

Self-consistent solutions of the Thomas-Fermi-Dirac equation including gradient and correlation corrections

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The effects of correlation forces and the inhomogeneity gradient correction on the atomic free energy are studied numerically within the framework of the Thomas-Fermi-Dirac model. Using the expressions presented by Gell-Mann and Brueckner [Phys. Rev. **106**, 364 (1957)] and Ma and Brueckner [Phys. Rev. **165**, 18 (1968)], an energy relation for the thermodynamical equilibrium state is derived. The strength parameter of the gradient term is expressed as $\sigma = \frac{1}{9} + 8\lambda n^{-1/3}$ where n is the electron density and λ is a structure parameter, $\lambda = 4.235 \times 10^{-3}$ a.u. The influence of these corrections on the equations of state of Al, Fe, Cu, and Mo was calculated. The results show that the net contributions of these correlation corrections to the binding energy are 6.78, 1.91, 1.80, and 1.04 parts per thousand, respectively. Results for the contributions to the cold pressure are also presented.

I. INTRODUCTION

The statistical Thomas-Fermi^{1,2} (TF) and Thomas-Fermi-Dirac³ (TFD) models, including gradient terms of the von Weizsäcker type⁴ (the TFW and TFDW theories), have been used intensively for the past several decades to calculate the equation of state (EOS) and other atomic properties of matter. The advantage of these models is the fact that the description of the many-particle atomic system depends on the local electron density only but not on the quantum state of the atom, thereby greatly decreasing the amount of computations.⁵⁻⁸ Results of these models for the atomic binding energies are within 1.7% of those of more accurate theoretical computations carried out using the Hartree-Dirac-Slater (HDS) model⁹ or 0.5% of experimental values.¹⁰ Even better accuracy, 0.5%–0.25%, is obtained with the TFDW model, deduced from the virial theorem.^{8,10} While this may be still insufficient for comparison with experimental atomic binding energies, which are now known to five or more significant figures of accuracy,¹¹ for the computation of EOS and related macroscopic parameters, the accuracy of results from the TFDW model is comparable to that of detailed configuration theories.

Of the various self-consistent models, the augmented-plane-wave (APW) method, which uses a complete quantum-mechanical band-structure calculation, yields the most accurate results over a large domain of densities characteristic of the solid state. The APW-tabulated data¹² for a few elements show impressive agreement with experimental cold curves in the solid phase. However, the extension of this theory to other temperature regimes is extremely complicated and simpler procedures of computation, which still provide reasonable accuracy, are therefore highly desirable.

In this paper we present from computations of EOS which incorporate the correlation forces into the TFDW model using the expressions developed by Gell-Mann and

Brueckner¹³ and Ma and Brueckner.¹⁴ These corrections are an improvement of the TFDW model. The results of EOS from these corrections, which we denote as the TFDWB model, are compared to those of other shell-oriented models as well as with experiment, to show its improved accuracy.

Though the generalization to high temperatures is straightforward,¹⁵ our treatment of this problem is limited to the zero-temperature ground state of the atom, since the correlation correction is well known only at that temperature.

II. THEORY

A. TFDW model

The main point of the TFDW model is the addition of a gradient correction to the statistical kinetic energy to account for the slow spatial variations of the electron density. This gradient correction to the Helmholtz free energy per particle has the form⁴

$$f_w = \frac{\zeta}{8} \left[\frac{\nabla n}{n} \right]^2, \quad (1)$$

where n is the local electron density and ζ is the strength parameter (atomic units $e^2 = m = \hbar = 1$ are used). There has been considerable discussion on the optimal value of ζ . Originally, $\zeta = 1$ was proposed by von Weizsäcker.⁴ Later, Kirzhnits¹⁶ and others^{17,18}, using perturbation theories, suggested that ζ should be $\frac{1}{9}$. In fact, the value of $1/5$ gives the best fit for cold-pressure curves⁸ at extremely high average electron densities (Ref. 10), $n > 6 \times 10^{25} \text{ cm}^{-3}$. On the other hand, computational results on binding energies^{19,10} showed that a value of $\frac{1}{5}$ to $\frac{1}{6}$ is in better agreement with the HDS theory or the experimental values. Other researches^{8,9,19} proposed a space-dependent ζ .

B. The correlation and gradient-correlation corrections

The correlation energy strongly depends on the electron-gas density.^{13,20} An expression for this energy density, which is valid in the high-density region, was derived by Gell-Mann and Brueckner,¹³

$$\varepsilon_C = -n \left[\frac{2}{3\pi^2} (1 - \ln 2) \ln \left[\frac{4\pi}{3} n \right] + 0.096 \right]. \quad (2)$$

According to Ma and Brueckner,¹⁴ it is possible to calculate the corresponding gradient correction to this term following a reverse procedure to that outlined in the density-functional theory (DFT).²¹ Their result indicates that a term of the form

$$\varepsilon_G = \lambda n^{-4/3} |\nabla n|^2, \quad (3)$$

should be added to Eq. (2).

