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THE CHARGED POINT DEFECT IN CLASSICAL FLUIDS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

Dah-Yang Kuan, B. Sc., M.Sc.

* * * * * *

The Ohio State University
1980

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CHAPTER I
INTRODUCTION

The behaviors of two different kinds of charged point defect in classical fluids are investigated in the present study. In part A, we focus our attention on the problem of an excess electron in rare gas fluids. Localized excess electron states in these gases will be examined within the density functional formalism and the electron bubble or droplet model. In part B, the clustering of atoms around a positive ion impurity in a classical fluid will be examined using both theories and computer simulations. The specific system considered is a potassium ion in argon gas.

A. Electrons

For the past few years much work has been done with the goal of understanding the physics of excess electron states in nonpolar fluids, especially those in rare gas fluids. The investigations have been focused on the elucidation of observed small electron mobilities on the order of $10^{-2} - 10^{-3}$ cm$^2$/volt-sec in liquid helium, dense gaseous helium, and liquid neon. Recently it also has been found that in gaseous xenon near the critical point there is a sharp decrease in the electron mobility.
This kind of low mobility electron state has been classified as a localized state in contrast to the quasi-free or extended electron states which are characterized by large mobilities on the order of $10^1 \text{ - } 10^4 \text{ cm}^2/\text{volt-sec}$.

Different models have been proposed to describe the localized electron states in helium and neon. The most widely accepted model is the so-called "bubble" model, according to which the electron creates a cavity or bubble around itself in the fluid and then becomes trapped within this bubble. Earlier calculations using this model predict that excess electron states should be localized in liquid helium and should be quasi-free in liquid argon. These results seem to be consistent qualitatively with experimental observations.

As for the localization of the electron in xenon near the critical point, it is believed to be small fluctuations in the local density of the fluid which serve as trapping centers for the electrons. A "droplet" model has been suggested to describe these localized electron states in highly-polarizable gases and it has been found that the localization of electrons in xenon is possible.

From the thermodynamics the condition that electron bubble (or droplet) states be stable relative to quasi-free electron states is that the free energy of the former be lower than that of the latter. A relatively simple and
A qualitatively correct theory for calculating the quasi-free electron states in monatomic fluids has been given by Springett, et al.\textsuperscript{20,26} The Wigner-Seitz method\textsuperscript{27} which assumes that each fluid particle occupies a sphere of volume equal to the inverse particle density was used. Also, they chose the interaction between the electron and a fluid atom to include the long-range attractive polarization potential and a short-range hard-core potential. The effective potential inside the Wigner-Seitz sphere is then the sum of the bare electron-atom interaction and the mean interaction produced by the other atoms of the fluid. Finally, the lowest energy quasi-free electron state is obtained by solving the one-electron Schrödinger equation within the sphere with boundary condition that the derivative of the wavefunction vanishes on the surface of the sphere.

A variety of procedures\textsuperscript{20,21} have been previously adopted to estimate the free energy of the fluid with a bubble state in it. Most of these theories have assumed that there is an abrupt boundary between the bubble and the fluid with the fluid density equal to zero inside and equal to the density of uniform fluid outside. The formation of the electron bubble states in the fluid will produce a free energy change which includes the ground state energy of the localized electron, the surface and volume free energy of
the bubble, and the polarization energy of the medium surrounding the bubble. Hence, the condition for a stable electron bubble state is that this free energy change is less than the free energy of an electron in a quasi-free state. The possibility of forming electron droplet states in rare gases was first investigated by Khrapak and Yakubov using the optimal-fluctuation method. They neglect the interatomic interaction and get a qualitative conclusion that the localization of an electron in xenon gas is possible through the formation of the droplet state.

Recently Ebner and Punyanita (Hereafter referred to as I) have applied the density functional formalism previously developed by Ebner, Saam, and Stroud to these systems. The correlations in the interacting fluid have been built into the theory which enables them to generate monotonic or possible oscillatory fluid density profiles around the bubble or droplet. The interparticle interaction has been chosen to be the Lennard-Jones (6-12) potential and the correlations between fluid particles have been treated using the Percus-Yevick approximation. A simple contact potential has been chosen for the electron-atom interaction. This choice has simplified the calculation to a great extent but fails to reveal the true significance of the polarization potential. Their results qualitatively agree with the previous theories in that localized bubble states are found
in dense helium gas and in liquid neon close to the liquid-gas coexistence curve. They also predict that the localized bubble states in neon become unstable at sufficiently large liquid densities. This contradicts previous findings using the ideal gas model\textsuperscript{31,32} that electron bubble states are stable even at higher liquid densities. In the search for droplet-like localized states, they find no such states in any rare gases and thus fail to give any support to the recent claim by Huang and Freeman\textsuperscript{13,14} that the observed decrease in the excess electron mobility in xenon vapor near the critical point is a consequence of such droplets. However, if the scattering length in the contact potential is given a plausible density dependence as suggested in Ref. 14, then droplet states will result.

The purpose of the present study is to improve the result in I by changing the electron-atom interaction from a simple contact potential to a physically more accurate pseudo-potential which includes a short-range core repulsion and a long-range polarization interaction. In fact, the short-range core potential should be taken to be the self-consistent Hartree-Fock potential. However, pseudo-potential theory uses the orthogonality requirements, imposed between the core orbitals and an excess electron wavefunction by the Pauli exclusion principle, to replace
the attractive Hartree-Fock potential by a fictitious potential. The effect of this is to eliminate the large oscillations of the excess electron wavefunction inside the core region and replace them by a smooth pseudo-wavefunction. Also, it has been shown from low-energy electron-atom scattering cross sections that the core pseudopotential must be positive for rare gas atoms.\textsuperscript{26,33} The effective hard core radius for rare gas atoms can be determined using low-energy electron-atom scattering phase shifts. Next, the electron-atom polarization interaction is screened in the liquid by the contribution to the local field induced from neighboring atoms. Numerical calculations performed by Lekner\textsuperscript{34} for liquid argon show that at distances greater than three halves of the atomic hard core diameter, the screening function can be accurately approximated by the Lorentz local field screening function.\textsuperscript{35}

For the electron-atom interaction we shall use a pseudopotential of the form,

\[ V(r) = \left(\frac{e^2}{2a_0}\right) \left[ (\sigma_e/r)^N - \alpha a_0/r_4 \right] \]  \hspace{1cm} (1-1)

where \( \alpha \) is the polarizability and \( \sigma_e \) and \( N \) are parameters to be determined so that first term will be an effective core potential. Thompson\textsuperscript{36} carried out phase shift calculations for electron scattering by atomic neon and argon
including the effect of polarization in a modified Temkin approximation. As discussed in Appendix A, we believe that the electron-atom scattering in classical fluids is dominated by the $l=0$ partial wave. Hence, the parameters $N$ and $\sigma_e$ will be determined in such a way as to reproduce the low energy part of the s-wave phase shifts.

In Appendix A we outline the procedures for fitting the parameters $N$ and $\sigma_e$. The detailed calculations of the lowest energy extended electron states are given in Appendix B. The density functional formalism used to treat the nonuniform fluid produced by the localized electron states is described in Section A of Chapter II. Results of these calculations are given in Chapter III. Finally, Chapter V comprises a summary and conclusions for both electron and ion systems.

B. Alkali Ions

The formation of alkali ion clusters in rare gases is mainly a consequence of the strongly attractive ion-atom polarization interaction. This can be seen from the large well depths for the ion-atom interactions as compared with those for the atom-atom interactions. For example, the well depth for $K^+ - Ar$ is about 0.12 ev, whereas for $Ar - Ar$ the value is only 0.012 ev. Alkali ion-rare gas clusters also are relatively simple to investigate theoretically in that the atoms are non-polar and there is no charge transfer when
clustering takes place. Thus we need not include complicated considerations concerning the detailed orientations of the molecules in the cluster, as has been the case in the previous Monte Carlo calculations on e.g. the ion-water aggregation by Kistenmacher et al. 38

In early experiments which measured the mobility of alkali ions in rare gases, the ion clusters were first observed as contaminants. 39-41 Subsequent experiments on the drift velocity of $K^+$ ions conducted by Beyer and Keller in 1971, 42 McDaniel et al in 1972, 43 and Thomson et al in 1973, 44 however, showed that a significant amount of clustering on $K^+$ ions takes place in nitrogen and argon at room temperature. In addition, small traces of clustering of a single molecule of CO₂, NO, CO, O₂, D₂, Ne, and He on $K^+$ ions were observed by the third group 44 when the drift tube was filled successively with the indicated gases.

Recently, a self-consistent formalism was developed by Etters et al 45 to determine the thermodynamic properties of $K^+$ - Ar clusters based on a many-body potential and Monte Carlo simulations. The detailed N-body potential, where N is the total number of particles in the system, includes the inductive and reactive interactions between the ion-atom and atom-atom pairs. The system is reactive in that the ion induces electric dipoles on the neutral atoms, and they modify not only the ion-neutral atom potential but also the interaction between neutral atoms.
Their calculations have shown that at low temperatures clusters form crystallites and when the temperature is increased a melting transition occurs. The crystallite structures were determined from the expectation values of the particle position vectors. Because of the complexity of the formalism, the number of neutral molecules in the system has been constrained to be below twelve.

The behavior of ions in classical fluids is quite different from that of electron as considered in part A. Most important of all, the ion has a much larger mass; usually it is comparable with that of fluid atoms. Therefore ions in the rare gas fluid can be regarded as a two-component system and the properties of ion-clusters then may be explored using the existing approximations for mixtures. One such approximation is a combination of the Percus-Yevick theory and the Ornstein-Zernike equations for a mixture. This approximation has been used previously by Perram and White; Henderson, Abraham, and Barker; Waisman, Henderson, and Lebowitz; and Saam and Ebner to treat various wall-fluid interface. The last authors have referred to this approximation as linearized Percus-Yevick (LPY) theory and the same name will be adopted throughout this work.

In the application of the LPY theory to the ion-rare gas system, we have assumed that the density of the ions approaches zero and there are no correlations between ions,
or no Coulombic interactions between ions need be considered. In the present study, we have limited our investigation to a $K^+ - Ar$ system. The interatomic interaction is still chosen to be the Lennard-Jones (6-12) potential. As for the $K^+ - Ar$ interaction, Budenholzer, Gislason, and Jorgensen used an $N-6-4$ potential of the form

$$V(r) = \frac{C_N}{R^N} - \frac{C_6}{R^6} - \frac{C_4}{R^4}$$

(1-2)

to represent this interaction. The parameters are determined from the total cross sections for $K^+ - Ar$ scattering. Their results are in good agreement with the previous results given by Kim and Gorden using a simple theoretical model. Here we shall use this simple potential for the $K^+ - Ar$ interaction in our calculation.

To test the validity of the LPY theory in this case, we also include computer experiments in the present work. The computer simulations were done using the grand-canonical-ensemble Monte Carlo method described by Adams. A more detailed review article on the Monte Carlo studies of simple classical fluids has been given by Wood.

The outlines of the LPY theory and the Monte Carlo simulation are given in Sections B and C of Chapter II, respectively. The results of these two methods are
compared in Chapter IV. Summary and conclusions are given in Chapter V.
CHAPTER II

FORMALISM

The theories used in this work are density functional, the so-called linearized Percus-Yevick equation, and computer simulation using Metropolis' Monte Carlo formalism. The density functional theory has been used mainly in treating an electron moving in a classical fluid. The models of the electron bubble and droplet are adopted here to account for the decrease in the electron mobility in the fluid at certain densities and temperatures. In the positive ion case, due to the lack of accurate correlation functions for systems with large density variations, the density functional has been limited to use in the low density gas region. Thus the linearized Percus-Yevick (LPY) equation and Monte Carlo (MC) calculation have been set up to deal with a positive ion in the fluid. The possibility of forming an ion-cluster is investigated. Because of the independent nature of these theories, we have separated this chapter into three sections, each dealing with one theory.

* This is the name given by Saam and Ebner, Ref. 49, to an approximate method in which the interaction of the fluid with the external potential is treated in the Percus-Yevick approximation.
A. Density Functional Theory

Given a system consisting of a classical fluid in the presence of an external potential \( v(\mathbf{r}) \) which couples to the fluid particle number density \( n(\mathbf{r}) \), the density functional theory states that there exists a functional \( \tilde{\Omega}[n] \) of \( n(\mathbf{r}) \) such that the minimum value of

\[
\Omega = \tilde{\Omega}[n] + \int d^3 r v(\mathbf{r}) n(\mathbf{r})
\]  

(2-1)

with respect to variation of \( n(\mathbf{r}) \) at constant \( \mu, T, V, \) and \( v(\mathbf{r}) \), is the equilibrium grand free energy of the system.\(^{55,56}\) The equilibrium number density is the final configuration \( n(\mathbf{r}) \) which minimizes \( \Omega \).

