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# Solution of the Thomas-Fermi Problem for Continuous, Spherical, Positive Charge Distribution

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A method to make an *ab initio* calculation of the free energy of small drops of liquid metal is presented. The model chosen involves the replacing of the positive ion cores by an equivalent continuous spherical distribution of charge. The Thomas–Fermi potential is calculated as a starting point for a Hartree–Fock self-consistent field calculation. The results of the Thomas–Fermi calculation are reported as an example of the preliminary calculations.

**KEY WORDS:** Thomas–Fermi potential; free energy calculations; liquid metal clusters.

## 1. INTRODUCTION

In order to study the qualitative effects of curvature on the thermodynamic properties of small drops of liquid metal, it is necessary to be able to estimate the free energies of these drops. The model we use, crude but simple, involves replacing the positive ion cores in the metal by an equivalent continuous spherical distribution of charge. The entropy $S(D)$ associated with the distribution $D$ can be estimated. Electrons are assumed to distribute themselves

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in their ground state, at energy $E(D)$. The electrons contribute no entropy since they are in their ground state. The partition function of the system can be approximated as

$$Q = \frac{(2\pi mkT)^{3N/2}}{h^{3N}} \sum_{D} e^{-S(D)/k} e^{-E(D)/kT} \tag{1}$$

where $T$ is the temperature, $k$ is Boltzmann's constant, $m$ is the mass of an ion core, $h$ is Planck's constant, and $N$ is the number of ion cores. The free energy $A$ can then be calculated from

$$A = -kT \ln Q \tag{2}$$

Clearly the central problem is the evaluation of $E(D)$. We are in the process of calculating this energy, using self-consistent field methods. As a starting point for these calculations it is useful to solve the Thomas–Fermi statistical potential for this system.(1) Consequently, we have undertaken the solution of the Thomas–Fermi equation for the above model. Since the solution was not trivial, and because it may have value in itself, we have decided to publish the results of this part of our investigation as a separate note.

## 2. METHOD

To solve the problem, we define a continuous spherical ion core distribution (equivalent to $N$ cores) out to a spherical boundary of radius $R_s$. The volume of the sphere is taken as $Nv$, where $v$ is the atomic volume of the metal. The total charge of the positive ion distribution is $Nz$, where $z$ is the number of free electrons assigned to the metal. The $Nz$ electrons can pass freely through the boundary surface. We define the positive charge density as $p_+(r)$.

The Thomas–Fermi model relates the electron charge density and electrostatic potential as follows:

$$p_-(r) = -(8\pi e/3h^3)[2meV(r)]^{3/2} \tag{3}$$

where $p_-(r)$ is the electron charge density, $V(r)$ is the electrostatic potential, $h$ is Planck's constant, $e$ is the charge of an electron, and $m$ is the mass of an electron. The potential energy is

$$U(r) = -eV(r) \tag{4}$$

By solving Poisson's equation

$$\nabla^2 V(r) = -4\pi P(r)/\epsilon_0 \tag{5}$$

$V(r)$ can be found by standard numerical integration techniques for any given $p_+(r)$. Here $P(r)$ is defined as

$$P(r) = p_+(r) + p_-(r) \tag{6}$$

Equation (4) is solved subject to the following boundary conditions:

$$dV_1(r)/dr = 0 \quad \text{at} \quad r = 0 \tag{7a}$$

$$dV_2(r)/dr = 0 \quad \text{at} \quad r = \infty \tag{7b}$$

$$V_2(r) = 0 \quad \text{at} \quad r = \infty \tag{7c}$$

$$V_1(r) = V_2(r) \quad \text{at} \quad r = R_s \tag{7d}$$

$$dV_1(r)/dr = dV_2(r)/dr \quad \text{at} \quad r = R_s \tag{7e}$$

where $V_1(r)$ refers to the potential inside $R_s$ and $V_2(r)$ to that outside.

The method used to obtain the potential is the following. Equation (3) is solved using a finite difference method. A guess is made for the value $V_0$, the potential at $r = 0$. Then the integration is carried toward $r = \infty$. $V_0$ is adjusted until the integration is well behaved out to $r = \infty$. Usually $r = \infty$ was approximated by $r = 10R_s$. A check on the solution was made by

