The Leading Correction to the Thomas-Fermi Model at Finite Temperature

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(Dated: December 9, 2014)

The semi-classical approach leading to the Thomas-Fermi (TF) model provides a simple universal thermodynamic description of the electronic cloud surrounding the nucleus in an atom. This model is known to be exact at the limit of \( Z \to \infty \), i.e., infinite nuclear charge, at finite density and temperature. Motivated by the zero-temperature case, we show in the current letter that the correction to TF due to quantum treatment of the strongly bound inner-most electrons, for which the semi-classical approximation breaks, scales as \( Z^{-1/3} \), with respect to the TF solution. As such, it is more dominant than the quantum corrections to the kinetic energy, as well as exchange and correlation, which are known to be suppressed by \( Z^{-2/3} \). We conjecture that this is the leading correction for this model. In addition, we present a different free energy functional for the TF model, and a successive functional that includes the strongly bound electrons correction. We use this corrected functional to derive a self-consistent potential and the electron density in the atom, and to calculate the corrected energy. At this stage, our model has a built-in validity limit, breaking as the L shell ionizes.

The richness of chemistry originates in the many-body character of the atomic problem, shadowing the simplicity of the underlying coulomb potential, and adding complexity to the solution. In order to solve this problem, one resorts to different approximations of the many-body quantum problem. A different approach, whose foundations lie in Density Functional Theory (DFT), is to formulate the problem in terms of the mean electron density. This is particularly useful when studying thermodynamic properties of a gas of atoms, at finite temperature and density. This research field of Warm and Dense Matter (WDM) is of central importance in astrophysics where the interior of main sequence stars is composed of such atomic plasma. In recent years, extreme thermodynamic conditions are achieved terrestrially using large scale experimental facilities, such as the Z-machine at Sandia National Laboratories, or the National Ignition Facility (NIF), where plasma can be produced at local thermodynamic equilibrium with temperatures of the order of 300 eV.

The first example of a density functional formulation of the atom has in fact been achieved long before the development of DFT in the Thomas-Fermi (TF) model [1, 2]. It is based on a semi-classical treatment of the electrons in the atom, combined with a spherical Wigner-Seitz cell approximation for the ions. Soon after its derivation the zero-temperature model has been corrected to include quantum “gradient” corrections to the kinetic energy and exchange effects [3, 4]. Scott, and following studies, have investigated the limits of the semi-classical approximation, by separating the strongly bound electrons from the semi-classical integration [5]. The basic TF model, as well as the gradient and exchange corrections, were generalized to finite temperature and densities [6-11]. TF model is a very crude and basic approximation for the atom, but its foundations are basic principles of physics, and in fact it is exact at \( Z \to \infty [11, 13] \), with \( Z \) the number of protons in the nucleus of the atom. Moreover, all physical properties predicted by TF model have a simple scaling property with \( Z \). TF model thus provides a universal description of all materials, differing only by a scaling factor.

The development of DFT [14-19] has highlighted the advantages of TF model. DFT ensures that the ground state properties of a quantum many body system are dictated by its density. However, DFT does not hint towards the structure of the density functional that governs the system properties. As a result, TF model is commonly used as the limit for phenomenological DFT models of heavy atoms [17], since TF depends merely on densities by construction. Moreover, Generalized Gradient Approximation (GGA) for the kinetic energy and an accurate exchange-correlation term, have been derived as corrections of the finite temperature TF model [18, 19]. A different approach to the corrections to TF model was taken by Schwinger and Englert [20-22]. Studying a TF description of an isolated atom, i.e., zero density and zero temperature model, they systematically ordered the corrections to the leading TF model by their \( Z \) dependence. They demonstrated that Scott’s correction, i.e., a quantum treatment of the strongly bound electrons, is the leading correction to TF model, suppressed by \( Z^{-1/3} \). Other corrections, such as quantum and exchange, are of lower order, suppressed by \( Z^{-2/3} \).

In the current letter we develop a generalization of Scott’s correction to the finite temperature and density TF model. We show that it is more dominant than the known quantum and exchange-correlation corrections, and thus conjecture that it is the leading correction at these thermodynamic conditions. As such, our study is the initial step to establish a systematic expansion of density functionals, whose different predictions represent the theoretical uncertainty.

We start by considering the assumptions leading to the TF model for a neutral atom of charge \( Z \) at finite temperature \( T \) and chemical potential \( \mu \). Neglect-
ing exchange and correlations contributions, the single electron Hamiltonian is $H_1 = H_n(r, ρ)$, the total entropy can be calculated combinatorially to be $S = k_B \text{Tr} (n \ln (n) + (1 - n) \ln (1 - n))$, and the electronic density is found to be the Fermi-Dirac distribution. Here, the single electron Hamiltonian is $H = \frac{p^2}{2m} + (-e) V(\vec{r})$.