The minimum of \( \Omega \) is determined by the condition that

\[
\frac{\delta \Omega}{\delta n(\mathbf{r})} = -v_n(\mathbf{r}) + v(\mathbf{r}) = 0 \quad (2-2)
\]

where

\[
v_n(\mathbf{r}) = -\frac{\delta \tilde{\Omega}(n)}{\delta n(\mathbf{r})} \quad (2-3)
\]

and the variations are at constant \( \mu, T, V, v(\mathbf{r}) \) and \( \mu, T, V, \) respectively. Note here that, for a given \( n(\mathbf{r}) \), \( v_n(\mathbf{r}) \) is just the external potential that would produce the same number density \( n(\mathbf{r}) \).
Recently an exact density functional that is applicable to the classical system considered here has been fully developed by Saam and Ebner.\textsuperscript{57}

They start with the formal definition of the direct correlation function $C(\mathbf{r}, \mathbf{r}')$, which is,\textsuperscript{58} if one uses Eq. (2-3),

\begin{equation}
\delta v_n(\mathbf{r}) = - \beta^{-1} \left[ \frac{\delta(\mathbf{r}-\mathbf{r}')}{n(\mathbf{r})} - C(\mathbf{r}, \mathbf{r}') \right], \tag{2-4}
\end{equation}

with $\beta^{-1} = kT$, and functionally integrate it to obtain $v_n(\mathbf{r})$. When constructed in this way, the functional gives the grand free energy relative to that of some reference state with density $n_0(\mathbf{r})$. Further simplification can be achieved by choosing $n_0(\mathbf{r})$ to be a constant, $n_0$, and by parametrizing densities $n'(\mathbf{r}; \alpha)$ intermediate between those of the reference and final states as

\begin{equation}
n'(\mathbf{r}; \alpha) = n_0(\mathbf{r}) + \alpha[n(\mathbf{r}) - n_0(\mathbf{r})], \tag{2-5}
\end{equation}

with $\alpha$ ranging from 0 to 1. The resulting simple expression for $v_n(\mathbf{r})$ is

\begin{equation}
\beta v_n(\mathbf{r}) = - \ln \left( \frac{n(\mathbf{r})}{n_0} \right) + \int_0^1 \! d\alpha \int d^3r' C(\mathbf{r}, \mathbf{r}'; \alpha) [n(\mathbf{r}') - n_0] \tag{2-6}
\end{equation}

where $C(\mathbf{r}, \mathbf{r}'; \alpha)$ is $C(\mathbf{r}, \mathbf{r}')$ at density $n'(\mathbf{r}, \alpha)$.
The exact expression for $\Omega$ can be obtained by further integration of Eq. (2-6) using Eq. (2-2) and has the form

$$\Omega - \Omega_0 = \int dr^* \omega(r^*) + \int dr^* v(r^*)[n(r^*) - n_0]$$

$$+ \frac{kT}{4} \int dr^* dr^{*'} \tilde{C}(r^*, r^{*'})[n(r^*) - n(r^{*'})]^2,$$  \hspace{1cm} (2-7)

where

$$\omega(r) = kT[n(r^*) \ln(n(r^*)/n_0) - [n(r^*) - n_0]$$

$$- \tilde{C}_0(r^*) \frac{[n(r^*) - n_0]^2}{2} ],$$ \hspace{1cm} (2-8)

$$\tilde{C}(r^*, r^{*'}) = 2\int_0^1 \alpha(1-\alpha)C(r^*, r^{*'}; \alpha),$$ \hspace{1cm} (2-9)

and

$$\tilde{C}_0(r^*) = \int dr^{*'} \tilde{C}(r^*, r^{*'}).$$ \hspace{1cm} (2-10)

In Eq. (2-7) the first integral has the appearance of being the difference of the local part of the free energy in that the integrand depends explicitly on the density at $r^*$ only,** the second integral accounts for the change in chemical

** It is implicitly a function of $n(r^*)$ for all $r^*$ through its dependence on the direct correlation function $C(r, r^*; \alpha)$. 
potential \( \mu \) due to the existence of the external potential \( v(\mathbf{r}) \), and the third integral gives the correlation energy of the fluid due to the non-uniformity in density. To further illustrate the physical meaning of Eq. (2-7), we consider a special case when the final density \( n(\mathbf{r}) \) is uniform. Then the integral involves the integral over \( v(\mathbf{r}) \) accounts for changes in \( \mu \) that occur when going from the initial to final uniform densities. It also can be shown that \( \omega(\mathbf{r}) \) is just the difference of the internal grand free energy density in going from \( n_0 \) to \( n \). The proof of the preceding assertion is as follows:

From Eq. (2-5), we have

\[
\alpha = \frac{n^* - n_0}{n - n_0} \quad \text{and} \quad d\alpha = \frac{dn^*}{n - n_0} \quad . \tag{2-11}
\]

The arguments have been suppressed when no ambiguity will result. The combination of Eqs. (2-9), (2-10), and (2-11) gives

\[
\tilde{C}_0(\mathbf{r}) = 2\int_0^1 d\alpha (1-\alpha) \int \tilde{C}(\mathbf{r}, \mathbf{r}^*; \alpha)
= 2\int_0^1 d\alpha (1-\alpha) \tilde{C}_0(\mathbf{r}; \alpha)
= 2\int_{n_0}^n \frac{dn^*}{n_0} \frac{(n-n^*)}{(n-n_0)^2} \tilde{C}_0(\mathbf{r}; n^*) \quad . \tag{2-12}
\]
Next substituting Eq. (2-12) back into Eq. (2-8) and integrating over \( \hat{r} \), we get

\[
\int \omega(r) d^3r = V kT \left\{ n \ln \left( \frac{n}{n_0} \right) - (n-n_0) \right\} - \int_{n_0}^{n} dn' (n-n') C_0(n') \right\}, \tag{2-13}
\]

where \( C_0(n) \) is the zeroth Fourier component of \( C(\hat{r};n) \) and

\[
C_0(n) = \int d^3r C(\hat{r};n) e^{-i\hat{q} \cdot \hat{r}}. \tag{2-14}
\]

Finally, by using the uniform system relations

\[
P(n) - P(n_0) = kT \int_{n_0}^{n} dn'[1 - n' C_0(n')] \tag{2-15}
\]

and

\[
\mu(n) - \mu(n_0) = kT \ln(n) - kT \int_{n_0}^{n} dn' C_0(n'), \tag{2-16}
\]

We obtain

\[
\int \omega(r) d^3r = V(-P + P_0 + n(\mu - \mu_0)) \tag{2-17}
\]

which is what we expected.

The application of the exact density functional theory to the system we are interesting in involves a great amount
of numerical work. To simplify the problem, we have chosen to use the approximate theory derived by the same authors plus Stroud on the basis of heuristic arguments prior to the derivations of the exact theory of Eqs. (2-7) through (2-10). It also has been shown that in one dimension this approximate theory and the exact theory give very close agreement even for relatively large and rapid density variations. The approximate theory looks very similar to Eq. (2-7) and takes the form

\[
\Omega - \Omega_0 = \int d^3r [\omega_0(n(\vec{r})) + v(\vec{r})(n(\vec{r}) - n_0)] + \frac{kT}{4} \int d^3r d^3r' C(|\vec{r} - \vec{r}'|; \bar{n}) [n(\vec{r}) - n(\vec{r}')]^2
\]

(2-18)

where

\[
\omega_0(n) = kT \left[ n \ln \left( \frac{n}{n_0} \right) - (n - n_0) + \int_{n_0}^n dn' C_0(n') (n' - n) \right].
\]

(2-19)

Here \(C(\vec{r}; \bar{n})\) is the direct correlation function in the uniform system at density \(n\) and temperature \(T\), and \(\bar{n}\) has been chosen to be the average of the densities at points \(\vec{r}\) and \(\vec{r}'\), i.e.
\[ \bar{n} = \frac{[n(\vec{r}) + n(\vec{r}')]}{2}. \] (2-20)

Eq. (2-19) has been derived using the compressibility sum rule, Eq. (2-15), and the Gibbs-Duhem relation. Note here that the first two terms of \( \omega_0(n) \) are just the change in grand free energy of an ideal gas when its density changes from \( n_0 \) to \( n \) and \( \omega_0 \) is itself the difference between the grand free energy densities of uniform fluids at densities \( n \) and \( n_0 \) when the chemical potential is \( \mu_0 \).

The direct correlation function \( C(\vec{r}) \) used in this work has been obtained by solving the Percus-Yevick equation and Ornstein-Zerike equation. The Lennard-Jones potential is used for the fluid's interparticle interaction.

Next we apply the above theory to a special case when there is an excess electron moving in a non-polar classical fluid at constant \( T, \mu, \) and \( V \). The grand free energy of the system is found by minimizing the functional

\[
\Delta \Omega[n] = \int d^3 r \frac{\hbar^2}{2m} |\psi(\vec{r})|^2 + \int d^3 r \omega_0(\vec{r}) \\
+ \int d^3 r d^3 r' |\psi(\vec{r})|^2 \nu(\vec{r} - \vec{r}')[n(\vec{r}') - n_0] \\
+ \frac{kT}{4} \int d^3 r d^3 r'' C(|\vec{r} - \vec{r}'|; \bar{n}) [n(\vec{r}) - n(\vec{r}'')]^2 \] (2-21)

with respect to variation of \( n(\vec{r}) \) and \( \psi(\vec{r}) \) subject to the constraint
\[ \int d^3r |\psi(r)|^2 = 1; \quad (2-22) \]

\( \psi(r) \) is the electronic wave function. The first two integrals in Eq. (2-21) are the electron kinetic energy and electron-fluid interaction energy, respectively. The latter is given in a mean field approximation in which the positions of the atoms and electron are not correlated. The electron-atom potential \( v(\vec{r}) \) is essentially a polarization potential at large distances and, within the context of pseudopotential theory, it is repulsive at short range. In those applications such that it need not be integrable, the potential is taken to have the form

\[ v(\vec{r}) = \left( \frac{e^2}{2a_0} \right) \left[ (\sigma_e/\vec{r})^N - \alpha a_0/\vec{r}^4 f(\vec{r}) \right] \quad (2-23) \]

where \( f(\vec{r}) \) is a dielectric screening function. The parameters \( \sigma_e \) and \( N \) have been fitted to reproduce s-wave scattering phase shifts as given by Thompson.\(^{36} \) When integrability is necessary, as in the mean field approximation of Eq. (2-21), \( v(\vec{r}) \) has been cut off at short distances. The detailed fitting procedure and the choice of \( f(\vec{r}) \) are discussed in Appendix A.

The constraint on the electron wavefunction \( \psi(\vec{r}) \) can be handled using a Lagrange multiplier. The resulting relation expressing the condition that \( \Delta \Omega \) be an extremum
with respect to variations of $\Psi^*(\vec{r})$ is just the Schrodinger equation for an electron moving in the mean field potential

$$v_e(\vec{r}) = \int d^3r \cdot v(\vec{r} - \vec{r}') [n(\vec{r}') - n_0]. \tag{2-24}$$

produced by the atoms of the fluid. For a given $n(\vec{r})$ we want the lowest eigen-energy of this Schrodinger equation and denote it by $E_e[n]$. Then the equilibrium number density is determined by minimizing the functional

$$\Delta \Omega[n] = E_e[n] + \int d^3r w_0[n(\vec{r})]$$

$$+ \frac{kT}{4} \int d^3r d^3r' C(\vec{r} - \vec{r}'; n)[n(\vec{r}) - n(\vec{r}')]^2 \tag{2-25}$$

with respect to variations of $n(\vec{r})$.

The free energy difference between a localized electron state (if any) which emerges from the preceding calculation and the lowest energy extended state in which the fluid density is a constant is simple $\Delta \Omega[n]$. This statement applies, of course, only if the mean field approximation is also used to compute the properties of the localized state.

An alternative procedure for finding the relative free energy of the localized state is to employ for the extended state the Wigner-Seitz cellular method$^{27}$ and $v(\vec{r})$ of Eq. (2-23). This leads to surprisingly accurate values of
the ground extended state energy in Ne and Ar fluids. This calculation is discussed in Appendix B.

To explain the drastic drop of the electron mobility observed in some classical fluids, the bubble and droplet models have been used here. The formation of the bubble state is preferable in fluids with relatively large repulsive short-range electron-atom potentials and weak attractive long-range polarization potentials. Such potentials are characterized by positive scattering lengths. The droplet state is favored in fluids with negative scattering length arising from strong polarization potentials. The localization of the electron causes a regional non-uniformity in the fluid density. Parametrized trial functions have been employed to simulate this non-uniformity. They were chosen to have the form

\[
  n(r) = n_0 (1 - \frac{\alpha}{e^{(r-\beta)/\gamma} + 1})
\]  

(2-26)

for the bubble state and

\[
  n(r) = n_0 (1 + \frac{\alpha}{e^{(r-\beta)/\gamma} + 1})
\]  

(2-27)

for the droplet state.

The minima of \[\Delta \Omega[n]\] are then obtained by starting from some initial set of variational parameters and evaluating
\[ A\Omega[n] \] for the given set and other sets located on a grid in the space of the parameters. After locating the minimum of \[ A\Omega[n] \] on this grid, the spacing of points is decreased to obtain a finer grid and the process repeated. This procedure is repeated until the minimum free energy difference is obtained. In those cases for which there is no minimum of \[ A\Omega[n] \] corresponding to a localized electron state, the bubble radius \( \beta \) would either vanish or diverge, yielding a uniform system.
B. Linearized Percus-Yevick Theory

A positive ion drifting in a non-polar classical fluid can be considered as a limiting case of a binary mixture in which the density of the positive ions approaches zero and ultimately reduces to only one ion left in the fluid.

The Ornstein-Zernike (OZ) equation for a mixture of \( m \)-species is

\[
h_{ij}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) = C_{ij}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2)
\]

\[
+ n_0 \sum_{k=1}^{m} x_k \int h_{ik}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_3) C_{kj}(\hat{\mathbf{r}}_3, \hat{\mathbf{r}}_2) d^3 r_3
\]

(2-28)

where \( h_{ij}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) \) and \( C_{ij}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) \) are the total and direct correlation functions, respectively, for an atom of species \( i \) at \( \hat{\mathbf{r}}_1 \) and an atom of species \( j \) at \( \hat{\mathbf{r}}_2 \); \( n_0 \) is the total number density, and \( n_0 x_k \) gives the number density of species \( k \).

