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Gradient correction to the statistical electronic free energy at nonzero temperatures: Application to equation-of-state calculations

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The gradient correction to statistical kinetic free energy, well known at zero temperature, is generalized to finite temperatures, following the prescriptions of the density-functional formalism. The coefficient of the gradient term, a function of electron density, is explicitly determined, and an accurate approximation, suitable for numerical computation, is given. The corrected kinetic free energy, with a phenomenological extrapolation to all temperatures of the exchange and correlation contribution, is applied to equation-of-state calculations. Results are presented in the case of Be, Al, and Cu, for temperatures up to 50 eV and compressions 0.1, 1, and 10, and the influence of the gradient correction is discussed.

I. INTRODUCTION

Since Von Weizsäcker's work,[1] the approach to many-electron systems which consists in deriving corrections to the statistical Thomas-Fermi (TF) and Thomas-Fermi-Dirac (TFD) models has been intensively explored.[2-13] When the statistical models express the total energy of a system in terms of the local electron density $n(\vec{r})$ only, the corrections introduce the gradient $\nabla n(\vec{r})$. The density-functional formalism[14-15] has given a rigorous theoretical background to the derivation of these corrections. Various applications to physical systems such as atoms,[16-18] metal surfaces,[19] and defects[20-22] may be found in the literature. In all these applications, the correction to the statistical kinetic energy has the following form:

$$K_1[n] = \int h_0 \frac{|\nabla n|^2}{n} \, d\vec{r} \,, \tag{1}$$

where h_0 is a numerical constant ranging from the Von Weizsäcker value of $\frac{1}{9}$ to the correct gradient-expansion value of $\frac{1}{72}$. In a previous paper, we have investigated the influence of the kinetic correction (1) on the zero-temperature equation of state of metals, particularly Li, Be, Al, and Cu.[23]

In the present work, we generalize the gradient expansion correction to the case of nonzero temperatures. Section II shows how such a generalization can be achieved in the framework of density-functional formalism, using the analytic expression of the free-electron gas polarizability for finite temperatures T. In order to investigate the effect of temperature in a model which reduces to the TFD one at absolute zero, an approximate treatment of exchange and correlation for all temperatures has been developed: it is described in Sec. III. In Sec. IV, the expressions derived in Sec. II and III are applied to the equation-of-state problem at nonzero temperatures. The numerical results obtained for Be, Al, and Cu are reported and discussed in Sec. V.

II. GRADIENT EXPANSION OF THE KINETIC FREE ENERGY

In their paper on the self-consistent equations for an inhomogeneous system of interacting electrons,[15] Kohn and Sham have shown how the density-functional formalism can be applied to finite temperature systems by considering the grand-canonical potential

$$\Omega[n] = \int v(\vec{r}) n(\vec{r}) \, d\vec{r} + \frac{1}{2} \int n(\vec{r}) \frac{1}{|\vec{r}-\vec{r}\,'|} n(\vec{r}\,') \, d\vec{r} \, d\vec{r}\,' + F_e[n] + F_{xc}[n] - \mu \int n(\vec{r}) \, d\vec{r} \tag{2}$$

where $v(\vec{r})$ is the external potential and μ is the chemical potential. The free energy of noninteracting electrons is $F_e[n]$, a unique functional of the electron density at a given temperature. $F_{xc}[n]$ is the exchange and correlation contribution to the free energy. The correct density of the system minimizes $\Omega[n]$, so that

$$v(\vec{r}) + \int n(\vec{r}\,') \frac{1}{|\vec{r}-\vec{r}\,'|} \, d\vec{r}\,' + \frac{\delta \mathcal{F}_e[n]}{\delta n(\vec{r})} + \frac{\delta \mathcal{F}_{xc}[n]}{\delta n(\vec{r})} = \mu \,, \tag{3}$$

where we have defined the free-energy density by the relation

$$F[n] = \int \mathcal{F}[n] \, d\vec{r} \,. \tag{4}$$

If the most simple approximation is made, which consists in using the uniform electron-gas free energy $\mathcal{F}_0$ for $\mathcal{F}_e$, then the statistical models are obtained: Eq. (3) reduces to the TF equation if exchange and correlation effects are neglected ($\mathcal{F}_{xc} \equiv 0$). The two well-known following equations define the free energy in this case:

$$\mathfrak{F}_0=(\sqrt{2}/\pi^2)\beta^{-5/2}[-\tfrac{2}{3}I_{3/2}(\eta)+\eta I_{1/2}(\eta)]\,, \tag{5a}$$

$$n=(\sqrt{2}/\pi^2)\beta^{-3/2}I_{1/2}(\eta)\,. \tag{5b}$$

I_α is the standard Fermi function[24] and $\beta^{-1}=kT$. An analytic form of $\mathfrak{F}_0(n)$ is given in Appendix A.