Summing all the single particle energies leads to double counting of the electrostatic energy between the electrons, thus we subtract it once, and write the free-energy functional as [23]

$$F = \text{Tr} ((H - \mu) n_{FD}) - \frac{1}{8\pi} \int d^3r \left( \nabla \left( V(\vec{r}) - \frac{eZ}{r} \right) \right)^2 + \mu Z,$$

where $\sigma = r_0^{-1} Z^{-\frac{4}{3}}$, $\tau = Z^{-\frac{4}{3}} T$. In the limit $Z \to \infty$ we recover the known value $f_{TF} \to -0.768745$.

One of the shortcomings of TF model are unphysical properties near the nucleus. This is a result of the fact that the semi-classical approximation breaks near the nucleus, as the electrons wavelength becomes comparable to the distance to the nucleus. This effectively imposes an ultraviolet cutoff $\mu_s$ on the semi-classical trace. However, such a cutoff neglects the energy of strongly bound electrons. At this level of approximation we neglect fluctuations in the strongly bound electrons population, i.e., their contribution to entropy vanishes.

We incorporate the strongly bound electrons perturbatively into the TF model by subtracting the semi-classical summation above the ultraviolet cutoff, and adding the quantum mechanical trace of the strongly bound electrons. We set-up a consistent perturbative calculation, thus calculating the trace for the strongly bound electrons using the leading order potential, i.e., the potential resulting from TF model. As the inner electrons are strongest bound, we follow Baker [24] and expand the TF potential about the nucleus [25]. Thus, at first order we get

$$V_{TF}(r) \approx V_B(r) = -\frac{Ze}{r} + B(\sigma, \tau) Z^\frac{4}{3},$$

i.e., a coulomb potential, leading to hydrogen atom wave functions and energies, up to the constant $BZ^{4/3}$. This approximation is valid for a shell $j$ with $n_j$ electrons, if $-\frac{Z^2 \alpha e^4}{2\hbar^2 n_j^2} + BZ^\frac{4}{3} \gg \langle eV(r) - eV_B(r) \rangle_{n_j}$. The deviation is at the percentage level for K-shell electrons, and about 10% for L-shell electrons. Finally,

$$F_{TFS} = F_{TF} - F_{\mu_s} + \left\langle \frac{p^2}{2m} - \frac{e^2 Z}{r} \right\rangle_{n_s} + \left\langle \frac{e^2 Z}{r} - eV(r) - \mu \right\rangle_{n_s},$$

where $n_s$ to be the quantum number of the highest energy level smaller than $\mu_s$. In addition, we introduced $F_{\mu_s}$, the semi-classical subtraction of the energy of particles whose energy is smaller than $\mu_s$. We use $n_{FD}$, the Fermi-Dirac distribution with chemical potential $\mu_s$, in order to select the electrons with energy less than $\mu_s$.

$\mu_s$ is chosen in the gap between the K-shell and L-shell, aiming to use a quantum mechanical treatment for the K-shell, i.e., $\mu_1 < \mu_s < \mu_2$ (therefore $n_s = 1$), where

$$\mu_j = -\frac{Z^2 \alpha e^4}{2\hbar^2 n_j^2} + \left\langle \frac{e^2 Z}{r} - eV(r) \right\rangle_{n_j}.$$
As a result,

\[ F_{\mu\nu} = \frac{1}{2} \sum_{j=1}^{2} F_{\mu j}, \]

(8)

Complying with the assumption that the strongly bound electrons fill complete shells, without fluctuations, dictates \( \mu_1 < \mu_2 \ll \mu \).

Taking the trace in Eq. (6), we deduce the energy functional for TF model at finite temperature with the strongly bound electron correction

\[ F_{\text{TFS}} = \int d^3r \left[ \frac{\sqrt{2}}{\pi^3 \hbar^3} \frac{m^2}{\beta^2} \left( -\frac{2}{3} I_2 (\beta(eV + \mu)) \right) - \frac{1}{8\pi} (\nabla(V(r) - eZ/r))^2 \right] + \mu Z \\
- \frac{1}{2} \sum_{j=1}^{2} \int d^3r \left( \frac{m^2 \sqrt{2}}{2 \pi^3 \hbar^3 \beta^2} \left( -\frac{2}{3} I_2 (\beta(eV + \mu_j)) + \beta(\mu_j - \mu) I_2 (\beta(eV + \mu_j)) \right) \right) \right] + \int d^3r \left( \frac{e^2 Z}{r} - eV(r) - \mu \right) \rho_{\sigma}(r) - \frac{Z^2 \rho e^4}{\hbar^2}, \]

(9)

with \( \rho_{\sigma}(r) \equiv 2|\psi_1(r)|^2 \), and \( \psi_1(r) \) is Hydrogen-like ground state wave function.

Similarly to the leading order, a variation of this functional with respect to \( \mu, V, \) and \( \mu_j \), leads to the number constraint and to Poisson equation. However, the electron density is now divided to the density of strongly bound electrons and the rest of the electrons,

\[ n(r) = \tilde{n}(r) + n_{\text{strong}}(r), \]

(10)

with

\[ n_{\text{strong}}(r) = \rho_{\sigma}(r) + \frac{1}{2} \sum_{j=1}^{2} Q_j |\psi_{\mu j}(r)|^2, \]

(11)

when we define

\[ Q_j = \frac{dF_{\mu\nu}}{d\mu_j} \]

(12)

\[ = \int d^3r \frac{m^2 \sqrt{2}}{2 \pi^3 \hbar^3 \beta^2} \left( I_2 (\beta(eV + \mu_j)) - \frac{1}{2} \sum_{j=1}^{2} \left( I_2 (\beta(eV + \mu_j)) + \beta(\mu_j - \mu) I_2 (\beta(eV + \mu_j)) \right) \right). \]

(13)

This correction, due to the strongly bound electrons, clearly does not change the chemical potential, since the correction does not change the dependence of the functional upon the number of electrons.