To apply the generalized OZ equation to our special binary mixture, we assume that ion-atom and atom-atom potentials depend on their relative distance only. Thus, \( h_{ij}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) \) and \( C_{ij}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) \) reduce to \( h_{ij}(\hat{\mathbf{r}}_1-\hat{\mathbf{r}}_2) \) and \( C_{ij}(\hat{\mathbf{r}}_1-\hat{\mathbf{r}}_2) \). The OZ equations become, in the limit of one ion (component 2 is the ion),
\[ h_{11}(\vec{r}_1 - \vec{r}_2) = c_{11}(\vec{r}_1 - \vec{r}_2) + n_0 \int h_{11}(\vec{r}_1 - \vec{r}_3)c_{11}(\vec{r}_2 - \vec{r}_3)d^3r_3 \]  
(2-29,a)

\[ h_{12}(\vec{r}_1 - \vec{r}_2) = c_{12}(\vec{r}_1 - \vec{r}_2) + n_0 \int h_{11}(\vec{r}_1 - \vec{r}_3)c_{12}(\vec{r}_2 - \vec{r}_3)d^3r_3 \]  
(2-29,b)

\[ h_{21}(\vec{r}_1 - \vec{r}_2) = c_{21}(\vec{r}_1 - \vec{r}_2) + n_0 \int h_{21}(\vec{r}_1 - \vec{r}_3)c_{11}(\vec{r}_2 - \vec{r}_3)d^3r_3 \]  
(2-29,c)

and

\[ h_{22}(\vec{r}_1 - \vec{r}_2) = c_{22}(\vec{r}_1 - \vec{r}_2) + n_0 \int h_{21}(\vec{r}_1 - \vec{r}_3)c_{12}(\vec{r}_2 - \vec{r}_3)d^3r_3 . \]  
(2-29,d)

Eq. (2-29,a) is just a one-component OZ equation which we used, in conjunction with the Percus-Yevick equation, to solve for \( C(\vec{r}) \) of a uniform fluid. Eq. (2-29,b) and Eq. (2-29,c) are equivalent since \( h_{12}(\vec{r}) = h_{21}(\vec{r}) \) and \( c_{12}(\vec{r}) = c_{21}(\vec{r}) \). Eq. (2-29,d) has no meaning here for only one positive ion is present in our mixture. The number density of the fluid is \( n_0 \). If we assume that the correlation function for a one-component uniform fluid is known, then the above OZ equations reduce to one two-component equation, i.e.
The solution of Eq. (2-30) can be obtained only if we have some closure relations to couple \( h_{12}(\vec{r}) \) with \( C_{12}(\vec{r}) \). Here we choose the two-component PY equation

\[
C_{12}(\vec{r}) = g_{12}(\vec{r})[1 - \exp(\beta v_{12}(\vec{r}))], \tag{2-31}
\]

where the pair distribution function \( g_{12}(\vec{r}) \) is related to \( h_{12}(\vec{r}) \) by

\[
g_{12}(\vec{r}) = h_{12}(\vec{r}) + 1. \tag{2-32}
\]

By combining Eqs. (2-30), (2-31), and (2-32), we obtain a linear integral equation

\[
g_{12}(\vec{r}) = \exp(-\beta v_{12}(\vec{r}))
\times [1 + n_0 \int d^3r' C_{11}(\vec{r}' - \vec{r})(g_{12}(\vec{r}') - 1)]. \tag{2-33}
\]

This equation will be called here the linearized Percus-Yevick equation (LPY). If \( v_{12}(\vec{r}) \) and \( C_{11}(\vec{r}) \) are given, Eq. (2-33) can be solved numerically to obtain \( g_{12}(\vec{r}) \). Thus
the density profile of the fluid with a positive ion at \( r = 0 \) is

\[
n_{12}(\vec{r}) = n_0 \xi_{12}(\vec{r}).
\]  

(2-34)

We remark that Eq. (2-33) can also be derived from the exact DF theory by expanding the exponential part of Eq. (2-6) and retaining only the term linear in the density deviations. The integral over \( \alpha \) gives a factor of unity, if we approximate \( C \) as the direct correlation function of a uniform fluid having density \( n_0 \). The result is Eq. (2-33).

A simple pseudopotential of the form

\[
v_{12}(r) = C_N/r^N - C_6/r^6 - C_4/r^4
\]  

(2-35)

has been used to represent the potential acting between the positive ion and an atom of the fluid. The term proportional to \( r^{-N} \) represents a short-range repulsive potential. The \( r^{-6} \) term is the dispersion potential due to the interaction of the two induced charge distributions. The last term is just the polarization potential of the fluid atom due to the excess positive charge of the ion; \( C_4 = e^2\alpha/2 \), where \( \alpha \) is the polarizability of fluid. The parameters \( C_N \), \( C_4 \) and \( N \) used in this work are taken from the paper by Budenholzer, Gislason, and Jorgensen. These parameters
are determined by making a least squares fit of the theoretical electron scattering cross sections calculated using $v_{12}(r)$ to the experimental cross section data.

C. Simulations

In this section we will deal with the computer simulation of the problem of a positive ion located in the classical fluid. This simulation is possible because the relative large size of the ion allows it to be treated classically. Here we have chosen to use the grand-canonical-ensemble (GCE) Monte Carlo (MC) method described by Adams.\textsuperscript{52,53} The outline of this method is given below.

The GCE average of a function $F$, which itself is a function of the particle positions, is

$$
\overline{F} = \frac{1}{X} \sum_{N=0}^{\infty} \frac{1}{N!} \left( \frac{2\pi mkT}{\hbar^2} \right)^{3N/2} \times \exp(N\mu/kT) \int \cdots \int F \exp(-U_N/kT) d^3r_1 \cdots d^3r_N,
$$

(2-36)

where $k$ is Boltzmann's constant, $d^3r_1 \cdots d^3r_N$ is a volume element in the $N$-particle configuration space, $U_N$ is the potential energy, and $X$ is the grand partition function defined by
\[ X = \sum_{N=0}^{\infty} \frac{1}{N!} \left( \frac{2\pi mkT}{\hbar^2} \right)^{3N/2} \times \exp(N\mu/kT) \int \ldots \int \exp(-U_N/kT) d^3r_1 \ldots d^3r_N. \]  

\[ (2-37) \]

In practice, it is convenient to remove the kinetic term \( \left( \frac{2\pi mkT}{\hbar^2} \right)^{3N/2} \) from the above expressions by substituting for the chemical potential \( \mu_0 + \mu \), where \( \mu_0 \) is the chemical potential of an ideal gas with the same particle mass and temperature and with density \( N_I/V \). The chemical potential of this ideal gas is

\[ \mu_0 = -kT[\ln(V/N_I) + \frac{3}{2} \ln \left( \frac{2\pi mkT}{\hbar^2} \right)]. \]  

\[ (2-38) \]

By transforming the integrals to dimensionless particle coordinates, \( d^3s = d^3r/V \), and making the substitution described above, we find that the grand partition function reduces to

\[ X = \sum_{N=0}^{\infty} \frac{1}{N!} \exp(N\mu^*/kT + N \ln N_I) \times \int \ldots \int \exp(-U_N/kT) d^3s_1 \ldots d^3s_N. \]  

\[ (2-39) \]
The MC procedure then can be implemented by setting $B = \mu^2/kT + \ln N_I$ as a specified parameter, along with volume and temperature.

A Markov chain whose steps each have two independent stages is used in this procedure. The condition for realization of a Markov chain is that the distribution of the state at time $t$ is independent of all previous states except for its immediate predecessor state. In the first stage, a particle is chosen at random and displaced to another random position within a predetermined interval about its original position. This new trial configuration is accepted according to the symmetric procedure first devised by Metropolis et al. The criterion is that if for a random number $\zeta$ in the interval $[0,1]$, the change in energy caused by this move satisfies

$$\exp(-\Delta E/kT) > \zeta, \quad (2-40)$$

then the move is accepted. The second stage proceeds regardless of the outcome of the first and attempts to add or remove a particle from the system.

In an attempt to add a particle to the system, the position of this new particle is generated randomly and the addition is accepted if

$$\zeta < \frac{N_I}{N} \exp(-\Delta E/kT) \quad (2-41)$$
where $\zeta$ is a new random number in $[0,1]$ and $\Delta E$ includes the change in energy due to the simultaneous addition of all periodic images. In an attempt to remove a particle from the system, the particle to be removed is picked randomly and the removal is successful if

$$
\zeta < \frac{N+1}{N} \exp(-\Delta E/kT)
$$

(2-42)

where $\zeta$ is yet another random number and $\Delta E$ includes the change in energy due to the simultaneous removal of all the periodic images.

The average energy per particle in the volume is given by $52,53$

$$
e = \frac{3}{2} kT + \frac{<U>}{<N>}
$$

(2-43)

where $\frac{3}{2} kT$ is the kinetic energy of the particle at temperature $T$, $<N>$ is the ensemble average of the number of particles in the system and

$$
<U> = \left< \sum_{i<j} \phi(r_{ij}) \right>.
$$

(2-44)

The pair interaction $\phi(\mathbf{r})$ between fluid particles is still chosen to be the Lennard-Jones potential. For computational convenience $\phi(\mathbf{r})$ is cut off at $6\sigma$. The fluid is confined
to a cubic box of volume \((15\sigma)^3\) and the positive ion is positioned at the center of the box. The presence of the positive ion acts as an external potential on the fluid and, under the periodic boundary condition, there will be one positive ion at the center of every image of the box. We will use the same ion-atom potential as described in section 2.B. The existence of the ion-cluster is checked by looking at the density profile of the fluid near the ion. This density profile is obtained by dividing the volume into concentric shells, centered at the ion, of thickness \(3\sigma/160\) and then accumulating the number of times a particle falls in each particular shell during the sampling process, divided by the volume of the corresponding shell.
A. Potential

The numerical procedure outlined in Appendix A has been used to compute the electron-atom scattering phase shifts for He, Ne, Ar, and Kr gases from the model electron-atom potentials. Here the results of s- and p-wave scattering are included in each calculation and the parameters \( N \) and \( a_e \) in Eq. (2-23) are varied in such a way as to determine those values which give the best s-wave phase shifts when compared with the existing data. The reason that only s-wave scattering has been used as a criterion is because as \( k \to 0 \) only the s-wave gives a finite contribution to the total scattering cross section; for the systems of interest to us, the electron energy is sufficiently small that s-wave scattering dominates. To justify this statement, we consider a typical electron bubble with diameter \( D = 10 \) Å. If we approximate this electron bubble as an infinite square well, then the electron wave number in the ground state is \( k_0 = \pi/D = 0.166 \) \( a_0^{-1} \) and the corresponding energy is simply

\[
E_0 = \frac{\hbar^2}{2m} \left( \frac{\pi}{D} \right)^2 = 0.38 \text{ (ev)},
\]
where $a_0$ is the Bohr radius. The first excited state of the electron has the energy $E_1 = 1.5$ ev which is much bigger than $E_0$. So it is quite reasonable to assume that the electron is always in its ground state and to neglect the contributions from the excited states. The angular momentum of interest is $h k_0 d$ where $d$ is the range of the potential and can be approximate by $\sigma_e$. If we substitute $\sigma_e$ which has the value somewhere between $1.5 a_0$ and $2.5 a_0$, as we will see later, into the above relation, then the corresponding angular momentum is about $1/3 h$. This also shows that only s-wave scattering is important in the potential fitting process.