Taking into account the first gradient correction leads to the free energy

$$\mathfrak{F}_e[n]=\mathfrak{F}_0(n)+h(n)\,|\nabla n|^2/n\,. \tag{6}$$

To our knowledge, the function $h(n)$ (for simplicity, we do not make explicit the dependence on temperature in the list of variables) has never been calculated up to now. The correct way to determine this function is to identify the polarizability of a system described by (3) and (6) with the exact polarizability of the noninteracting electron gas at large wavelengths.[14] With the free energy (6), Eq. (3) becomes

$$U+\frac{\partial\mathfrak{F}_0}{\partial n}-|\nabla n|^2\frac{\partial}{\partial n}\left(\frac{h}{n}\right)-2h\frac{\Delta n}{n}+\frac{\delta\mathfrak{F}_{xc}}{\delta n}=\mu\,, \tag{7}$$

provided that the boundary condition $\nabla n=0$ on the surface enclosing the system is fulfilled. Let us now consider the linear response δn of a noninteracting system ($\mathfrak{F}_{xc}\equiv 0$) described by (7) to a small localized variation δU of the effective (total) potential U:

$$\delta U+\left[\frac{\partial^2\mathfrak{F}_0}{\partial n^2}-|\nabla n|^2\frac{\partial^2}{\partial n^2}\left(\frac{h}{n}\right)-2\Delta n\frac{\partial}{\partial n}\left(\frac{h}{n}\right)\right]\delta n$$
$$-2\frac{\partial}{\partial n}\left(\frac{h}{n}\right)\nabla n\cdot\nabla\delta n-2\frac{h}{n}\Delta\delta n=0\,. \tag{8}$$

The polarizability of the system is defined as the ratio of δn to δU in reciprocal space

$$\Pi(q,n)=\delta n(q,n)/\delta U(q)\,. \tag{9}$$

Specializing to the case of the uniform electron gas of density n_0, we find

$$\Pi(q,n_0)=-\left(\frac{\partial^2\mathfrak{F}_0}{\partial n^2}+2\frac{h(n)}{n}q^2\right)^{-1}_{n_0}\,. \tag{10}$$

It is clear that h can be determined by requiring the identity of the expansions in $q(q\to 0)$ up to order q^2 of $\Pi(q,n_0)$ and $\Pi_{\mathrm{RPA}}(q,n_0)$, the random-phase-approximation polarizability defined by[25]

$$\Pi_{\mathrm{RPA}}(q,n_0)=2(2\pi)^{-3}\int\frac{f_{\vec{k}}-f_{\vec{k}+\vec{q}}}{\epsilon_{\vec{k}}-\epsilon_{\vec{k}+\vec{q}}}\,d\vec{k}\,, \tag{11}$$

where $f_{\vec{k}}$ is the Fermi-statistics occupation number

$$f_{\vec{k}}=[1+\exp(\beta\epsilon_{\vec{k}}-\eta)]^{-1}\,, \tag{12a}$$

with

$$\epsilon_{\vec{k}}=\tfrac{1}{2}k^2\ \text{(a.u.)} \tag{12b}$$

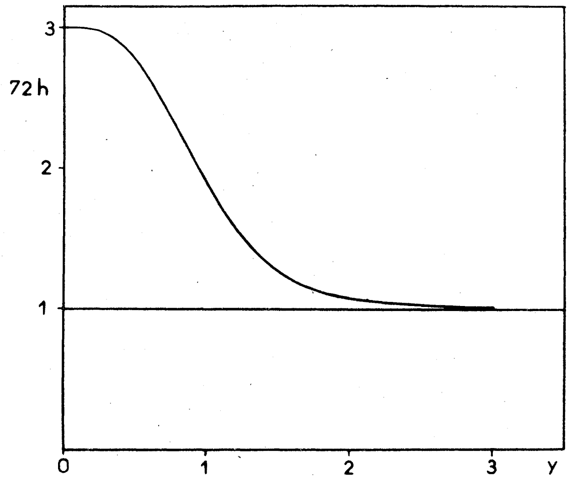

FIG. 1. Coefficient of the gradient term of the kinetic free energy as a function of the reduced variable y.

and η is related to $n=n_0$ by (5b).