An analytical derivation, using the charactereristics method, leads to the scaling properties of the model [24].

\[ F_{\text{TFS}} = f_{TF} (\sigma, \tau) Z^{3} + \frac{1}{2} Z^2 + O(Z^{3}), \]

(14)

predicting that the prefactor to Scott’s \( Z^2 \) term is density and temperature independent. This is verified numerically in Fig. 1, where we demonstrate this scaling as derived from the free energy, and invariant of (scaled) temperature \( \tau \). Similar constant behavior is verified for the (scaled) density \( \sigma \). The scaling clearly shows that the generalized Scott’s correction is suppressed by \( Z^{-1/3} \), with respect to the bare TF result. Moreover, as \( Z \rightarrow \infty \) grows, the coefficient goes to \( \frac{1}{2} \) monotonically, validating our analytic derivation.

![Figure 1](image-url)

Figure 1: Left panel: \( Z \) dependence of the Scott coefficient. The red curve is a fit to the analytical dependence of this coefficient [25], showing asymptotic approach to Scott’s value of \( \frac{1}{2} Z^2 \). Right panel: Dependence of the energy on \( \tau \), for the TFS models scaled in \( Z \). Accomplished for \( Z = 30, 50, 80, 100, 200, 300, 500, 1000 \) and \( \rho = 1 \text{ cm}^{-3} \). Essentially no dependence is found. Similar independence is found as a function of \( \sigma \).

The TFS correction affects atomic potential, and as a result the electronic densities. In Fig. 2 and Fig. 3 we demonstrate this for Mercury (\( Z=80 \)) at \( \rho = 1 \text{ cm}^{-3} \).
Table I: Numerical value of the TFS model. Calculation for $Z = 80$, and $\rho = 1 \text{ g cm}^{-3}$. (Hartree Atomic Units are used)

| $T$ [eV] | $\tau$ | $\mu_1$ | $\mu_2$ | $Q_1$ | $Q_2$ |
|----------|--------|---------|---------|-------|-------|
| 1        | 0.0001 | -2724   | -443.8  | 0.867 | 5.126 |
| 10       | 0.001  | -2727   | -444.9  | 0.866 | 5.125 |
| 100      | 0.010  | -2742   | -459.8  | 0.866 | 5.111 |
| 500      | 0.053  | -2813   | -529.3  | 0.859 | 4.835 |
| 1000     | 0.106  | -2886   | -598.5  | 0.838 | 4.148 |

Changes in screening factor, Fig. 3, reach up 1%, reproducing the result in Ref. [22]. The electronic densities show the expected near nucleus shell structure, and are temperature dependent.

In Table I we show some numerical results of the models’ parameters. The low-temperature limit in Fig. 2 and Table I reproduces the results of Ref. [21]. The model breaks when the condition $\mu_1 < \mu_2 \ll \mu$ is broken. This breaking indicates L-shell ionization, and thus a change in $Q_2$. Indeed, in Fig. 4 we can see that, for Mercury at $\rho = 1 \text{ g cm}^{-3}$, $Q_2$ is of the same order until it reaches its minimum at $T = 1250$ eV. For higher temperatures it starts to increase rapidly adding a growing number of quantum mechanical electrons, while not subtracting enough semi-classical ones. For even higher temperatures $\mu_2$ and $Q_2$ do not converge. For Mercury with $\rho = 1 \text{ g cm}^{-3}$, it occurs at about $T = 1550$ eV. Thus, $Q_2$ behavior can be used to probe the validity of the model.

In summary, we have established a consistent method to estimate a $Z^{-1/3}$ correction to the TF energy at finite thermodynamic conditions, in a functional form. The model is valid as long as the L-shell is not ionized. In the regime of validity, the correction to the TF energy is independent of temperature and density, namely $\frac{1}{2}Z^2$. The model presented here takes into account the electron screening potential when dealing with the strongly bound electrons. This accounts for the differences comparing to Ref. [26–29].

These results lead us to conjecture that TFS correction is the leading correction for the TF model at finite temperature. In particular due to the fact that gradient and exchange-correlation corrections to the TF energy are of order $Z^2$ [30]. As such, it is essential to include TFS correction as a starting point when studying these further corrections, as well as relativistic corrections. Such successive construction of functionals will allow to better estimate theoretical uncertainties.

The authors thank Samuel B. Trickey for valuable com-
ments on earlier versions of this paper. E. S. thanks the hospitality of the University of Florida during the completion of this work.

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[33] \[ I_u(\eta) = \int \frac{dx}{\exp(x-\eta)+1}. \quad z \geq -1 \]