Since the most complete phase shifts available to us are those given by Thompson for Ar and Ne gases with wave number ranging from $k = 0.1 a_0^{-1}$ to $k = 2.0 a_0^{-1}$, we will begin our discussions with the Ar gas. In Table 1 the s- and p-wave phase shifts are calculated by setting $N = 10$ and varying $\sigma_e$ until the best fit in the small $k$ region is obtained at $\sigma_e = 2.07 a_0$. The results from Thompson's paper are also included in this and the following Tables. In Tables 2 we list the phase shifts calculated with different $N$ and $\sigma_e$ along with the best fit appearing from Table 1. We find that $N = 10$ gives us better agreement over a wider range of wave numbers. Actually there is no reason why we cannot select some other number for the value of $N$. Here for simplicity we have decided to let $N = 10$ for all the
Table 1: The S- and P-Wave Phase Shifts for Electron-Ar Scattering with N=10 and Different Values of $\sigma_e$

<table>
<thead>
<tr>
<th>$\sigma_e(a_0)$</th>
<th>s-partial wave</th>
<th>p-partial wave</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k(1/a_0)$</td>
<td>$\delta^*$ 2.0 2.05 2.07 2.1</td>
<td>$\delta^*_1$ 2.0 2.05 2.07 2.1</td>
</tr>
<tr>
<td>0.1</td>
<td>0.034 0.064 0.042 0.034 0.023</td>
<td>0.015 0.020 0.019 0.019 0.019</td>
</tr>
<tr>
<td>0.2</td>
<td>-0.061 -0.014 -0.047 -0.059 -0.077</td>
<td>0.027 0.062 0.060 0.059 0.057</td>
</tr>
<tr>
<td>0.4</td>
<td>-0.374 -0.302 -0.348 -0.365 -0.390</td>
<td>-0.051 0.115 0.101 0.095 0.086</td>
</tr>
<tr>
<td>0.6</td>
<td>-0.722 -0.633 -0.687 -0.708 -0.739</td>
<td>-0.245 0.052 0.022 0.011 -0.007</td>
</tr>
<tr>
<td>0.8</td>
<td>-1.063 -0.967 -1.029 -1.053 -1.089</td>
<td>-0.479 -0.106 -0.149 -0.166 -0.191</td>
</tr>
<tr>
<td>1.0</td>
<td>-1.382 -1.296 -1.366 -1.394 -1.434</td>
<td>-0.714 -0.317 -0.371 -0.392 -0.424</td>
</tr>
<tr>
<td>1.2</td>
<td>1.468 1.523 1.445 1.415 1.370</td>
<td>-0.933 -0.556 -0.620 -0.646 -0.683</td>
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<tr>
<td>1.4</td>
<td>1.204 1.207 1.122 1.089 1.039</td>
<td>-1.132 -0.810 -0.884 -0.913 -0.956</td>
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<td>1.8</td>
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<tr>
<td>2.0</td>
<td>0.548 0.298 0.192 0.150 0.087</td>
<td>1.520 1.537 1.439 1.400 1.342</td>
</tr>
</tbody>
</table>

* From Ref. 36.
Table 2: The S- and P-Wave Phase Shifts for Electron-Ar Scattering with Different Values of N and $\sigma_e$

<table>
<thead>
<tr>
<th>k(1/(a_o))</th>
<th>s-partial wave</th>
<th>p-partial wave</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta^*$</td>
<td>$\sigma_e$=2.07</td>
</tr>
<tr>
<td>0.1</td>
<td>0.034</td>
<td>0.034</td>
</tr>
<tr>
<td>0.2</td>
<td>-0.061</td>
<td>-0.059</td>
</tr>
<tr>
<td>0.4</td>
<td>-0.374</td>
<td>-0.365</td>
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<td>0.8</td>
<td>-1.063</td>
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<tr>
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<td>-1.382</td>
<td>-1.394</td>
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<td>1.204</td>
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<td>0.964</td>
<td>0.770</td>
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<td>0.747</td>
<td>0.457</td>
</tr>
<tr>
<td>2.0</td>
<td>0.548</td>
<td>0.150</td>
</tr>
</tbody>
</table>

* From Ref. 36.
elements. In the above calculations the polarization potential has been chosen to have the polarizability \( \alpha = 11a_0^3 \) as given by O'Malley. The polarizabilities given in the same paper will be used in the remaining calculations. Now we conclude that \( N = 10, \sigma_e = 2.07a_0, \) and \( \alpha = 11a_0^3 \) are indeed a satisfactory choice for the parameters of the Ar-electron potential in Eq. (2-23).

In Table 3 we show the results for the Ne gas. Given the polarizability \( \alpha = 2.65a_0^3 \) and \( N = 10 \), the best fit is determined to be at \( \sigma_e = 1.48a_0 \). We remark here that the s-wave phase shifts calculated here and those given by Thompson are in very close agreement not only at small \( k \) but also at relatively large \( k \). Also, at sufficiently small \( k \), our choice of parameters gives close agreement for the p-wave. We will come back to discuss the p-wave results further later. In Table 4 we list the phase shifts of He in comparison with the data given by Naccache and McDowell. We have normalized our phase shifts such that they fall between \( \pm \pi/2 \). The phase shifts are given here up to relatively high energy; the best match at low energies is obtained at \( \sigma_e = 1.75a_0 \). Finally in Table 5 we present the results for krypton gas. The phase shifts are compared with those given by Heidorff, Hofft, and Dabkiewicz and the parameters so obtained are \( N = 10, \alpha = 16.6a_0^3 \) and \( \sigma_e = 2.3a_0 \).
Table 3: The S- and P-Wave Phase Shifts for Electron-Ne Scattering with N=10 and Different Values of $\sigma_e$

<table>
<thead>
<tr>
<th>$\sigma_e(a_0)$</th>
<th>(\delta^*)</th>
<th>1.45</th>
<th>1.48</th>
<th>1.49</th>
<th>(\delta^*)</th>
<th>1.45</th>
<th>1.48</th>
<th>1.49</th>
</tr>
</thead>
<tbody>
<tr>
<td>k(1/a_0)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>-0.040</td>
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<td>-0.042</td>
<td>0.004</td>
<td>0.005</td>
<td>0.005</td>
<td>0.005</td>
</tr>
<tr>
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<td>-0.112</td>
<td>-0.115</td>
<td>0.009</td>
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<td>0.015</td>
<td>0.014</td>
</tr>
<tr>
<td>0.4</td>
<td>-0.302</td>
<td>-0.279</td>
<td>-0.300</td>
<td>-0.304</td>
<td>-0.008</td>
<td>0.032</td>
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<td>0.027</td>
</tr>
<tr>
<td>0.6</td>
<td>-0.516</td>
<td>-0.483</td>
<td>-0.508</td>
<td>-0.517</td>
<td>-0.074</td>
<td>0.017</td>
<td>0.009</td>
<td>0.007</td>
</tr>
<tr>
<td>0.8</td>
<td>-0.735</td>
<td>-0.696</td>
<td>-0.727</td>
<td>-0.738</td>
<td>-0.173</td>
<td>-0.037</td>
<td>-0.052</td>
<td>-0.057</td>
</tr>
<tr>
<td>1.0</td>
<td>-0.946</td>
<td>-0.912</td>
<td>-0.948</td>
<td>-0.961</td>
<td>-0.285</td>
<td>-0.128</td>
<td>-0.149</td>
<td>-0.159</td>
</tr>
<tr>
<td>1.2</td>
<td>-1.147</td>
<td>-1.127</td>
<td>-1.169</td>
<td>-1.183</td>
<td>-0.398</td>
<td>-0.246</td>
<td>-0.274</td>
<td>-0.283</td>
</tr>
<tr>
<td>1.4</td>
<td>-1.334</td>
<td>-1.340</td>
<td>-1.387</td>
<td>-1.403</td>
<td>-0.505</td>
<td>-0.383</td>
<td>-0.417</td>
<td>-0.428</td>
</tr>
<tr>
<td>1.6</td>
<td>-1.508</td>
<td>-1.552</td>
<td>1.538</td>
<td>1.521</td>
<td>-0.602</td>
<td>-0.533</td>
<td>-0.573</td>
<td>-0.586</td>
</tr>
<tr>
<td>1.8</td>
<td>-1.474</td>
<td>1.381</td>
<td>1.325</td>
<td>1.306</td>
<td>-0.691</td>
<td>-0.692</td>
<td>-0.738</td>
<td>-0.753</td>
</tr>
<tr>
<td>2.0</td>
<td>1.326</td>
<td>1.174</td>
<td>1.114</td>
<td>1.094</td>
<td>-0.770</td>
<td>-0.857</td>
<td>-0.908</td>
<td>-0.925</td>
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* From Ref. 36.
Table 4: The S- and P-Wave Phase Shifts for Electron-He Scattering with N-10 and $\sigma_e = 1.75\sigma$

<table>
<thead>
<tr>
<th>Energy (ev)</th>
<th>$k$ ($l/a_o$)</th>
<th>$\delta_0^*$</th>
<th>$\sigma_e=1.75$ ($a_o$)</th>
<th>$\delta_1^*$</th>
<th>$\sigma_e=1.75$ ($a_o$)</th>
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</thead>
<tbody>
<tr>
<td>1.5</td>
<td>0.332</td>
<td>-0.41</td>
<td>-0.412</td>
<td>0.054</td>
<td>-0.013</td>
</tr>
<tr>
<td>2.5</td>
<td>0.429</td>
<td>-0.54</td>
<td>-1.541</td>
<td>0.089</td>
<td>-0.037</td>
</tr>
<tr>
<td>5.1</td>
<td>0.612</td>
<td>-0.78</td>
<td>-0.789</td>
<td>0.154</td>
<td>-0.111</td>
</tr>
<tr>
<td>7.1</td>
<td>0.723</td>
<td>-0.91</td>
<td>-0.938</td>
<td>0.188</td>
<td>-0.177</td>
</tr>
<tr>
<td>9.1</td>
<td>0.818</td>
<td>-1.01</td>
<td>-1.066</td>
<td>0.214</td>
<td>-0.242</td>
</tr>
<tr>
<td>11.1</td>
<td>0.903</td>
<td>-1.09</td>
<td>-1.181</td>
<td>0.237</td>
<td>-0.308</td>
</tr>
<tr>
<td>13.1</td>
<td>0.981</td>
<td>-1.15</td>
<td>-1.285</td>
<td>0.257</td>
<td>-0.372</td>
</tr>
<tr>
<td>15.1</td>
<td>1.054</td>
<td>-1.20</td>
<td>-1.381</td>
<td>0.274</td>
<td>-0.436</td>
</tr>
<tr>
<td>17.1</td>
<td>1.121</td>
<td>-1.24</td>
<td>-1.470</td>
<td>0.291</td>
<td>-0.496</td>
</tr>
<tr>
<td>19.1</td>
<td>1.185</td>
<td>-1.27</td>
<td>-1.554</td>
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<td>-0.556</td>
</tr>
<tr>
<td>26.1</td>
<td>1.385</td>
<td>-1.34</td>
<td>1.326</td>
<td>0.354</td>
<td>-0.752</td>
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<tr>
<td>31.1</td>
<td>1.512</td>
<td>-1.37</td>
<td>1.162</td>
<td>0.384</td>
<td>-0.882</td>
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<tr>
<td>36.1</td>
<td>1.629</td>
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<td>-1.005</td>
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<td>50.0</td>
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<td>0.482</td>
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<tr>
<td>100.0</td>
<td>2.711</td>
<td>-1.48</td>
<td>-0.317</td>
<td>0.528</td>
<td>0.958</td>
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Table 5: The S- and P-Wave Phase Shifts for Electron-Kr Scattering with N=10 and Different Values of $\sigma_e$

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>$k$ (1/(a_0))</th>
<th>$\delta^*$</th>
<th>$\sigma_e=2.2$</th>
<th>$\sigma_e=2.28$</th>
<th>$\sigma_e=2.3$</th>
<th>$\delta^*$</th>
<th>$\sigma_e=2.2$</th>
<th>$\sigma_e=2.28$</th>
<th>$\sigma_e=2.3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>0.469</td>
<td>-0.527</td>
<td>-0.437</td>
<td>-0.520</td>
<td>-0.540</td>
<td>-0.195</td>
<td>0.144</td>
<td>0.103</td>
<td>0.093</td>
</tr>
<tr>
<td>5.0</td>
<td>0.606</td>
<td>-0.832</td>
<td>-0.701</td>
<td>-0.792</td>
<td>-0.814</td>
<td>-0.387</td>
<td>0.055</td>
<td>-0.002</td>
<td>-0.016</td>
</tr>
<tr>
<td>7.0</td>
<td>0.717</td>
<td>-1.064</td>
<td>-0.914</td>
<td>-1.011</td>
<td>-1.035</td>
<td>-0.548</td>
<td>-0.053</td>
<td>-0.122</td>
<td>-0.139</td>
</tr>
<tr>
<td>9.0</td>
<td>0.813</td>
<td>-1.250</td>
<td>-1.095</td>
<td>-1.199</td>
<td>-1.224</td>
<td>-0.683</td>
<td>-0.165</td>
<td>-0.243</td>
<td>-0.262</td>
</tr>
<tr>
<td>9.79</td>
<td>0.848</td>
<td>-1.317</td>
<td>-1.161</td>
<td>-1.267</td>
<td>-1.292</td>
<td>-0.734</td>
<td>-0.208</td>
<td>-0.289</td>
<td>-0.309</td>
</tr>
<tr>
<td>10.5</td>
<td>0.878</td>
<td>-1.368</td>
<td>-1.216</td>
<td>-1.325</td>
<td>-1.351</td>
<td>-0.773</td>
<td>-0.247</td>
<td>-0.331</td>
<td>-0.351</td>
</tr>
</tbody>
</table>

* From Ref. 61.
As we should have noticed by now, for our choice of parameters the p-wave phase shifts provide us poor agreement except in some cases (Ar, Ne) at very low energy. Actually we should expect this lack of agreement because the requirement that incoming partial waves be orthogonal to the core orbitals are not the same for s- and p-waves. The simplest case is the helium atom which has two electrons in the 1s orbital. The incoming s-wave will see a larger repulsive potential because it must be made to orthogonal to 1s core orbital by the Pauli-exclusion principle. The p-wave, on the other hand, will see a 'softer' repulsive potential because it is already orthogonal to the 1s orbital anyway. Although the cases of Ne, Ar, and Kr are more complicated, the above argument should at least give us part of the explanation for the discrepancies. An angular-momentum-dependent model potential has the necessary flexibility to overcome this problem.

Finally we consider xenon gas, the heaviest rare gas element. Unfortunately there are not many phase shifts for electron-xenon scattering extant in the literature. We have decided to choose $\sigma_e$ to yield the same scattering length as that given by Ramsauer and Kollath. The scattering length $a_s$ is defined by

$$a_s = - \lim_{k \to 0} \frac{\delta_0(k)}{k}$$

(3-1)
where $\delta_0(k)$ is the s-wave phase shift. Eq. (3-1) also means that the scattering length is just the negative of the first derivative of $\delta_0(k)$ as $k \to 0$. The same computer program has been used to calculate the phase shifts down to $k = 0.001/a_0$ and the slope is derived accordingly. The parameter $\sigma_e$ is chosen so that the negative of the slope is equal to the scattering length $a_s = -6.5a_0$ as given by Ramsauer and Kollath. The parameters are $N = 10$, $\alpha = 27.0a_0^3$, and $\sigma_e = 2.45a_0$.