Expressions (11) and (12) can be treated by elementary means in order to obtain the expansion at small q:

$$\Pi_{\mathrm{RPA}}(q,n_0)=-(2\pi^2)^{-1}\left(\frac{2}{\beta}\right)^{1/2}\left(I_{-1/2}(\eta)-\tfrac{1}{12}\beta q^2\frac{d}{d\eta}\right.$$
$$\left.[I_{-1/2}(\eta)]+O(q^4)\right)\,. \tag{13}$$

The first term of (13) is exactly $-(\partial^2\mathfrak{F}_0/\partial n^2)^{-1}$; from the term in q^2 we get

$$\frac{h(n)}{n}=-\frac{\sqrt{2}}{24}\pi^2\beta^{3/2}\frac{d}{d\eta}\left(\frac{1}{I_{1/2}(\eta)}\right)\,. \tag{14}$$

Elimination of η between (5b) and (14) entirely determines h, which is shown in Fig. 1. The correct limit $h=\frac{1}{72}$ at zero temperature is recovered. At very high temperatures, the limit is $h=\frac{1}{24}$. It is easy to see that h is a function of the reduced variable

$$y=(\pi^2/\sqrt{2})\beta^{3/2}n \tag{15}$$

only. An analytic approximation of $h(y)$ is given in Appendix B.

III. APPROXIMATE TREATMENT OF EXCHANGE AND CORRELATION EFFECTS

Our purpose here is to derive an expression of the exchange (and correlation) functional $\mathfrak{F}_{xc}(n)$ which could be considered as a reasonable extrapolation to non-zero temperatures of the 0 °K Kohn-Sham exchange functional. The theoretical difficulty of this task lies in the impossibility of treating temperature dependent exchange effects alone: correlations must be considered simultaneously in order to avoid an anomalous behavior of the specific heat C_v at low temperatures.[26] The correct calculation of the electron-gas specific heat is a very difficult work[27] beyond the scope of the present paper. The results obtained by different authors are not in full agreement and the question remains open. Here we shall restrict ourselves to define a phenomenological functional $\mathfrak{F}_{xc}(n)$ having the following properties: $\mathfrak{F}_{xc}(n)$ gives the exact exchange energy in both limits of zero and very high temperatures; the corresponding specific heat vanishes at absolute zero.

Let $\mathfrak{F}_x(n)$ be the exchange (only) contribution to the free-energy density. Its formal expression in momentum space, up to first order in the interaction, is[26]

$$\mathfrak{F}_x(n) = -(2\pi)^{-6} \int\int d\vec{k}\, d\vec{k}' \frac{4\pi}{|\vec{k}-\vec{k}'|^2} f_{\vec{k}} f_{\vec{k}'}, \quad (16)$$

which can be transformed, by elementary means, to

$$\mathfrak{F}_x(n) = -\frac{1}{2\pi^3\beta^2} \int_{-\infty}^{\eta} [I_{-1/2}(\eta)]^2\, d\eta. \quad (17)$$

The occupation numbers in (16) are defined by (12a), and η is related to the density n by (5b). Using the asymptotic form of the Fermi functions for $\eta \to -\infty$ in (17) leads to

$$\mathfrak{F}_x(n) \to -\tfrac{1}{2}\pi^2\beta n^2 \quad (18)$$

at high temperatures, showing that for a given density, $\mathfrak{F}_x(n)$ decreases as $1/T$. Horovitz and Thieberger have shown that the expression of $\mathfrak{F}_x(n)$ at low temperatures is[26]

$$\mathfrak{F}_x(n) = -\frac{3}{4}\left(\frac{3}{\pi}n\right)^{1/3} n + \frac{1}{6\pi\beta^2}\ln(\beta\mu_0) + O(\beta^{-2}), \quad (19)$$

where μ_0 is the Fermi energy at 0 °K. The first term is the classical exchange energy at $T = 0$; the temperature-dependent part gives a contribution to the specific heat

$$C_{vx} \sim \beta^{-1}\ln(\beta\mu_0) + O(\beta^{-1}) \quad (20)$$

which dominates the specific heat of the noninteracting electron gas, proportional to β^{-1} only. This result is unphysical and Horovitz and Thieberger have pointed out that $C_{vx}(20)$ must be cancelled by other terms in the expansion of $\mathfrak{F}_{xc}[n]$.

