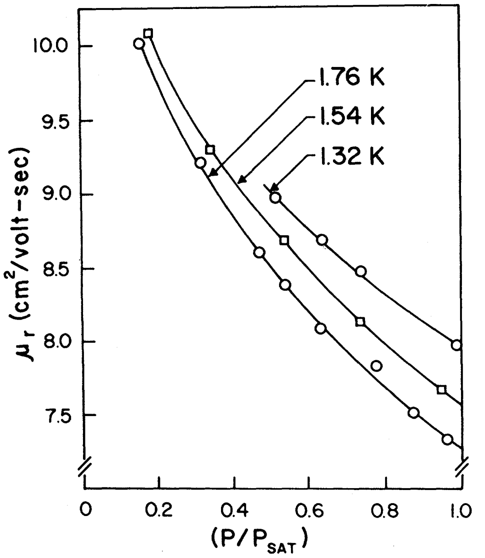

FIG. 1. Experimental reduced mobility μ_r vs saturation ratio ($p/p_{\rm sat}$), at three different temperatures.

Representative experimental measurements of the reduced mobility versus the saturation ratio are shown in Fig. 1. The obvious decrease of μ_r with increading pressure provides unambiguous evidence of a density-dependent ion-atom interaction, and thus of droplet growth. Previous measurements by Henson[12] of mobility at higher temperatures and pressures do not clearly show this behavior. This may not be surprising, however, since as we will show later, at the densities he studied the binary-collision hypothesis is almost certainly invalid.

In order to obtain quantitative information about the size of these droplets it is necessary to adopt a model relating to the mobility to an appropriate ion–vapor-atom cross section. When only binary collisions are important, the Chapman-Enskog expression for the reduced low-field mobility is[11]

$$\mu_r = (3e/16n_{\rm ref})(2\pi/m_r kT)^{1/2}/\bar{\Omega}^{(1,1)}, \qquad (2)$$

where m_r is the reduced mass (indistinguishable from the mass of helium atom in our case), and the collision integral $\bar{\Omega}^{(1,1)}$ is a suitably averaged momentum-transfer cross section. While this expression is valid in general only for elastic collisions, it applies in some situations to inelastic collisions also.[9,13] Consequently, we will define an experimental effective radius, $b_{\rm expt} = (\bar{\Omega}^{(1,1)}/\pi)^{1/2}$ in terms of the collision integral obtained by applying Eq. (2) to our data. The result is displayed in Fig. 2 as a function of saturation ratio for two different temperatures, where it may be compared with the theoretical drop size R obtained from Eq. (1). An immediate qualitative observation is that the drop "appears" much larger than it ought to be.

We can understand this apparent discrepancy by considering the nature of the interaction potential between a vapor atom and a charged droplet. For reasonably large separations it will have two terms. The first is the polarization potential arising from the central charge, and the second is the van der Waals potential[14] ($-c_6/r^6$) between the vapor atom and each of the remaining atoms in the drop. Assuming pairwise additivity we can integrate over a uniform drop of radius R to obtain the model potential[15]

$$u(r) = -C/r^4 - AR^3/(r^2 - R^2)^3, \qquad (3)$$

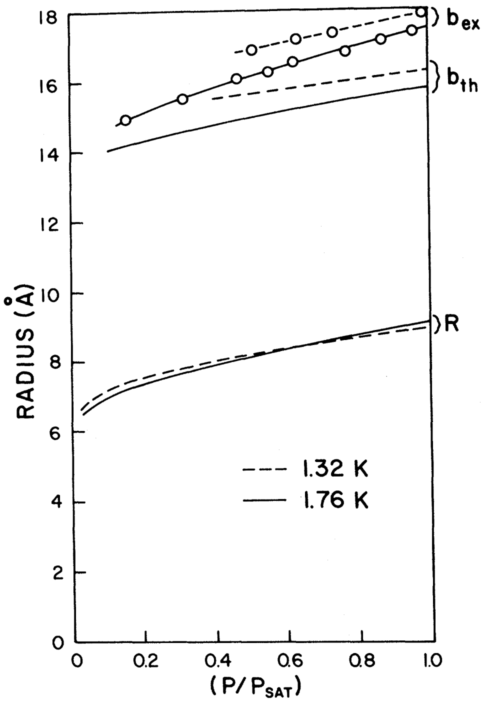

FIG. 2. Calculated droplet radius R, experimental effective radius b_{expt}, and theoretical effective radius b_{theor}, vs saturation ratio at two different temperatures.