To conclude this section we list all the potential parameters, including those used in the interatomic Lennard-Jones potential in Table 6.

B. Density Profiles and Free Energies

Before we turn our discussion to the results of the density functional calculations, we will examine how good is the ground state energy $E_0$ of the quasifree electron obtained by the Wigner-Seitz method described in Appendix B as compared with the experimental data. For helium gas we have done the calculation at high temperature to avoid quantum effects arising from its small atomic mass. The energy $E_0$ at $T^* = 7.7$ and $n_0^* = 0.30$ is 1.62 ev which is compared with the measured energy $E_0 = 1.05 \pm 0.05$ ev given by Sommer at $T^* = 0.41$ and $n_0^* = 0.36$. (From now on the temperature $T$ and density $n_0$ will be given in units of $\epsilon/k$ and $1/\sigma^3$ respectively, where $k$ is Boltzmann's constant and $\epsilon$, $\sigma$ are...
Table 6: Parameters of the Interatomic and Electron-Atom Interactions

<table>
<thead>
<tr>
<th>Element</th>
<th>Lennard-Jones Potential</th>
<th>Electron-Atom Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\varepsilon/k (K^o)$</td>
<td>$\sigma (\AA)$</td>
</tr>
<tr>
<td>He</td>
<td>10.2</td>
<td>2.556</td>
</tr>
<tr>
<td>Ne</td>
<td>35.7</td>
<td>2.789</td>
</tr>
<tr>
<td>Ar</td>
<td>119.76</td>
<td>3.405</td>
</tr>
<tr>
<td>Kr</td>
<td>171.0</td>
<td>3.600</td>
</tr>
<tr>
<td>Xe</td>
<td>221.0</td>
<td>4.100</td>
</tr>
</tbody>
</table>

From Ref. 63.
parameters for the Lennard-Jones potential listed in Table 6). The calculated quasifree electronic ground state energy is much larger than the one given by experiment. We believe the difference is due, in part, to the fact that the system we are considering has much higher temperature. Unfortunately, there is no measurement of \( E_0 \) in the classical regime. Next we look at neon gas at \( T^* = 0.70 \) and \( n_0^* = 0.80 \). The calculated \( E_0 \) is 0.60 ev as compared with the experimental value 0.67±0.05 ev given by Tauchert at \( T^* = 0.70 \) and \( n_0^* = 0.805 \). The agreement here is surprisingly good which may be attributed to our having fit the potential to the scattering phase shifts over a wide range of energy. If this is the case then we would expect that the Ar gas will also give us good agreement. The result for the Ar gas is \( E_0 = -0.298 \) ev at \( T^* = 0.70 \) and \( n_0^* = 0.85 \) which is very encouraging as compared with \(-0.20\pm0.02\) ev given by Tauchert and Lekner et al. at \( T^* = 0.73 \) and \( n_0^* = 0.846 \). The above results are obtained using the screening function given by Eq. (B-7). We have also examined the case when there is full screening, i.e.

\[
f(r) = \left(1 + \frac{8}{3} \pi n_0 \alpha \right)^{-1} \quad \text{for all } r,
\]

and the case when there is no screening at all. In the Ne gas, and at \( T^* = 0.70 \) and \( n_0^* = 0.80 \), we find \( E_0 = 0.566 \) ev for
no screening and $E_0 = 0.65$ ev for full screening. In the Ar gas, and at $T^* = 0.70$ and $n_0^* = 0.85$, the energy $E_0$ is found to be $-0.443$ ev for no screening and $-0.093$ ev for full screening. The results for $E_0$ are summarized in Table 7 accompanied with the experimental data. The overall results show that the partial screening proposed earlier is the satisfactory choice insofar as calculations of $E_0$ are concerned.

The result for the Kr gas using partial screening is $E_0 = -0.581$ ev at $T^* = 0.70$ and $n_0^* = 0.80$. This may be compared with $-0.45 \pm 0.05$ ev given by Tauchert$^6$ at $T^* = 0.72$ and $n_0^* = 0.826$. The last element is Xe and for it we find $E_0 = -1.105$ ev at $T^* = 0.70$ and $n_0^* = 0.90$ which is about twice as much as the experimental value of $-0.61 \pm 0.05$ ev given by Tauchert$^6$ at $T^* = 0.75$ and $n_0^* = 0.936$. Probably, this discrepancy can be reduced if we have enough low energy scattering phase shifts, instead of a single scattering length, to fit our potential. Also, for xenon, a small change in the screening function can produce a relatively large change in $E_0$. We note that only He and Ne have positive ionization energies.

We have also suggested two different cutoff schemes in Appendix B to ensure that our choice of the electron-atom potential is applicable in the mean field approximation. In scheme I the potential has been set to zero for distances smaller than the cutoff radius $r_c$ while in scheme II the
Table 7: Calculated and Experimental Ionization Energies

<table>
<thead>
<tr>
<th>Element</th>
<th>Experimental</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T$ ($\epsilon$/K)</td>
<td>$n_0$ (1/$a^3$)</td>
</tr>
<tr>
<td>He</td>
<td>0.41 0.36 1.05$+0.05^1$</td>
<td>7.70 0.30 1.62</td>
</tr>
<tr>
<td>Ne</td>
<td>0.70 0.805 0.67$+0.05^1$</td>
<td>0.70 0.80 0.60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.70 0.80 0.56$^4$</td>
</tr>
<tr>
<td>Ar</td>
<td>0.73 0.846 $-0.2+0.02^2,3$</td>
<td>0.70 0.85 $-0.298$</td>
</tr>
<tr>
<td>Kr</td>
<td>0.72 0.826 $-0.40+0.05^2$</td>
<td>0.70 0.80 $-0.581$</td>
</tr>
<tr>
<td>Xe</td>
<td>0.75 0.936 $-0.46+0.05^2$</td>
<td></td>
</tr>
</tbody>
</table>

1. From Ref. 64.
2. From Ref. 65.
3. From Ref. 34.
4. With no screening.
5. With full screening.
potential inside the cutoff radius has been set equal to the potential at \( r = r_c \). Eqs. (B-11), (B-13) have been used to determine the value of \( r_c \) for these two procedures. For example, at \( T^* = 1.1 \) and \( n_0^* = 0.9 \), scheme I gives \( r_c = 1.130a_0 \); the potential is 180 ev at this point and drops to zero for \( r < r_c \). At the same temperature and density, scheme II gives \( r_c = 1.329a_0 \) and the constant potential inside \( r_c \) is 28.43 ev. Here remember that the repulsive potential was introduced originally to simulate the exchange and correlation potentials between the incoming electron and core electrons. It will make more sense to have this potential uniform through the core region as represented by scheme II, instead of a large and sharp potential barrier as given in scheme I. The electron-atom potential specified by scheme II has been adopted in all mean field calculations.

Next we proceed to discuss our results for the free energies and density profiles obtained from the density functional formalism. The relative functional \( \Delta \Omega[n] \) given in Eq. (2-25) is minimized by substituting in the trial function of Eq. (2-26) or (2-27), depending on whether the state sought is the bubble or droplet. The parameters \( \alpha, \beta, \) and \( \gamma \) are adjusted on grids of varying sizes until the minimum of \( \Delta \Omega[n] \) are obtained. Different starting points have been chosen to ensure that physically reasonable results are obtained and also that the results are
reproducible. In Eq. (2-26), \( n(\vec{r}) \) can be negative at small \( r \) if \( \alpha \) becomes sufficiently large. Wherever this happened, we set \( n(\vec{r}) \) equal to zero.

A trial function which includes more parameters to allow for possible oscillatory behavior of \( n(\vec{r}) \) near the bubble-liquid interface has been used in I. Oscillatory profiles have actually been predicted in the case when a fluid is pressed against a hard wall or when the fluid is in contact with a wall that exerts a long-range van der Walls force on the fluid atoms. The result given in I shows that such a trial function fails to predict any non-monotonic behavior even at very high densities at the bubble-liquid interface. One might think that it is important to include this more complicated trial function in our more refined calculation. We may argue, on the basis of similar calculations for a model one-dimensional system, that oscillations are only likely when the interface is narrow and the fluid density change, large. This is the case only for bubble states in fluids at high pressure and density. In those materials for which bubble states are stable anywhere (Helium and Neon) we find that they are stable at high densities for monotonic profiles. Even if a non-monotonic profile should lower the free energy, that would not affect the qualitative conclusion that the bubble is stable. Hence we did not feel that the added complexity and consumption of computer time necessitated by a
non-monotonic trial function was desirable, and we have confined ourself to the use of the simple trial function of Eq. (2-26). Now we proceed to discuss in turn our results for helium, for neon, and for argon, krypton, and xenon. In each case comparison is made with the results of I.

(1). Helium

In I, a simple positive delta function i.e., a contact potential has been used to simulate the interaction between the electron and the helium atom. It was found that the free energy difference $\Delta \Omega$ between the bubble and quasifree states as given by the density functional formalism is larger than that obtained from an ideal gas model. The main purpose of the present computation is to examine corrections introduced by including the long-range polarization potential. The same temperature $T^* = 7.7$ was used. In Fig. 1 we show the free energy difference $\Delta \Omega$ between the bubble and quasifree states in units of $\epsilon$ plotted against $n_0^*$. The curve $I$ results from the ideal gas model while curves $DF1$ and $DF2$ are predicted by the previous and current calculations respectively. For $n_0^* > 0.10$, our results show that $\Delta \Omega$ is much more negative than the previous calculations and signify the existence of more stable bubble states. These are consistent with our inclusion of an attractive polarization potential in the interaction
The grand free energy difference $\Delta \Omega$, in units of $\varepsilon$, between the bubble and quasifree states is plotted against the bulk density $n_0^* = n_0 \sigma^3$ in helium gas at $T=78.5 K$. The curve $IG$ is the result of the ideal gas model while $DF1$ and $DF2$ are predicted by the previous and current density functional calculations, respectively. The density at which the bubble becomes unstable is $n_0^* = 0.112$ in the ideal gas model, $n_0^* = 0.126$ in $DF1$, and $n_0^* = 0.106$ in $DF2$. The parameters $\varepsilon$ and $\sigma$ for rare gases are given in Table 6.
Fig. 1
which tends to lower the electronic energy in the bubble by lowering the potential energy of the electron in this region of space. As the density becomes smaller, the present $\Delta \Omega$ approaches those found from the ideal gas model and in I. Also, the density at which the bubble becomes unstable, i.e. $\Delta \Omega = 0$, is $n_0^* = 0.106$ which is somewhat smaller than in the ideal gas approximation ($n_0^* = 0.112$) and in I ($n_0^* = 0.126$).

In Fig. 2 we compare the density profiles at $n_0^* = 0.13$ for the three different formalisms. Curves IG and DF1 are very similar in that they have a smooth interface between the vapor and liquid phases. The present calculation, as shown by DF2, gives a sharper bubble boundary and manifests no vapor at distances less than $2\sigma$. The deep potential well inside the bubble produced by the polarization potential from the fluid atoms outside enables the electron to have a relatively large kinetic energy. At $T^* = 7.7$ and $n_0^* = 0.13$ the depth of the potential well is 0.433 ev while the kinetic energy of the localized electron is 0.2852 ev. This may partly explain why there is no vapor at the central region of the bubble.

Another possible reason for this might be the presence of a large positive core potential in our electron-atom interaction. Any attempt by the fluid atom to enter into the bubble will inevitably raise the electron potential in the bubble which certainly is not favored by the localized
Fig. 2

The density profile of the electron bubble, in units of $\sigma^{-3}$, is plotted as a function of $r(\sigma)$ in helium gas at $n_0^*=0.13$ and $T=78.5K$. The results of the previous and current density functional calculations are identified by DF1 and DF2 along with the result of the ideal gas model which is marked by IG. The present calculation predicts that no vapor is allowed within a distance of $2\sigma$ of the bubble center at this density and temperature.
Fig. 2
electronic state. Instead the bubble will try to expel the fluid atoms far enough that no substantial amount of the repulsive part of the potential is felt within the bubble, while keeping it close enough that the deepest part of the potential can reach into the bubble. This kind of delicate balance between the negative and positive parts of the electron-atom potential can undoubtedly be used to explain the predicted sharp bubble-liquid interface.