One can easily be convinced of the extreme sensitivity of the specific heat to the approximations made in the treatment of interactions. A simple calculation of (16) using a screened interaction $e^{-\lambda|\vec{r}-\vec{r}'|}/|\vec{r}-\vec{r}'|$ instead of the bare interaction gives evidence of this sensitivity. Applying the Sommerfeld method to

$$\mathfrak{F}_{xc}(n) = -(2\pi)^{-6} \int\int d\vec{k}\, d\vec{k}' \frac{4\pi}{|\vec{k}-\vec{k}'|^2+\lambda^2} f_{\vec{k}} f_{\vec{k}'}, \quad (21)$$

we find a thermal component $\Delta\mathfrak{F}_{xc}$ at $T \to 0$:

$$\Delta\mathfrak{F}_{xc}(n) = \frac{1}{6\pi\beta^2}\left[\left(\frac{1}{2}+\frac{1}{\theta}\right)\ln(1+\theta) - 1\right] \quad (22)$$

with $\theta = 9\mu_0/\lambda^2$ or $\theta = \pi\sqrt{2\mu_0}$ with the reasonable choice of the Thomas-Fermi screening length. The quantity $\Delta\mathfrak{F}_{xc}(n)$ compares with the thermal component of the free energy for the noninteracting electrons

$$\Delta\mathfrak{F}_0(n) = -(1/6\pi\beta^2)\theta, \quad T \to 0. \quad (23)$$

In the range of metallic densities ($n > 10^{-2}$; $\theta > 2$ a.u.), the ratio $s = \Delta\mathfrak{F}_{xc}(n)/|\Delta\mathfrak{F}_0(n)|$ is always small: $s = 0.050$ at $\theta = 2$, $s = 0.052$ at $\theta = 4$, and $s = 0.044$ at $\theta = 10$; s decreases as $\theta^{-1}\ln\theta$ for larger values of θ. The results of this model differ strongly from those obtained with the bare interaction. Although not rigorous, they support the opinion according to which the relative magnitude of the exchange and correlation corrections to the noninteracting specific heat is small, about 10%.[28]

After the previous remarks, and keeping in mind that we are not concerned here with an accurate study of temperature-dependent exchange and correlation effects, and they only included in order to allow the extrapolation of the cold TFD model, we adopted the following form for $\mathfrak{F}_{xc}(n)$:

$$\mathfrak{F}_{xc}(n) = -\tfrac{1}{2}\pi\beta n^2 \tanh(a_0 y^{-2/3} + b_0 y^{-2}), \quad (24)$$

where y is the dimensionless variable defined by (15). At high temperatures ($y \to 0$), Eq. (24) has the correct asymptotic behavior [Eq. (18)]. The numerical constant a_0 is such that the Kohn-Sham exchange is recovered at $T = 0$ [$a_0 = \frac{1}{4}(3\sqrt{2})^{4/3}$]. In the absence of reliable result on the exchange and correlation part of the specific heat ($T \to 0$), we have chosen the second term in the argument of the hyperbolic function in order to cancel the term in T^2 ($b_0 = \frac{27}{16}$). The asymptotic form (18) is reached for $y = 1$ approximately, or $\beta = 0.7 r_s^2$, where r_s is the standard density parameter.

IV. APPLICATION TO EQUATION OF STATE

A. Self-consistent calculation of the electron density

We want now to solve Eq. (7) for a density $n(r)$ describing an atom confined in a spherical volume V of radius S. The boundary conditions are

$$n(0) = n_0, \quad (25a)$$

$$\left.\frac{dn}{dr}\right|_{r=S} = 0, \quad (25b)$$

$$\int_V n(\vec{r})\,d\vec{r}=Z\,. \tag{25c}$$

Following our experience of the zero-temperature case, we have determined the density $n(r)$ by an iterative procedure, writing at the step $i+1$,

$$n_{i+1}(r)=n_i(r)+\delta n_i(r)\,, \tag{26a}$$

$$U_{i+1}(r)=U_i(r)+\delta U_i(r)\,, \tag{26b}$$

and linearizing Eq. (7). Choosing the new function

$$w(r)=r\big(\delta U_i(r)-\mu\big)\,, \tag{27}$$

and relating it to $\delta n_i(r)$ by the Poisson equation, leads to

$$w''''+\frac{h_1}{h}\frac{n_i'}{n_i}w'''+Q_i(r)w''+\frac{1}{h}\,2\pi n_i w=S_i(r)\,, \tag{28a}$$