The proportionality constant in Eq. (3) accounts for the long-range density variation effects. Ma and Brueckner computed this constant to be 4.235×10^{-3} a.u. based on the collective motion effects in a uniform electron gas.¹⁴ Their results were found, however, to be in poor agreement with experimental data.

We introduced the following expression into the equations of the TFDW free energy per particle, to account for the correlation effects:

$$f_c = \frac{1}{2}(\varepsilon_C/n) = - \left[\frac{1}{3\pi^2} (1 - \ln 2) \ln \left[\frac{4\pi}{3} n \right] + 0.048 \right]. \quad (4)$$

The factor of $\frac{1}{2}$ was introduced into Eq. (4), to account for the two possible spin directions in the Fermi electron gas. The characteristic energy equation of the system is obtained by applying the variational principle to minimize the total free-energy density, following the DFT formalism.²¹ The new energy equation is

$$\frac{1}{2}(3\pi^2 n)^{2/3} - \frac{1}{\pi}(3\pi^2 n)^{1/3} - \left[c_1 + c_2 \ln \left[\frac{4\pi}{3} n \right] \right] + \frac{\sigma}{8} \left[\left[\frac{\nabla n}{n} \right]^2 (1 - \gamma) - \frac{2\nabla^2 n}{n} \right] + V(r) = \mu, \quad (5)$$

where $V(r)$ and μ are the central and chemical potentials of the atom, and

$$\begin{aligned} c_2 &= \frac{1}{3\pi^2} (1 - \ln 2), \\ c_1 &= c_2 + 0.048, \\ \gamma &= \frac{\partial \ln \sigma}{\partial \ln n}. \end{aligned} \quad (6)$$

The sum of the correlation gradient correction, Eq. (3), and the von Weizäcker term, Eq. (1), can be cast into a form similar to Eq. (1), with a modified, density-dependent strength parameter

$$\sigma = \lambda + 8\lambda n^{-1/3}. \quad (7)$$

It is this σ which should be used in Eq. (5). It combines the short-range density variation effects, represented by the term $\lambda = \frac{1}{9}$, as predicted by the random-phase approximation theory,²¹ and the long-range density variation effects expressed by the parameter λ .

C. Self-consistent solutions and boundary conditions

The solutions of Eqs. (5–7) under finite spherical boundary conditions, as defined by the ion-sphere model (ISM),¹ should satisfy two self-consistency conditions: namely, that the electrostatic potential $V(r)$ is a solution of the Poisson equation,

$$\nabla^2 V(r) = -\frac{Z}{r} + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}', \quad (8)$$

and the charge neutrality condition,

$$Z = \int_V n(\mathbf{r}, \mu) d^3\mathbf{r}, \quad (9)$$

which, in practice, is used to calculate the chemical potential μ .

Equation (5) is a fourth order differential equation which requires four boundary conditions in order to give a unique solution. These boundary conditions are

$$V(r_0) = \partial n / \partial r(r_0) = 0, \quad (10a)$$

$$rV(r)|_{r=0} = -Z, \quad (10b)$$

$$\sigma(n) \frac{\partial n / \partial r}{n} \Big|_{r=0} = -2Z, \quad (10c)$$

where r_0 is the ion-sphere radius.

D. EOS and the virial theorem

After solving the electron spatial distribution Eq. (5) with the complimentary conditions Eqs. (8)–(10), one can calculate the total free energy of the atom. From this function the basic thermodynamic quantities of the atom can be derived: namely, the atomic pressure, energy and volume. Finally the EOS can be obtained. The result is the decomposition of the total pressure into the sum of five terms. Three^{8,10} of them are the kinetic, electrostatic, and exchange components, whereas the other two, the gradient and the correlation terms, derived from Eqs. (1) and (4), are given by

$$P_G = -\frac{\sigma[n(r_0)]}{4} \nabla^2 n(r_0), \quad (11a)$$

$$P_C = -\frac{1}{3\pi^2} (1 - \ln 2) n(r_0), \quad (11b)$$

In Eqs. 11, $n(r_0)$ is the electron density at the atom boundaries. P_G of Eq. (11a) includes the correlation gradient contribution

$$P_{CG} = -2\lambda[n(r_0)]^{-1/3} \nabla^2 n(r_0). \quad (12)$$

The energy E , at $T=0$, is the sum of the contribution of the corresponding partial free energy densities,

$$E = E_K + E_R + E_X + E_W + E_C = \int n f(n) d^3\mathbf{r}. \quad (13)$$

TABLE I. Contribution of the computed correlation corrections to the atomic binding energy in some elements compared to various theoretical and experimental quantities.

