Region of validity of the Thomas–Fermi model with quantum, exchange and shell corrections

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Abstract. A novel approach to calculate thermodynamically consistent shell corrections in wide range of parameters is used to predict the region of validity of the Thomas–Fermi approach. Calculated thermodynamic functions of electrons at high density are consistent with the more precise density functional theory. It makes it possible to work out a semi-classical model applicable both at low and high density.

1. Introduction
Development of wide-range equations of state is of current interest in modern physics of extreme states of matter. Calculation of thermodynamical properties of warm dense matter (WDM) is a challenging problem for a variety of models existing nowadays. The most precise approaches based on the density functional theory (DFT) provide us with high quality data for matter at near-normal densities and temperatures up to tens of eV [1, 2]. Recently, it was shown [3] that the Thomas–Fermi (TF) model gives reasonable results at moderate temperatures; this opens a possibility to construct a wide-range semiclassical model of satisfactory quality.

The finite-temperature Thomas–Fermi (FTTF) model is the simplest average atom approach [4–6]. Initially this semi-classical model was formulated without important quantum effects such as exchange interaction and a bound electrons spectrum. The former problem was solved by introduction of quantum and exchange corrections [7–9], the latter one actually arises for low density plasma and requires more sophisticated analysis [10].

In the recent research [11] the possibility of a proper linking of the Thomas–Fermi and Saha models was demonstrated. The other way, however, is to take into account the shell effects by a procedure of including of discrete states of bound electrons into the Thomas–Fermi model. This approach was introduced by Shpatakovskaya for low density hot plasma [12–14].

A method of calculating the shell corrections was modified by us to obtain thermodynamically consistent values in a wide range of parameters. The region of validity for the Thomas–Fermi model with shell corrections has not been before investigated. It is done by the comparison of basic thermodynamical functions with corrections to them, similar to the work [3].
2. Model description

The FTTF model [4] is based on the assumption that electrons of an atom are distributed around the nuclei in a self-consistent field in accordance with the Fermi–Dirac statistics. Using the atomic system of units \((e = 1, \hbar = 1, m_e = 1)\) and considering \(U(r)\) as a potential of the field, \(T\) as the temperature, \(V\) as the volume, and \(\mu\) as the chemical potential one can directly obtain the spatial electron density:

\[
\rho_{TF}(r) = \frac{2}{(2\pi)^3} \int_0^\infty \frac{4\pi p^2 \, dp}{1 + \exp \left( \frac{p^2/2 - U(r) - \mu}{\frac{3}{2}} \right)}.
\]  

In this case the consistency between the potential \(U(r)\) and the electron density \(\rho\) can be easily found from the Poisson equation:

\[
\Delta U(r) = 4\pi \rho(r).
\]  

In the TF approximation a boundary value problem [5] is solved in a spherical atomic cell of the radius \(r_0 = (3V/4\pi)^{1/3}\). It gives satisfactory results for thermodynamic properties of WDM in most cases. By replacing \((U(r) + \mu)/T\) with a dimensionless potential \(\phi(x)/x\), where \(x = r/r_0\), pressure and energy can be expressed as follows:

\[
P_{TF} = \frac{2\sqrt{2}}{3\pi^2} V T^{5/2} I_{3/2}(\phi(1)),
\]

\[
E_{TF} = \frac{\sqrt{2}}{\pi} VT^{5/2} \left[ 2I_{3/2}(\phi(1)) - 3 \int_0^1 x^2 I_{3/2} \left( \frac{\phi(x)}{x} \right) \, dx \right] - E_0,
\]

where \(E_0 = -0.76874512422Z^{7/3}\), \(I_k(x)\)—the Fermi–Dirac function.

This simple model does not take into account the exchange interaction between electrons and non-uniformity effect. The first order expansion of the density matrix in the semiclassical parameter \([7]\) includes both effects. The resulting FTTF model with quantum and exchange corrections (FTTFQE) \([5,9]\) contains additions to pressure and energy:

\[
\Delta P = \frac{T^2}{3\pi^2} \left[ \psi(1) I_{1/2}(\phi(1)) + Y(\phi(1)) \right],
\]

\[
\Delta E = \frac{2T^2}{3\pi^2 r_0^3} \left[ \int_0^1 x\psi(x) I_{1/2} \left( \frac{\phi(x)}{x} \right) \, dx + \int_0^1 2x^2 Y \left( \frac{\phi(x)}{x} \right) \, dx \right] + \frac{Z\sqrt{2T}}{6\pi} \psi'(0) - \Delta E_0.
\]

Here \(\Delta E_0 = -0.26990017Z^{5/3}\), \(\psi(x)\)—the correction to the potential defined from the problem:

\[
\begin{align*}
\frac{d^2\psi}{dx^2} &= a \left[ I_{1/2}' \left( \frac{\phi(x)}{x} \right) + xY_{1/2}' \left( \frac{\phi(x)}{x} \right) \right], \\
\psi(0) &= 0, \quad \psi'(1) = \psi(1),
\end{align*}
\]

and the \(Y\)-function:

\[
Y(x) = I_{1/2} I_{1/2}'(x) + 6 \int_x^{-\infty} \left[ I_{1/2}'(t) \right]^2 \, dt.
\]