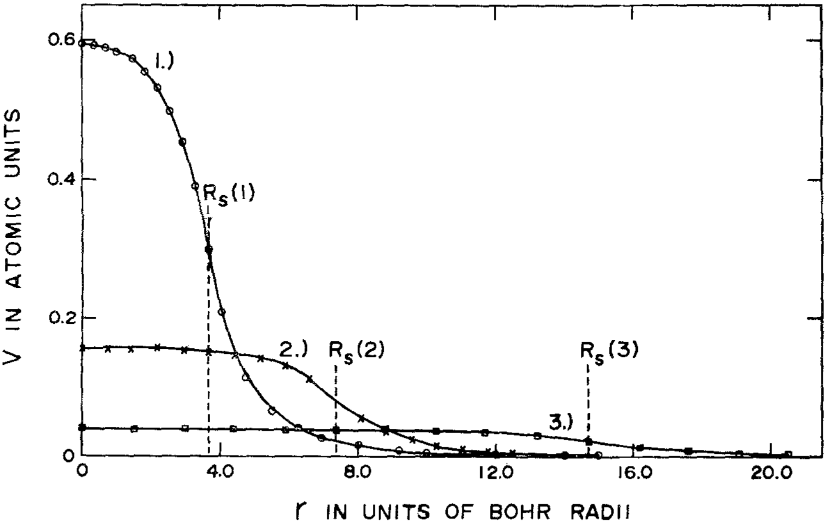

Fig. 1. Thomas–Fermi electrostatic potentials for spheres of constant $p_+$ but of differing radii. Curve 2 represents a sphere of volume $10v$, where $v$ is the atomic volume of Hg. Curve 1 is for the case where $R_s(1) = \frac{1}{2}R_s(2)$, and curve 3 is for the case where $R_s(3) = 2R_s(2)$. Each sphere contains the equivalent number of positive charges. $V$ is in atomic units and $r$ is in units of Bohr radii.

solving for $p_-(r)$ and integrating over all space. This integral should exactly balance the total positive charge. The choice of the starting potential was found to be extremely critical. On the order of 20 iterations were required, with $V_0$ being varied only in the fifth decimal place, in order to obtain a stable and self-consistent function.

## 3. RESULTS AND DISCUSSION

Results obtained for a cluster of ten metal atoms each the size of a Hg atom are reported as an example. In Fig. 1 the electrostatic potential for distributions of three differing radii $R_s$, but containing the same number of atoms, is presented. The positive charge density $p_+(r)$ was assigned a constant value equal to the total positive charge divided by the volume inside $R_s$. Values of $r$ are given in units of Bohr radii. The potential is given in atomic units, where $e = 1$, $m_e = 1$, and $h = 2\pi$. $z$ is taken as equal to one.

Figure 2 gives an indication of the effect of a nonconstant $p_+(r)$. For this

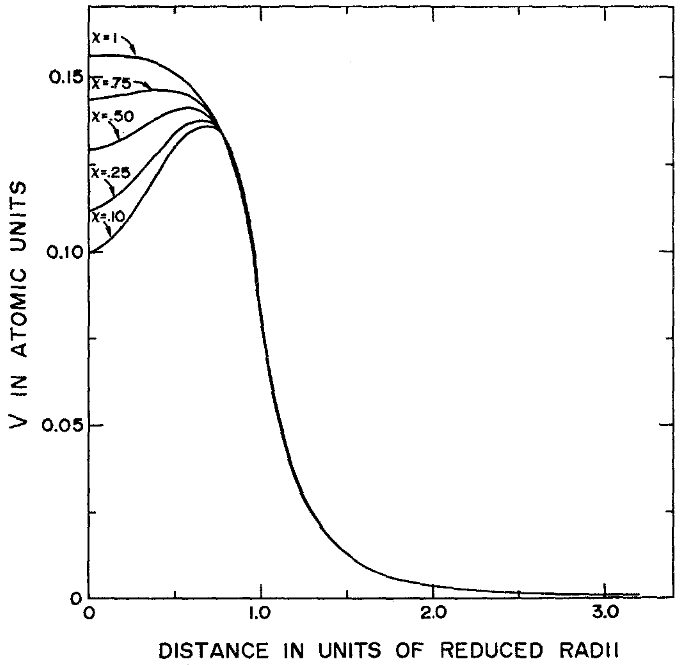

Fig. 2. Thomas–Fermi electrostatic potentials for spheres of constant $R_s$ but of differing $p_+(r)$. Here $p_+$ is a linear function of $r$, where $p_{\min} = xp_{\max}$, $p_{\min}$ is the value of $p_+$ at $r = 0$, and $p_{\max}$ is the value of $p_+$ at $r = R_s$. The volume of the sphere is $10v$, where $v$ is the atomic volume of Hg. $V$ is in atomic units and $r_a$ is in reduced units of $r/R_s$.

calculation $p_+$ increases linearly with $r$ from a $p_{\text{min}}$ at the center to $p_{\text{max}}$ at $R_s$. The total positive charge is, however, kept the same; $p_{\text{min}}$ is equal to $xp_{\text{max}}$, where $x$ is equal to or less than one but always greater than zero. Units of $r$ are given in terms of reduced radii, where $R = r/R_s$.

The potential behaves as expected. For the case where there is more positive charge near $R_s$ the electron density is seen to be greater there also. However, it should be noted that $V(r)$ is not very sensitive to the choice of $p_+(r)$. In Fig. 2 it is seen that a tenfold variation in $x$ causes only about a 30% change in the value of $V_0$. Also, beyond $R_s$, where the shape of the potential is approximately Coulombic in nature, there is very little effect. This result is the same as that predicted by classical electrostatic theory. Finally, it can be noted that as the positive charge density is decreased by increasing $R_s$ the potential energy decreases, and the electronic charge density becomes more diffuse.

The solution to this model suggests that a simple choice of the functional form of $p_+(r)$ can be made without sacrificing much accuracy in the determination of the starting potential energy for a Hartree–Fock calculation. Either a simple shell of positive charge lying on $R_s$ or a constant positive charge density model could be chosen. The choice of the value $R_s$ is seen to be the more important consideration.

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