Element	Z	Binding energy (a.u.)			Energy calculations with the TFDWB model			
		Expt ^a	HDS ^b	TFDW ^c	$-E$ (a.u.)	E_{CG} (a.u.)	$-E_C$ (a.u.)	$1000 \Delta E/E $
Al	13	242.704	240.714	261.43	252.35	2.26	0.55	6.78
Fe	26	1272.57	1267.80	1345.51	1320.06	3.81	1.30	1.90
Cu	29		1649.47	1747.65	1713.81	4.57	1.49	1.80
Mo	42		4040.75	4174.87	4122.65	6.62	2.32	1.04

^aReference 11.

^bReference 24.

^cPresent work.

The terms originating at the TFDWB model are¹⁴

$$E_C = \int n f_c(n) d^3\mathbf{r} \quad (14a)$$

and

$$E_{CG} = \int \lambda n^{-4/3} |\nabla n|^2 d^3\mathbf{r}. \quad (14b)$$

The last contribution, E_{CG} , is included in the gradient term E_W of Eq. (13) through the strength parameter σ , Eq. (7).

A more balanced way of expressing the total energy E is by means of the virial theorem which has been shown to hold true for the generalized TF atom.^{1,2} The following procedure described in Ref. 8, in the case of the TFDWB model, E can be also calculated by the formula

$$E = (3PV + E_R + E_X - E_{GC})/2 + E_C, \quad (15)$$

where E_{GC} is given by

$$E_{GC} = -6 \int \lambda n^{-1/3} \nabla^2 n d^3\mathbf{r} - \frac{(1 - \ln 2)}{\pi^2} Z. \quad (16)$$

III. NUMERICAL PROCEDURE

Equation (5) is solved numerically by means of the Milne Predictor-Corrector method.²² The values of $n''(r_0)$ and $n(0)$ are determined by carrying out an inward-outward integration procedure, requiring the equalization of the logarithmic derivative at the turning point.²³

The results for the binding energy obtained by this method were compared with the values calculated by means of the virial theorem, Eqs. (15) and (16). For the studies reported here, a typical difference of the order of 0.1–0.5% relative to the virial theorem was obtained.

IV. RESULTS

A. Binding energy

Table I summarizes the computational results obtained for the binding energy and the correlation corrections in the elements of Al, Fe, Cu, and Mo, according to the TFDW and TFDWB statistical models. These parameters are compared, in Table I, to either experimental¹¹ or computational results using the HDS model.²⁴

The incorporation of the new terms to the energy equation (5), causes a decrease in the energy contribution of each term. This lowering of the binding energy (calculated around the crystalline state density), is much larger than the addition of the single corrections E_{CG} and E_C to the unperturbed energy computed by the TFDW model (see Table I). Only at very high compressions do both procedures give the same results. Nevertheless, the improvement of the predictions of the TFDWB relative to the TFDW model, both compared with experimental or HDS results, is still insufficient.

The size of the total correlation contribution to the energy, shown in Table I by ΔE , follows an approximate scaling law of $Z^{0.77}$, compared with the factor $Z^{7/3}$ followed by the total binding energy. This fact indicates that this correlation becomes insignificant with increasing values of Z , as can be seen in the last column of Table I.

B. Cold pressure

Similar computations have been carried out for the cold pressure. In Table II are shown the value of this pressure and its corrections at the normal density for the elements of Table I. The expected value of zero for the total pressure is not attained, in spite of the fact that the

TABLE II. Contribution of the computed correlation corrections to the cold pressure at the normal density for the same elements quoted in Table I.

Element	Z	ρ (g/cm ³)	TFDW	P (GPa)	TFDWB	
			P (GPa)		$-P_{GC}$ (GPa)	$-P_C$ (GPa)
Al	13	2.7	8.617	-15.483	5.679	5.084
Fe	26	7.874	115.380	56.952	12.267	12.952
Cu	29	8.93	130.013	68.427	12.835	13.666
Mo	42	10.2	70.559	26.015	10.100	10.424