The information about bound electronic energy levels which is necessary to reproduce the shell effects is not used in the basic FTTF model [12]. However, it is possible to split the total
number of states $N$ between discrete $N_b$ and continuous $N_{TF}$ spectra in the Thomas–Fermi potential:

$$N_b = 2 \sum_{n,l} \frac{2l + 1}{1 + \exp \left( (\varepsilon_{nl} - \mu)/T \right)}, \quad (9)$$

$$N_{TF} = \int \rho_{TF}(r)|_{\varepsilon > \varepsilon_b} d^3r, \quad (10)$$

The energy levels $\varepsilon_{nl}$ can be found by using the Bohr–Sommerfeld quantization condition for the Thomas–Fermi potential:

$$S_{nl} = \int_{r_1}^{r_2} p_{nl}(r)dr = \pi \left( n - l - \frac{1}{2} \right). \quad (11)$$

Here $p_{nl}$ is a classical radial momentum:

$$p_{nl}(r) = \sqrt{2 \left[ \varepsilon_{nl} - U(r) - \frac{(l + 1/2)^2}{2r^2} \right]} \quad (12)$$

The total number of states $N$ must be equal to the total number of electrons in the atom $Z$, but the chemical potential $\mu$ for that case will differ from the Thomas–Fermi one $\mu_{TF}$ by some value $\delta\mu_{sh}$ which is defined as the shell correction:

$$N(\mu) = N_b(\mu) + N_{TF}(\mu) = Z, \quad (13)$$

$$\mu = \mu_{TF} + \delta\mu_{sh}. \quad (14)$$

By varying $\delta\mu_{sh}$ one can solve equation (13). Then the appropriate corrections to pressure and energy can be expressed through the correction to the chemical potential [12]:

$$\Delta P_{sh} = \rho_{TF}(r_0)\delta\mu_{sh}, \quad (15)$$

$$\Delta E_{sh} = \left[ \frac{3}{2} Z - \int \frac{\partial \rho_{TF}}{\partial \mu} (\mu_{TF} + U(r)) d^3r \right] \delta\mu_{sh}. \quad (16)$$

3. Quantum and exchange corrections

The region of validity of the Thomas–Fermi model can be defined by the comparison of basic thermodynamic functions $P$ and $E$ with the corrections to them $\Delta P$ and $\Delta E$. This region was already determined in our previous research [3]. Here we perform calculations for the relations $\Delta P/P$ and $\Delta E/E$ in a wide range of temperatures and densities for Cu (figures 1a and 1b) to get more reliable overview.

The well known fact that the TF model is applicable at high pressures and temperatures is clearly seen now. It should be also mentioned that the region of validity for the pressure is wider than that for the energy. But both figures show that the region near the normal density $\rho_0$ (between $\rho/\rho_0 = 0.1$ and $\rho/\rho_0 = 10$) at relatively low temperatures turns out to be irrelevantly described by the FTTF theory. The applicability at such densities is achieved only for temperatures higher than tens of eV.
Figure 1. The region of validity for the FTTF model with respect to quantum and exchange corrections on pressure and energy calculated for Cu. The model is assumed valid at negative values of logarithm (the ratio of the correction to the value itself is less than 1).

Figure 2. The region of validity of the FTTF model with respect to the shell corrections on pressure and energy for Cu. At high densities we observe bad convergence for the developed method. The shell effects are clearly seen at near-normal densities and high temperatures. The region of invalidity is almost the same as in figure 1.

4. Shell corrections

The method for calculating the shell corrections described above works well in a wide range of parameters. The only problem was found in the region of high pressures and low temperatures. The region of validity of the FTTF model with respect to the shell corrections is presented in figures 2a and 2b.

The region of validity of the FTTF model relative to the shell corrections is similar to the one for the quantum and exchange corrections (figure 1): both models cannot be applicable at low temperature and density. The shell effects are clearly seen at temperatures higher than 10 eV.

One might suppose that the quantum, exchange, and shell corrections can somehow compensate each other and extend the region of validity to lower temperatures. In figure 3 the relations of the total correction to the corresponding thermodynamic function (pressure and energy) are shown. One can see that the assumed compensation does not take place and the region of validity actually remains the same.
Figure 3. The region of validity of the FTTF model with respect to the quantum, exchange, and shell corrections on pressure and energy calculated for Cu. Corrections do not compensate each other.

Figure 4. Thermal pressure calculated for Cu by the FTTF model with different corrections in comparison with DFT-VASP calculations. At low temperatures there are no correspondence between different methods, but at high temperature Thomas–Fermi curves with corrections tend to the DFT results.

The problem of such invalidity in the region of low temperatures and near-normal densities is generally connected with the model formulation based on the approximate TF potential. The DFT provide more precise description of the electronic structure and material properties for that region. The algorithm of such calculations takes into account only bound states of electrons and therefore becomes very expensive computationally for temperatures higher than tens of eV. We use the well-known VASP code [15, 16] with a 17-electron pseudopotential for Cu and the PBE generalized gradient approximation exchange–correlation functional [17, 18]. For the plane wave representation of the basic functions in the interstitial region the cut-off energy was taken as $E_{\text{cut}} = 800$ eV, the number of bands above the Fermi level—as $N_{\text{bands}} = 240$. 
Hopefully, it is possible to coordinate both approaches in the region between 10 and 100 eV as shown in figure 4. One can see that the density functional theory and corrected Thomas–Fermi results for the pressure come closer at high temperatures.

5. Conclusion
The TF model with quantum, exchange, and shell corrections appears to be valid from low to high densities and high temperatures. Direct comparison with DFT calculations shows better agreement between models at high temperatures near the edge of the validity region. This fact may be useful for the development of wide-range equations of state in combined direct DFT/TF approach.

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