(2). Neon

As we mentioned earlier, helium and neon are the only two elements among the rare gases whose fluids have positive ionization energies and positive electron scattering lengths. This means that neon is another candidate for possible bubble states. In I bubble states have been shown to be stable ($\Delta \Omega < 0$) within the reduced temperature range from 0.7 to 1.5. The results also show that at given temperature the bubble states become metastable when the density is either increased or decreased. For temperatures lower than the gas-liquid critical temperature ($T^* = 1.3$), decreasing the density of the liquid will eventually lead to a region where the liquid is metastable against formation of the gas phase. The radius of the bubble will grow indefinitely and $\Delta \Omega$ approaches negative infinity. In Fig. 3 we show our results for $\Delta \Omega$ in units of $\varepsilon$ vs $n_0^*$ at selected
The grand free energy difference $\Delta \Omega$, in units of $\varepsilon$, is plotted against the bulk density $n_0^* = n_0 \sigma^3$ in neon gas at $T^* = 0.7, 1.1, 1.3, 1.4, 1.5, \text{ and } 1.6 \varepsilon/k$. Each curve is labeled with the appropriate value of $T^*$. At high densities and $T^* < 1.4$, the present calculations predict increasingly stable bubble states in contrast to the previous DF calculations which predict the collapse of the bubble in this region.
Fig. 3
temperatures between 0.7 and 1.6. Behavior similar to that given in I has also been observed at low densities in our calculations. But at high densities our results show that the bubble tends to be more stable which is in contrast with the results given in the previous calculations which predict the collapse of the bubble in this region. We believe that this also results from the inclusion of the polarization potential which makes the potential well inside the bubble relatively more negative to accommodate the electron. In this case the fluid is totally expelled from the bubble and a sharp interface is found. We show the density profiles $n^*(r)$ as functions of $r^*$ at $T^*=1.5$ for several densities in Fig. 4. A vacuum region and a sharp boundary which form a well defined bubble are observed at reduced densities larger than 0.5. The radius $R$ is defined, as in I, to be such that

$$\frac{4}{3}\pi R^3 = \int d^3r [1-n(r)]/n_0.$$  \hfill (3-2)

in Fig. 5 the radius $R$ in units of $\sigma$ is plotted against $n_0^*$ for temperatures such that $0.7 < T^* < 1.6$. In general they are about $0.5\sigma$ smaller than those given in I at the same temperatures and densities.
The density profile of bubbles in neon gas are shown as functions of $r^*$ at $T^*=1.5$ and $n_0^*=0.3, 0.4, 0.5, 0.6,$ and $0.7$. A vacuum region and a sharp boundary forming a well-defined bubble are observed for $n_0^* > 0.5$. 

Fig. 4
Fig. 4
The bubble radius $R(\sigma)$, defined in Eq. (3-2), is plotted as a function of the bulk density $n_0^*$ in neon gas at $T^*=0.7, 1.1, 1.3, 1.4, 1.5,$ and $1.6$. Each curve is labeled with the appropriate value of $T^*$. 
(3). Argon, Krypton and Xenon

It is known that no bubble-like localized electron states exist in the heavier rare gas fluids Ar, Kr, and Xe. Our search for such states did not yield any metastable or stable bubbles which is in agreement with this observation. However, it has been proposed\textsuperscript{13,14} that droplet-like localized states may possibly appear in the gas phase at some \(n_0^*\) and \(T^*\) close to the phase boundary. The previous model calculation predicts no droplet formation is likely in these gases which implies that the observed decrease in the excess electron mobility in xenon vapor near the critical point is not a consequence of such droplets. To investigate this question calculations have been done here for Ar and Xe at \(T^*=1.2\) and 1.3 in the gas phase region. The results for Ar predict no such states at \(T^*=1.2\), but at \(T^*=1.3\) there are metastable droplet states at reduced densities between 0.10 and the phase boundary \((n_0^*=0.175)\). The relative free energies in units of \(\varepsilon\) are 1.91 at \(n_0^*=0.10\) and 0.82 at \(n_0^*=0.15\). If the number of excess fluid particles embedded in this high density region is defined by

\[
N = \int (n(r) - n_0) d^3r, \tag{3-3}
\]
then the number of particles involved in this metastable Ar droplet is about 44 at both densities. For the xenon gas at $T^* = 1.3$ and the same density ranges, $\Delta \Omega$ has been found to be negative and equal $-5.12 \varepsilon$ at $n_0^* = 0.10$ and $-13.34 \varepsilon$ at $n_0^* = 0.15$. The total number of particles associated with the droplet has been found to be 78 at $n_0^* = 0.10$ and 99 at $n_0^* = 0.15$.

Since the localized state is only slightly lower in free energy than the extended state, large fluctuations in free energy and particle number density near the critical region can easily work against the formation of such droplets. To show this is the case, we have estimated the size of fluctuations in the droplet at $T^* = 1.3$ and $n_0^* = 0.15$. The minimum of $\Delta \Omega$ occurs at $\alpha = 2.167 \sigma$, $\beta = 1.00 \sigma$, and $\gamma = 4.90$ (see Eq. 2-27), and the corresponding density profile is given in Fig. 6. If we approximate this high density region by a simple droplet of radius $3.5 \sigma$ and uniform density $0.50 \, 1/\sigma^3$, then the total number of fluid particles inside the droplet is about 90. To estimate the fluctuations in the particle number density $n$ and energy $E$ within the droplet, we use the following relations given in the grand canonical ensemble:

$$\frac{(\Delta n)^2}{\bar{n}^2} = \frac{kT}{V} k_T,$$

(3-4)
The density profile of the droplet, $n^*(r^*)$, is shown as a function of $r^*$ in xenon gas at $n_0^* = 0.15$ and $T^* = 1.3$. The number of excess xenon atoms in this droplet is estimated to be 100 using Eq. (3-3). For simplicity, this profile has been approximated by a step function of radius $3.5\sigma$ and height $0.50\sigma^{-3}$ to estimate the fluctuations in the particle number and energy.
Here $k_T$ is the isothermal compressibility of the droplet, $C_v = \frac{3}{2}k$, and $U$ is given by the virial theorem

$$U = \frac{3}{2}NkT + \frac{N^2}{2V} \int g(r)v(r)d^3r,$$  \hspace{1cm} (3-6)

where $v(r)$ is the Lennard-Jones (6-12) potential. The isothermal compressibility $k_T$ can be calculated using the differential form of Eq. (2-15), i.e.,

$$\left(\frac{3P}{\partial n}\right)_T = kT[1 - nC(0)]; \hspace{1cm} (3-7)$$

Further $nC(0) = 0.788$ at $n_0^* = 0.15$ and $T^* = 1.3$, and $C(0)$ is the zeroth Fourier component of the direct correlation function as given in Eq. (2-14). Simple thermodynamic relations have also been used to relate $\left(\frac{3P}{\partial n}\right)_T$ to $k_T$, i.e.

$$\left(\frac{3P}{\partial n}\right)_T = \left(\frac{\partial P}{\partial V}\right)_{T,N}\left(\frac{\partial V}{\partial n}\right)_T$$

$$= -\frac{V^2}{N}\left(\frac{\partial P}{\partial V}\right)_{T,N}$$

$$= \frac{V}{N}\frac{1}{k_T}.$$  \hspace{1cm} (3-8)
Hence the root-mean-square fluctuation in the particle number is

\[ \left( \frac{\Delta N}{\langle N \rangle} \right)^2 = \left( \frac{N}{0.212} \right)^2 \approx 20. \]  

(3-9)

The corresponding fluctuation in energy is given, in units of \( \epsilon \), by

\[ \left( \frac{\Delta E}{\langle E \rangle} \right)^2 \approx 76. \]  

(3-10)

which is much larger than \( \Delta \Omega = -13.3^4 \epsilon \) at the same temperature and density.

Our conclusions coincide with the recent observations by Freeman and Huang.\(^{13,14}\) They found that "of the order of a hundred molecules are involved in a 'quasidroplet' that quasi-localized an electron" and "the extent of the electron quasi-localization in dense argon gas near the critical region is less than that in xenon at the same relative density and temperature". The term 'quasidroplet' has been used because the density fluctuations that serve as trapping centers in the vapor are not true long-lived droplets.
A. Potential

Here we consider only the two-body intermolecular forces between closed shell atoms and ions, or more specifically the interactions between rare gas atoms and alkali ions. As we know, at large distances these interactions can be fairly well represented by the dispersion and polarization potentials. But once an ion and an atom approach each other, the effects of electron exchange and electron correlation become important and result in a repulsive interaction at short distances. The exact formulation of this short-range force is a tedious and complicated problem which is certainly beyond our present interest. But before we proceed to describe the procedures used to fit the model potential of Eq. (2-35), namely

$$v(r) = C_N/r^N - C_6/r^6 - C_4/r^4,$$  \hspace{1cm} (4-1)

we remark that a simple model for calculating the forces between closed-shell atoms and molecules at short distances has been developed by Kim and Gordon. They have taken
both the overlap of the separate atomic densities and electron correlations into account by using the electron gas model. Tabulated potential values, which are in good agreement with available measures of ion mobilities and diffusion coefficients, are given for rare gas pair and alkali-rare gas interactions. Instead of using these tabulated potentials as input to our computer program and interpolating them whenever needed, we have decided to use simple 4-6-N potentials of Eq. (4-1) suggested by Budenholzer, Gislason, and Jorgensen.\textsuperscript{50} In Eq. (4-1) the parameter $C_4$ is chosen to give the polarization potential at large distances. The parameters $N$, $C_N$, and $C_6$ are allowed to vary in such a way that Eq. (4-1) gives the best calculated ion-atom scattering cross sections as compared with the experimental results. Because of the slow motion and large mass of ions and atoms, this scattering process can be treated classically using Smith's theory,\textsuperscript{68} instead of the quantum mechanical phase shift analysis described in Appendix A.

Smith has derived the following relation between the deflection angle $\theta$ and the impact parameter $b$:

$$E_{rel} \theta = \tau(b) + (E_{rel})^{-1}\tau_1(b) + (E_{rel})^{-2}\tau_2(b) + \ldots.$$  

(4-2)
Here $E_{\text{rel}}$ is the relative kinetic energy and $\theta$ is measured in the center of mass coordinates. The functions $\tau(b)$, $\tau_1(b)$, etc., can be computed from the intermolecular interaction $v(r)$ of Eq. (4-1). At high energies and small deflection angles, only the first term in the expansion need be retained. In addition, at high energies,

$$E_{\text{rel}} \theta = E\theta,$$

(4-3)

where $E$ is the kinetic energy of incoming particle while the target particle is at rest, and $\theta$ is the deflection angle in the laboratory coordinates. Thus, we have a simple relation between the deflection angle and the impact parameter:

$$E\theta = \tau(b).$$

(4-4)

The classical differential cross section $\rho_0(\tau)$ in this case reduces to

$$\rho_0(\tau) = (\tau/2) |d(b^2)/d\tau|,$$

(4-5)

which depends on $\tau$ only. If one defines

$$\sigma(\tau_0) \equiv \int_{\tau_0}^{\infty} d\tau \rho_0(\tau)/\tau$$

(4-6)
which depends on $\tau_0$ only, the total cross section $q$ is simply the integral of $\sigma(\tau)$ over $\tau$ weighted by the derivative of the resolution function $K(\tau, \tau_R)$:

$$q(\tau_R) = -\int_0^\infty \sigma(\tau_0) K'(\tau_0; \tau_R) d\tau_0. \quad (4-7)$$

Here $K'(\tau_0; \tau_R) = dK/d\tau_0$ and the resolution function $K(\tau_0; \tau_R)$ has the form

$$K(\tau_0; \tau_R) = \exp[-(\ln 2)(\tau/\tau_R)^2]. \quad (4-8)$$

The quantity $\tau_R$ is the product of the kinetic energy $E$ and the nominal apparatus resolution angle $\theta_R$, i.e., $\tau_R = E\theta_R$. This shows that the total cross section only depends on the simple variable $\tau_R$. The computation of the total cross section $q(\tau_R)$ is straightforward once the function $\tau(b)$ is given as a function of $V_{12}(r)$. The relation between $\tau(b)$ and $V_{12}(r)$ is as follows:

$$\tau(b) = -b \int_b^\infty dR (dV_{12}(r)/dR)/(R^2-b^2)^{3/2}. \quad (4-9)$$

For our simple choice of the potential $V_{12}(r)$, an analytical expression can be obtained for $\tau(b)$ as has been shown by Smith,
The function $\tau(b)$ in this case is positive at small $b$ and passes zero and reaches a minimum value of $-\tau_r$ at the so-called rainbow impact parameter. The function then goes smoothly to zero as $b \to \infty$. For a given value of $\tau_0$ and $|\tau_0| \leq \tau_r$, the cross section $\sigma(\tau_0)$ of Eq. (4-6) can be obtained by determining the three values of $b$ which solve the equation $\tau(b) = \pm \tau_0$. If the solutions are ordered so that $b_1 < b_2 < b_3$, then

$$\sigma(\tau_0) = \sigma_1(\tau_0) + \sigma_2(\tau_0), \quad (4-10a)$$

where

$$\sigma_1(\tau_0) = \pi b_1^2, \quad (4-10b)$$

$$\sigma_2(\tau_0) = \pi (b_3^2 - b_2^2). \quad (4-10c)$$

For $\tau_0 > \tau_1$, $\sigma_2(\tau_0)$ simply vanishes. The total cross section of Eq. (4-7) reduces to

$$q(\tau_R) = q_1(\tau_R) + q_2(\tau_R), \quad (4-11a)$$

where
Eqs. (4-11) then can be used to reproduce the experimental cross section by varying the parameters \( N, C_N \) and \( C_6 \) in \( v(r) \). The parameters for the potassium ion-rare gas potentials have been given in Table 1 of Ref. 50. These parameters are obtained by the least square fit of the theoretical \( q(T_R) \) described above to 36 experimental data points.