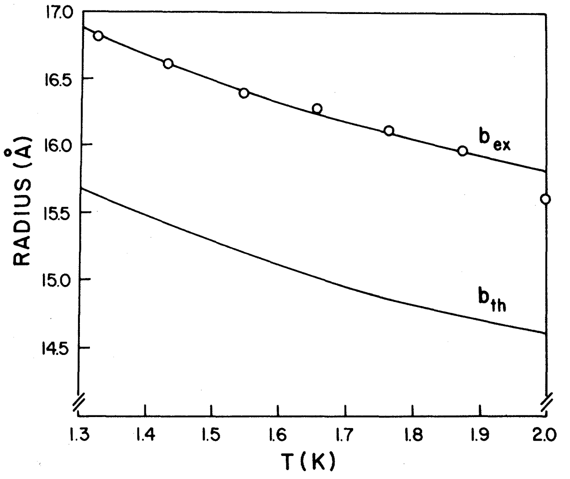

FIG. 3. Experimental effective radius b_{expt}, and theoretical effective radius b_{theor}, vs temperature for the fixed saturation ratio $p/p_{\text{sat}} = 0.5$.

where $A \equiv \frac{4}{3}\pi n_l c_6$ and $C \equiv \alpha e^2/2$.[16] The classical trajectories in this "sharp-edged" potential are characterized by a rapid transition from small deflections to orbits which spiral into the droplet surface as the impact parameter decreases. For example, when $R = 9$ Å and the incident energy is 4 K an atom will be deflected by less than 30° if its impact parameter is greater than 15.86 Å, yet it will spiral into the surface if its impact parameter is less than 15.33 Å. Recent surface scattering measurements[17] indicate that an atom incident on the surface of bulk liquid helium is almost certainly absorbed. It is thus reasonable to assume that incident vapor atoms which reach the droplet surface are also absorbed and thermalized. To compensate the drop must be evaporating at a rate which maintains it size and internal energy relatively constant. Since evaporation is isotropic in the droplet rest frame, it produces no net change in momentum of the core droplet. The net momentum exchange for the entire process should then be on average nearly the same as if every incident atom which reaches the surface were scattered randomly but elastically. Consequently, we will adopt the following simplified classical model of the scattering process. We will treat exactly the momentum exchange from trajectories which do not intersect the droplet surface, and we will assume that those which do intersect it result in random isotropic elastic scattering. With these assumptions we can obtain a theoretical value of the collision integral, $\bar{\Omega}_{\text{theor}}^{(1,1)}$, in terms of the drop radius R and the temperature by evaluating numerically the three usual integrals[11] for the deflection angle, the momentum-exchange cross section, and the collision integral. In order to compare the model with our experimental results we first evaluate the drop size from Eq. (1) for a particular temperature and saturation ratio. We then perform the triple integration to obtain $\bar{\Omega}_{\text{theor}}^{(1,1)}$ for this drop size and temperature. Finally, we define the theoretical effective radius, $b_{\text{theor}} \equiv (\bar{\Omega}_{\text{theor}}^{(1,1)}/\pi)^{1/2}$ and plot it in Fig. 2 for comparison with b_{expt}. The theoretical curves thus obtained are low in magnitude by roughly 8%, but the agreement as to pressure dependence is quite good. In particular, the change in slope with temperature mirrors the experimental results nicely. In order to display the temperature dependence more clearly we have plotted in Fig. 3 the results from these and several other temperatures for a constant saturation ratio of 0.5. Apart from a difference in magnitude of 1.3 Å the agreement is excellent. It must be emphasized that the model as presented has *no* adjustable parameters, and that 1.3 Å is only slightly greater than the effective radius of a helium atom.

It is appropriate at this point to check whether the binary-collision hypothesis is internally consistent with these results. If we take b_{expt} as a number characterizing the range of the interaction, we can define an interaction volume, V_I, as a sphere of this radius. One reasonable criterion for the validity of the hypothesis is that the vapor density should be low enough so that the mean number of atoms in any volume V_I, nV_I, is less than 1. All the data we have presented above meet or exceed this criterion if we take $b_{\text{expt}} = 16$ Å. In addition, we have observed that other data obtained at higher densities show qualitative departures from the predictions of our model. None of the measurements described by Henson[12] meet this criterion and thus our model should not apply to them.

We feel that the good agreement between our calculated and experimental mobilities, particularly as to their dependence on pressure and temperature, provides convincing evidence that the central features of the model are correct. In particular, it is reasonable to conclude that droplets form with radii $R(p, T)$ close to that predicted by the classical Thompson equation, and that their dominant interaction with the vapor is through the van der Waals or dispersion force.[18] It is tempting to try to improve the model in order to account for the difference of 1.3 Å remaining between b_{theor} and b_{expt}. There are certainly several effects which have been neglected and which could result in changes of this order. Among them are curvature dependence of the surface tension, a diffuse surface profile, density variations within the drop, and dynamical deformations of the drop. Probably most important are quantum mechanical effects in the scattering process.[19] It seems unlikely, however, that a more sophisticated model will allow us to extract with confidence much more detailed structural information from simple mobility measurements. Such information is probably better acquired by more discriminating experimental methods than by more detailed analysis.

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