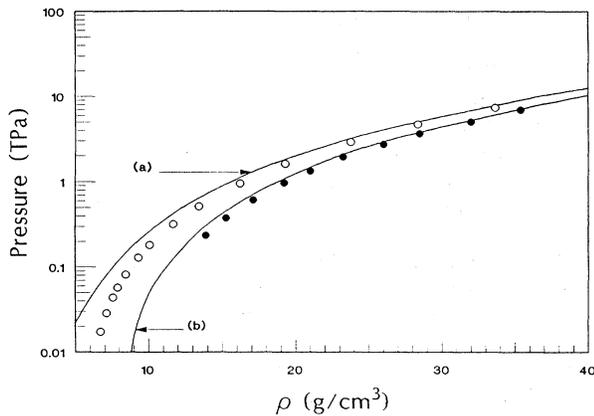


FIG. 1. Zero-degree Kelvin pressure isotherms for iron according to present calculations compared to similar graphs from Ref. 25 (1 TPa=10 Mbar). The abscissa units are density expressed in g/cm^3 as given by the same reference. (a) Computations according to the TFDW model. (b) Experimental cold curve (Ref. 25). (●) Computed values with the INFERNO code (Ref. 26). (○) Present computations with the TFDWB.

correlation correction has a more significant influence on the pressure than on the binding energy. Furthermore, in the case of aluminum, the computed TFDWB value of the pressure is negative. A more complete description of the improvements introduced by the TFDWB model in the cold curve is shown in Fig. 1. This figure shows a comparison between the cold-pressure curves for iron, as obtained from the present calculations (TFDW and TFDWB models) and similar graphs of Ref. 25.

It can be seen that, for iron, the TFDWB is in better agreement with the experimental cold curve than the TFDW computations, particularly at the low pressures region.

In Fig. 2 the contribution of the various terms composing the total pressure are plotted from 3 to 1000 g/cm^3 . From a comparison of Fig. 2 with a similar analysis carried out with the TFDW model,⁸ one finds that the introduction of correlation forces appreciably changes the relative contributions of the various terms at low pressures. For example, at a density of 100 g/cm^3 , when the effect of the correlation term in the expression of σ [see Eq. (7)] is small, the gradient contribution is around 0.61 of the exchange component, compared to 0.5 as predicted by the TFDW computations. Near the crystalline state this gradient contribution becomes as high as the kinetic term, in sharp contrast to the TFDW theory. In the range of density shown in Fig. 2, the correlation term constitutes approximately only $\frac{1}{10}$ of the gradient pressure. In the liquid phase, when the density is below 10 g/cm^3 (see Fig. 2), the correction terms exceed the kinetic contribution in the pressure and even becomes negative, reflecting the tensile forces opposing the interatomic binding forces during expansion.

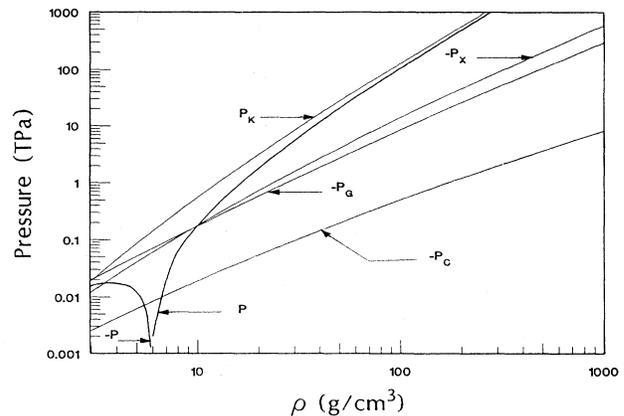


FIG. 2. Electronic pressure in iron as obtained from the TFDWB scheme. P_K and P_X (absolute value) are the known kinetic and exchange components of the total pressure P . The absolute values of the gradient (P_G) and correlation (P_C) terms defined by Eq. (11) are also plotted as functions of the density.

V. DISCUSSION AND CONCLUSIONS

The effects of the TFDWB model were analyzed numerically. We have found that the introduction of correlation and gradient corrections to the TFDW energy equations improve the results for the pressure near the crystalline state as well as for the binding energies. The size of the correlation corrections at very high compression varies between 0.7% and 0.1% of the total energy for $13 \leq Z \leq 42$, which is close to the accuracy of the numerical integration. This means that, seemingly, there is no advantage to adding new terms to the Hamiltonian in order to describe the macroscopic properties of matter for this region of densities. Nevertheless, the inclusion of these corrections in the Hamiltonian may significantly improve the solutions for atomic properties, particularly at low pressures. It is, however, doubtful that the incorporation of more terms in the gradient expansion^{18,21} could produce better agreement with the experimental data. In fact, the statistical nature of the TF models avoids the possibility that a continuous gradient expansion will provide a correct description of the atomic quantum properties.²¹ At present it seems that for further improvements more realistic expressions for the Dirac exchange term and the correlation contributions should be worked out.

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