In Fig. 7 we show the \( K^+ - Ar \) potential curves obtained by Kim and Gordon\(^5\) and the 4-6-N model potential. As far as our present application is concerned, the agreement is quite good. The parameters for \( K^+ - Ar \) potential are \( N = 11.02, C_N = 1.198 \times 10^4 \text{ (ev)}(\text{\AA})^N, C_6 = 27.56 \text{ (ev)}(\text{\AA})^6, \) and \( C_4 = 11.80 \text{ (ev)}(\text{\AA})^4. \)

B. Density Profiles

The main purpose of our present calculation is to investigate the possibility of forming an ion-cluster in classical fluids. With the ion-rare gas atom potential given in Eq. (4-1), we expect that at high temperatures and low densities the density profiles of the fluid with the ion located at the origin will have forms close to those of an ideal gas, i.e.
The potential $v(r)$, in units of ev, between a potassium ion and an argon atom is plotted as a function of $r(\text{Å})$. The curve marked with KG is given by Kim and Gordon (Ref. 51) and the one marked with MP is obtained by using the 4-6-N model potential defined in Eq. (4-1).
\[ n(r) = n_0 \exp(-v(r)/kT). \quad (4-12) \]

Here, \( n_0 \) is the uniform gas density at distances far away from the origin. We also believe that at high temperatures and low densities the density functional theory, the linearized Percus-Yevick equation and Monte Carlo simulation should yield densities comparable with those given by Eq. (4-12). Furthermore, the clustering of a single molecule of argon gas around a potassium ion has been observed in drift tube experiments at room temperature by Thomson et al.\textsuperscript{43,44} Hence we decided to do our calculation beginning with a potassium ion in argon gas at \( n_0^* = 0.01 \) and room temperature (\( T^* = 2.505 \)).

A trial function appropriate for the density functional formalism in this case is

\[ n(r) = n_0 \exp(\alpha/r^{11.02} - \beta/r^6 - \gamma/r^4). \quad (4-13) \]

The exponents for the \( r \) dependence have been chosen to equal those of \( v(r) \) in Eq. (4-1). The minimum of the relative free energy given by Eq. (2-18) occurs at \( \alpha = 1.23, \beta = 3.27, \) and \( \gamma = 5.0 \). If the total number of particles attached to the ion is defined by

\[ N = \int[n(r) - n_0]d^3r, \quad (4-14) \]
then N = 1.5 for the density functional formalism at $n_0^* = 0.01$ and $T^* = 2.505$. The peak of the fluid density profile is $n_{\text{max}}^* = 0.78$ which is about the highest density for which accurate correlation functions are available to us at this temperature. For densities higher than 0.8 the solution of Percus-Yevick equation which gives the pair correlation function converges extremely slowly. Thus the application of the density functional has been restricted to systems with small maximum density.

The result of the LPY theory is equivalent to solving the integral equation Eq. (2-33) self-consistently for $g_{12}(r)$. Eq. (2-33) can be simplified to a one-dimensional form if the ion is positioned at the origin, i.e.

$$g_{12}(r) = \exp(-\beta v(r))[1 + \frac{2\pi n_0}{r} \int_0^\infty r'^2 dr'[g_{12}(r') - 1]$$

$$[I(r + r') - I(r - r')]}, \quad (4-15)$$

with

$$I(x) = \int_0^x yC_{11}(y)dy. \quad (4-16)$$

The integral $I(x)$ is determined solely by the correlation function of a uniform system at density $n_0$ and only needs to be computed once before the iteration process begins.

During the iteration process combinations of two immediate
predecessors of \( g_{12}(r) \) have been used as input to the right hand side of Eq. (4-15) to ensure fast convergence. The criterion for the iteration process to terminate is when two consecutive solutions of Eq. (4-15) differ by less than some positive number \( \epsilon(<10^{-5}) \) at each point. To see how fast the integral equation is converging, we have also calculated for each iteration the \( L_1 \) norm of the difference of two successive solutions, \( g_{12}^{(1)} \) and \( g_{12}^{(2)} \), i.e.

\[
\|g_{12}^{(1)}(r) - g_{12}^{(2)}(r)\| = \int |g_{12}^{(1)}(\mathbf{r}) - g_{12}^{(2)}(\mathbf{r})| \, d^3r.
\]  

(4-17)

By definition the \( L_p \) norm for a function \( f(x) \) is given by

\[
\|f(x)\|_p = \left( \int |f(x)|^p \, dx \right)^{1/p}.
\]  

(4-18)

The initial input to the right hand side of Eq. (4-15) is \( \exp(-v(r)/kT) \) and it only takes 17 iterations for the equation to satisfy the convergence criterion set above at \( n_0^* = 0.01 \) and \( T^* = 2.505 \). The \( L_1 \) norm of Eq. (4-17) for the last two solutions is \( 2.7 \times 10^{-5} \). The total number of particles attached to the ion is approximately equal to 1.9 in this LPY calculation.

Next we compare density profiles resulting from density functional and LPY with the Monte Carlo simulations.
In Fig. 8 the density profile of an ideal gas attached to an ion as given by Eq. (4-12) at $T^* = 2.505$ and $n_0^* = 0.01$ is plotted against that of the MC simulation computed at the same temperature and density. In the following discussions the MC results are shown as histograms with a bin width equal to the thickness of concentric shells around the ion as mentioned in Section C, Chapter 2. The pair interaction between fluid particles tends to lower the peak of the density profile. In Figs. 9 and 10 density profiles from the density functional and LPY are plotted against the MC profiles at $T^* = 2.505$ and $n_0^* = 0.01$. The result of LPY fits the result of MC extremely well while the result of density functional shows a closer peak to the ion.

The surprisingly good agreement between the results of the LPY and MC has inspired us to further investigate the validity of the LPY at higher densities. In Figs. 11 to 14 we have shown the results of the LPY versus MC at $T^* = 2.505$ and $n_0^* = 0.021, 0.042, 0.063$, and $0.097$ respectively. The mounting cost of computer time has prevented us from doing more MC computations at densities higher than $0.097$. But for the existing data, the LPY gives very consistent agreement with computer simulations in the potassium ion-rare gas system at room temperature. Note in Fig. 14 the result of the LPY also shows signs of forming a second 'bump' as
Fig. 8

The density profile of an ideal gas in the presence of an ion, as given by Eq. (4-12) using the interaction of Eq. (4-1), at $n_0^* = 0.01$ and $T^* = 2.505$ is compared with that of the MC simulation of the interacting gas at the same density and temperature.
Fig. 9

The density profile of a potassium ion cluster in argon gas obtained from the density functional formalism is plotted against that of the MC simulation at $n_0^* = 0.01$ and $T^* = 2.5$. 
$n^* (r^*) \times 10^2$

Fig. 9
Fig. 10

The density profile of a potassium ion cluster in argon gas obtained from the LPY theory is plotted against that of the MC simulation at $n_0^* = 0.01$ and $T^* = 2.505$. 
Fig. 10

\[ n^*(r^*) \times 10^2 \]

\[ r^* \]

Fig. 10
Fig. 11

The density profile of a potassium ion cluster in argon gas obtained from the LPY theory is plotted against that of the MC simulation at $n_0^* = 0.021$ and $T^* = 2.505$. 
The density profile of a potassium ion cluster in argon gas obtained from the LPY theory is plotted against that of the MC simulation at $n_0^* = 0.042$ and $T^* = 2.505$. 
Fig. 13

The density profile of a potassium ion cluster in argon gas obtained from the LPY theory is plotted against that of the MC simulation at $n_0^* = 0.063$ and $T^* = 2.505$. 

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Fig. 13

\[ n^*(r^*) \times 10^2 \]
The density profile of a potassium ion cluster in argon gas obtained from the LPY theory is plotted against that of the MC simulation at $n_0^* = 0.097$ and $T^* = 2.505$. 
has been seen in the case of argon fluid pressed against a hard wall.\textsuperscript{66}

The interesting question to ask next is what will happen when the temperature is lowered, for example, near the critical point. The LPY calculation at $T^* = 1.5$ and $n_0^* = 0.011$ is given in Fig. 15 along with its MC counterpart. For temperatures lower than 1.5 the convergence of the integral equation (4-15) is extremely slow. Sometimes our algorithm tends to diverge although we know the solution must exist. But even when the temperature is only lowered to $T^* = 1.5$ a large discrepancy between the LPY and MC is evident. In this case the LPY gives a much larger ion cluster than that predicted by the computer simulation. Previously it has also been shown that the LPY gives much larger oscillations of the fluid density profiles than those produced by the density functional and MC formalisms in one-dimensional square well problems.\textsuperscript{67} Our calculations thus suggest that although LPY can give very consistent results in the ion cluster system as compared with computer simulations at room temperature, it shows large discrepancies at temperatures closer to the critical point.
The density profile of a potassium ion cluster in argon gas obtained from the LPY theory is plotted against that of the MC simulation at $n_0^* = 0.011$ and $T^* = 1.5$. A large discrepancy between the LPY and MC is evident in this case.
Two different kinds of charged point defect in classical fluids have been considered in the present work. In the first part of this thesis, we have applied the density functional formalism to the problem of an excess electron in rare gas fluids. It has been pointed out previously in Punyanitya's thesis that there are four major approximations made in applying density functional formalism to classical fluids. We reiterate here as follows:

a) The atom-atom interaction is assumed to be pairwise additive. The pair potential is taken to be a Lennard-Jones (6-12) potential. 

b) The pair correlation function is determined from the Percus-Yevick approximation.

c) The kernel in the non-local term in the free energy functional, Eq. (2-25), is calculated at the average density $\bar{n} = (n(\hat{r}) + n(\hat{r}^-))/2$. 

d) The local term involving $w_0[n(r)]$ in the free energy functional, Eq. (2-25), is taken to be the difference between the grand free energy densities of uniform fluids at densities $n(\hat{r})$ and $n_0$ when the chemical potential is $\mu_0$. 

After an excess electron is introduced into the fluid system, further approximations are made. These are listed below.

e) A pseudopotential consisting of the attractive polarization potential and an effective repulsive core potential has been used to represent the interaction between the electron and a fluid atom. The parameters of the pseudopotentials for rare gases are determined by the phase shifts of the $\ell=0$ partial wave as outlined in Appendix A and are given in Table 6. The exception is xenon gas where the parameter is chosen to reproduce the same scattering length as that given by Ramsauer and Kollath.62

f) The Lorentz local field screening function of Eq. (B-7) has been used to approximate the screening effect due to the presence of other atoms in the fluid. This screening function will affect the long range part of the pseudopotential only.

g) The lowest energy extended electronic state in the fluids was calculated using the Wigner-Seitz cellular method described in Appendix B. The energies so calculated are in good agreement with experimental data.

h) The electron bubble and droplet models were used to simulate the non-uniformity in fluid density produced by the self-trapped electron states (if any).

In He gas, our calculations show that $\Delta \Omega$ is significantly more negative than that calculated in I at $T^* = 7.7$ and $n_0^* > 0.10$. A sharper bubble boundary is also predicted.
This is consistent with our inclusion of the attractive polarization potential whose effect is to lower the energy of the electron localized in the bubble.

In Ne gas, our results also show that electron bubble states are to be expected close to the critical point and in the liquid along the liquid-gas coexistence curve. At high densities our results indicate that the bubble states tend to be even more stable which contradicts the previous predictions that bubble states collapse in this region. Once again we believe this result to be a consequence of the inclusion of the polarization interaction in the present calculations. It is found that at high density the fluid is totally expelled from the bubble and a sharp interface is formed. Our results have been obtained by using a simple monotonic trial function given by Eq. (2-26). One might think that a more complicated trial function which can simulate the possible oscillations at this sharp interface would give us a still lower free energy. We argue that even if this is true it would not affect the qualitative conclusion that the bubble states are stable anywhere in He and Ne at high densities. Hence we did not feel the need to pursue any further along this line of investigation.

The previous calculations with simple contact potentials predicted no droplet-like electron state is likely in any of the rare gases. With our more physically reasonable potential, we found that there are metastable droplet
states in Ar and stable droplet states in Xe at $T^*$ close to 1.3 and reduced densities between 0.10 and the phase boundary. At $T^* = 1.3$ the number of particles involved in the metastable Ar droplet is around 44 in this region and the number of particles associated with the Xe droplet is 78 at $n_0^* = 0.10$ and 99 at $n_0^* = 0.15$. We have also shown that the fluctuations in energy in the droplet at this density and temperature, which is close to the critical point, are much larger than the free energy difference $\Delta \Omega$ between the droplet and uniform gas at the same density and temperature. This means that these droplet states are not stable and have a finite lifetime only. At $T^* = 1.2$ our calculations predict no such states in Ar, but there are metastable states in Xe at reduced densities between 0.05 and the phase boundary. The number of particles involved in these metastable Xe droplets is around 10 to 20 at $0.05 \leq n_0^* \leq 0.10$. These results are consistent with the recent observations by Freeman and Huang who found that of the order of a hundred molecules are involved in electron "quasidroplet" states and the extent of the electron quasilocalization in Ar is less than that in Xe near the critical region. They use "quasidroplet" to indicate that the density fluctuations which serve as trapping centers in the vapor are not true long-lived droplets.

In the second part of this thesis, we have dealt with the problem of ion-clustering in classical fluids. A
specific system we have investigated is a potassium ion in Ar gas at room temperature ($T^* = 2.5$) and at $T^* = 1.5$. Because the density inside the cluster is large and accurate correlation functions at these high densities are not obtainable via the Percus-Yevick approximation, the density functional has been found to be inapplicable, at least within the Percus-Yevick approximation, in this case. Instead the linearized Percus-Yevick approximation and computer simulations were used. The interatomic potential was still assumed to be pairwise additive and taken to be the Lennard-Jones potential, and the ion-atom interaction was chosen to be the N-6-4 potential of Eq. (2-35) as suggested by Budenholzer, Gislason and Jorgensen. The LPY approximation is presented in Eq. (2-33). Our computer simulation was done in the grand canonical ensemble (constant $\mu$, $V$, $T$) using the Monte Carlo method described by Adams. Periodic boundary conditions were adopted to overcome the limitations imposed by the finite size of the system. The results showed that the LPY approximation and computer simulations are in good agreement at room temperature for densities ranging from 0.01 to 0.1. Calculations at higher densities were not attempted because of the expenditure of computer time. But when the temperature was lowered to near the critical point, large discrepancies appeared between the results found using these two procedures. At $T^* = 1.5$ the LPY gives a much larger ion
cluster than that predicted by the MC method. This result is consistent with the previous finding by Ebner, Lee and Saam\textsuperscript{67} that the LPY gives much larger oscillations of the fluid density profiles than those produced by the DF and MC formalism in one-dimensional potential well problems.

We conclude here that the results of the first part of this thesis show that the density functional formalism can be used to predict the existence of localized electronic states in the rare gas fluids. Although at the present stage there is no experimental data available to support our finding that the electron bubble states in Ne are stable even at higher densities and T* <1.2, the same calculations on the electron droplet states in Ar and Xe gases give results consistent with the results of recent electron mobility measurements in these gases. Thus we feel quite satisfied with the approximations made in the calculation and have confidence in the results of our present study on the electronic states in the rare gas fluids.

In the investigation of ion-clustering in the rare gases, our results using the LPY approximation and computer simulations are in moderate agreement with results of the ion mobility and diffusion coefficient measurement.\textsuperscript{43,44} Our calculations estimate about two Ar molecules attached to the K\textsuperscript{+} ion at T* = 2.5 and P\textless1 torr as contrasted to one molecule observed in experiments. We believe that our present results on ion-clustering calculations can be
Improved by including the screening of the N-6-4 potential whose effect is to reduce the attractive long-range potential.
APPENDIX A

DETERMINATION OF THE ELECTRON-ATOM POTENTIAL
FROM SCATTERING PHASEhiftS

Here we describe how we determine the parameters $\sigma_e$ and $N$ in the unscreened electron-atom interaction,

$$v(r) = \left(\frac{2e^2}{\alpha_0 r}\right) \left[\left(\frac{\sigma_e}{r}\right)^N - \frac{\alpha_0}{r^4}\right], \quad (A-1)$$

to give correct electron-atom scattering phase shifts. Eq. (A-1) represents the interaction between an electron and a single fluid atom only and the presence of a positive term in the expression represents the effect of exchange repulsive in the spirit of the pseudopotential theory. Within this theory the requirement that the excess electron wave function be orthogonal to the core orbitals imposed by the Pauli-exclusion principle has been replaced by a fictitious repulsive potential. If the potential $v(r)$ is used as an interaction between an electron and an atom in the fluid, the long-range polarization potential will be screened by the presence of other atoms.

The parameters $\sigma_e$ and $N$ can be determined using the method of partial waves. In this method the radial wave
function $R_\ell(r)$ of the electron at $r>r_0$, where $r_0$ is radius beyond $\nu(r)$ is negligible, is:

$$R_\ell(r) = A_\ell (\cos \delta_\ell j_\ell(kr) - \sin \delta_\ell n_\ell(kr)) \quad (A-2)$$

where $\ell$ is the angular momentum quantum number, $\delta_\ell$ is the phase shift of the $\ell$-th partial wave, $k$ is the wave number and $j_\ell(kr), n_\ell(kr)$ are spherical Bessel and Neumann functions respectively.

As for the radial wave function $R_\ell(r)$ at $r<r_0$, it can be found by solving the following differential equation numerically:

$$-\frac{\hbar^2}{2m} \frac{d^2u_E}{dr^2} + V(r)u_E = Eu_E, \quad (A-3)$$

where

$$V(r) = \frac{\ell(\ell+1)\hbar^2}{2mr^2} + v(r), \quad (A-4)$$

and

$$u_E = rR_\ell(r). \quad (A-5)$$

Eq. (A-3) can be further simplified if we introduce dimensionless variables, parameters, and functions as follows:
\[ x = r/a; \quad \varepsilon = 2\text{mea}^2/h^2; \]
\[ V_e(x) = 2mV(x)a^2/h^2; \quad (A-6) \]

and

\[ f_e(x) = \sqrt{a} u_E(x). \]

Here \( a \) is some constant length usually chosen to be that distance over which \( V(x) \) varies appreciably. Eq. (A-3) then becomes

\[ f_e(x) - \gamma(x) = g_e(x)f_e(x) \quad (A-7) \]

where

\[ g_e(x) = V(x) - \varepsilon. \quad (A-8) \]

A simple and accurate algorithm for solving Eq. (A-7) has been given by Fox and Goodwin; the recurrence relation for \( f(x) \) is given by

\[
f_e(x_{n+1}) = \left\{ \frac{2}{6} g_e(x_n) \right\} f_e(x_n)
- \left[ 1 - \frac{2}{12} g_e(x_{n-1}) \right] f_e(x_{n+1}) / \left[ 1 - \frac{2}{12} g_e(x_{n-1}) \right],
\]

(A-9)
where

\[ x_{n+1} = x_n + \delta \]

and \( \delta \) is some suitable chosen stepsize.

To start the recurrence algorithm in Eq. (A-9), we need to know at least two initial values of \( f_e(x) \). These values can be obtained by looking at the behavior of \( f_e(x) \) at a small \( x \) region where the only dominant term in \( V(x) \) is just the \( 1/x^N \) term. Here Eq. (A-7) reduces to

\[ f_e(x) = \frac{2ma^2}{h^2} (\sigma_e/a)^N f_e(x), \quad (A-10) \]

and the asymptotic solution of this equation is

\[ f_e(x) = A \exp(-\beta/x^p) \quad (A-11) \]

where

\[ p = (N-2)/2, \quad (A-12) \]

and

\[ \beta = \frac{2}{N-2} \left( \frac{2ma^2}{h^2} \right)^{3/2} (\sigma_e/a)^{N/2}; \quad (A-13) \]
A is a normalization constant which is not important in this case.

Once the interior radial wave function is found, the boundary condition requires that \( R_\ell(r) \) be logarithmically continuous at \( r = r_0 \), i.e.

\[
\left. \frac{1}{R_\ell} \frac{dR_\ell}{dr} \right|_{r=r_0^-} = \left. \frac{1}{R_\ell} \frac{dR_\ell}{dr} \right|_{r=r_0^+}. \tag{A-14}
\]

If we let \( \gamma \) be this ratio for the interior radial wave function and use Eq. (A-2) for the external radial wave function, then Eq. (A-14) gives

\[
\gamma_\ell = \frac{k[j_\ell(ka)\cos \delta_\ell - n_\ell(ka)\sin \delta_\ell]}{j_\ell(ka)\cos \delta_\ell - n_\ell(ka)\sin \delta_\ell}. \tag{A-15}
\]

Finally, Eq. (A-15) can be rewritten as

\[
\tan \delta_\ell = \frac{kj_\ell(ka) - \gamma_\ell j_\ell(ka)}{kn_\ell(ka) - \gamma_\ell n_\ell(ka)}. \tag{A-16}
\]

and used to compute the phase shifts for each \( V(r) \).
APPENDIX B

THE QUASIFREE ELECTRON STATES IN RARE GAS FLUIDS

The calculation of the lowest extended state energy $E_0$ of an electron in a classical fluid involves solving the following one-electron wave equation:

$$[-\frac{\hbar^2}{2m} \nabla^2 + v(\vec{r})]\psi_0(\vec{r}) = E_0\psi_0(\vec{r})$$

(B-1)

where $v(\vec{r})$ is the potential exerted on the electron by the fluid and $\psi_0$ is the ground state electron wave function. Since there is no translational symmetry of the lattice in the fluid, it is best to do the calculation using the Wigner-Seitz cellular method.\(^{27}\) We now proceed along the conventional lines of this method and assume that each atom in the fluid occupied a sphere of radius $r_s$ defined by, with the nucleus at the center of sphere,

$$r_s = (3/4\pi n_0)^{1/3}, \quad (B-2)$$

where $n_0$ is the uniform fluid density. In the Wigner-Seitz method, it is assumed that the potential is spherically symmetric around any nucleus within the sphere surrounding
that nucleus. Hence, the ground state wave function is also symmetric about the nucleus and so the boundary condition for \( \psi_0 \) at \( r_s \) is

\[
\left. \frac{d\psi_0}{dr} \right|_{r=r_s} = 0. \tag{B-3}
\]

Consequently, if the potential within the Wigner-Seitz sphere is known, the ground state energy \( E_0 \) can be easily obtained by solving the equation

\[
[-\frac{\hbar^2}{2m} \nabla^2 + V(r)]\psi_0(r) = E_0 \psi_0(r) \tag{B-4}
\]

where \( \psi_0 \) is subjected to the boundary condition Eq. (B-3) and an appropriate condition at \( r \to 0 \).

Next we proceed to find a suitable potential \( V(r) \) within the sphere. It will certainly contain the bare electron-atom potential produced by the atom at the origin and the potentials from the other atoms in the fluid. We have chosen the bare electron-fluid atom potential to have the form

\[
v(r) = (e^2/2a_0)[(g_e/r)^N - \frac{a_0}{r^4}], \tag{B-5}
\]
and the parameters $g_e$ and $N$ have been determined using electron-atom scattering data. The contribution of the potential from the atom outside the Wigner-Seitz sphere can be expressed in the form

$$V_{\text{electron-fluid}}(\vec{r}) = n_0 \int_{\Omega} V(\vec{r}-\vec{r}^\prime)f(\vec{r}-\vec{r}^\prime)g(\vec{r}^\prime)d^3r^\prime, \quad (B-6)$$

where the integration over the volume $\Omega$ excludes the Wigner-Seitz sphere. Here $g(\vec{r})$ is the pair distribution function of the uniform fluid at density $n_0$; it is related to the direct correlation function $C(\vec{r})$ used in Eq. (2-18) through the Percus-Yevick approximation. Since the electron-atom potential is screened by the presence of the other atoms in fluid, the dielectric screening function $f(\vec{r})$ is included in Eq. (B-6). Here because of the short range of the repulsive term in $V(\vec{r})$, the screening effect will affect the polarization potential only. The Lorentz local field screening function of the form\(^2\)

$$f(r) = \begin{cases} 1, & r < r_s, \\ (1 + \frac{8}{3}\pi n_0 a) r_s^{-1}, & r > r_s, \end{cases} \quad (B-7)$$

has been used to approximate this screening effect. Different screening approximations have been tried in Chapter III,
but the above choice gives us the best results for the extended state energy in comparison with the existing data. The combination of equations (B-3) to (B-7) then can be used to solve for $E_0$.

We mentioned in Chapter II that our choice of the electron-atom potential $v(\mathbf{r})$ faces serious difficulty if it is to be used in the mean field approximation. To make it also applicable in this approximation, we have cut it off at short distances. Physically it is plausible to make this cutoff, since the positions of the electron and the atom are actually correlated with each other. The potential energy of the electron in the fluid at density $n(\mathbf{r})$ should be

$$V_1 = \int |\psi(\mathbf{r})|^2 g_e(\mathbf{r}-\mathbf{r}')v(\mathbf{r}-\mathbf{r}')n(\mathbf{r}')d^3\mathbf{r}' , \quad (B-8)$$

where $\psi(\mathbf{r})$ is the electron wave function and $g_e(\mathbf{r})$ is the pair distribution function for the electron and a fluid particle. In the case when the fluid is uniform with density $n_0$ and the electron is equally probably distributed in the volume $V$, Eq. (B-8) reduces to

$$V_0 = n_0 \int v(\mathbf{r})g_e(\mathbf{r})d^3\mathbf{r} . \quad (B-9)$$

Given a potential with a hard core, such as that in Eq. (B-5), $g_e(\mathbf{r})$ is zero at distances less than about the hard
core diameter, and there is no contribution to $V_0$ from this region of the integral. In the simplest mean field approximation $g_e$ is taken equal to unity everywhere. Given a potential with a hard core, such a procedure will produce an infinite $V_0$. However, if we cut the potential off at a distance on the order of the hard core diameter, $V_0$ is thereby rendered finite and, in fact, this scheme approximates closely the effect that $g_e$ has upon $V_0$. That is, the presence of $g_e$ in Eq. (B-9) amounts to cutting off the potential $v(r)$ at some short distance. Two different cutoff schemes have been tested. In the first scheme $v(r)$ is chosen to be

$$v(r) = 0, \quad r \leq r_c,$$

(B-10)

$$v(r) = \left(\frac{e^2}{2a_0}\right)\left(\frac{\sigma_e}{r}\right)^N - \frac{aa_0}{r^4}, \quad r > r_c,$$

where $r_c$ is determined by

$$E_0 = \int_{r_c}^{\infty} v(r) d^3r.$$

(B-11)

In the second scheme it is chosen to be
\[ v(r) = r(r_c), \quad r \leq r_c, \quad (B-12) \]

\[ v(r) = \frac{e^2}{2a_0}[(\sigma_e/r)^N - \frac{aa_0}{4r^4}], \quad r > r_c, \quad (B-13) \]

where \( r_c \) satisfies the following relation:

\[ E_0 = \int v(r) d^3r. \quad (B-13) \]

We note that in the mean field approximation there is no electron kinetic energy in the ground state and so \( V_0 = E_0 \). That is why in Eqs. (B-11) and (B-13) the mean field potential energy has been set equal to the total electron energy. It has been shown in Chapter III that the second choice gives better results.
LIST OF REFERENCES


27. E. Wigner and F. Seitz, Phys. Rev. 43, 804 (1933).


40. L. B. Loeb, *Basic Processes of Gaseous Electrons* (University of California, Berkeley, 1955), Chaps. I and II.


59. It is implicitly a function of $n(r^*)$ for all $r$ through its dependence on the direct correlation function $C(r, r^*; \alpha)$.