$$\begin{aligned}Q_i(r)={}&\frac{h_2}{2h}\left(\frac{n_i'}{n_i}\right)^2+\frac{h_1}{h}\left(\frac{n_i''}{n_i}+\frac{n_i'}{rn_i}\right)\\&-\frac{1}{2h}\left(n\frac{\partial^2\mathfrak{F}_0}{\partial n^2}+n\frac{\partial^2\mathfrak{F}_{xc}}{\partial n^2}\right)_{n_i}\,,\end{aligned} \tag{28b}$$

$$\begin{aligned}S_i(r)={}&-4\pi rn_i\left\{\frac{1}{2h}\left[U_i+\left(\frac{\partial\mathfrak{F}_0}{\partial n}+\frac{\partial\mathfrak{F}_{xc}}{\partial n}\right)_{n_i}\right]\right.\\&\left.-\frac{h_1}{2h}\left(\frac{n_i'}{n_i}\right)^2-\frac{\Delta n_i}{n_i}\right\}.\end{aligned} \tag{28c}$$

The primes correspond to derivation with respect to the coordinate r.

The functions h_1 and h_2 are related to the function h of the gradient correction by

$$h_1=y\frac{dh}{dy}-h\,, \tag{29a}$$

$$h_2=y^2\frac{d^2h}{dy^2}-2h_1\,. \tag{29b}$$

h, h_1, and h_2 are calculated in (28a)–(28c) with the argument y_i corresponding to n_i.

Equation (28a) has been integrated using the numerical technique described in detail for the similar equation at zero temperature.[23] The electron density found in the TFD approximation [Eq. (7) without gradient correction term in $\mathfrak{F}_e[n]$], modified in a small region near origin in order to cancel the singularity at $r=0$, has been used as starting density for the first iteration. A relative accuracy of 5×10^{-4} was reached after five iterations.

B. Energy and pressure

As a consequence of the stationarity of $\Omega[n]$, the energy of the system can be expressed as

$$E=\frac{\partial}{\partial\beta}\left[\beta(\Omega+\mu Z)\right]_{V,n(r)}\,, \tag{30}$$

where the derivation is at constant volume V and density n. With the functional forms of the free energies (cf. Appendix A)

$$\mathfrak{F}_0(n)=\beta^{-1}nf(y) \tag{31}$$

and (24),

$$\mathfrak{F}_{xc}(n)=-\beta n^2 j(y)\,, \tag{32}$$

the total energy becomes

$$E=K+W+X\,, \tag{33}$$

where the three contributions appear (kinetic, potential, and exchange-and-correlation):

$$K=\tfrac{3}{2}\beta^{-1}\int_V ny\frac{df}{dy}\,d\vec{r}+\int_V\left(h+\tfrac{3}{2}y\frac{dh}{dy}\right)\frac{|\nabla n|^2}{n}\,d\vec{r}\,, \tag{34}$$

$$W=\int_V-\frac{Z}{r}n\,d\vec{r}+\frac{1}{2}\int\int_V n(r)\frac{1}{|\vec{r}-\vec{r}\,'|}n(r')\,d\vec{r}\,d\vec{r}\,'\,, \tag{35}$$

$$X=-\beta\int_V n^2\left(2j+\tfrac{3}{2}y\frac{dj}{dy}\right)d\vec{r}\,. \tag{36}$$

The kinetic energy is the sum of the homogeneous part K_0 and the gradient correction K_1.

The pressure is also deduced from the grand potential

$$P=-\frac{\partial}{\partial V}\left[\Omega+\mu Z\right]_{\beta,nS^3}\,; \tag{37}$$

the partial derivative is at constant density under the constraint of normalization when the volume changes. Equation (37) leads to the virial theorem in the form

$$3PV=2K+W+3\int_V\left(n\frac{\partial\mathfrak{F}_{xc}}{\partial n}-\mathfrak{F}_{xc}\right)d\vec{r}\,. \tag{38}$$

A more interesting expression of the pressure, which avoids the important numerical cancellations occuring in (38), can be derived. We shall not give the detailed demonstration of this equivalent expression here, but only indicate how it can be worked out. The main point is to transform the kinetic energy K [Eq. (34)], integrating the first term by parts. A surface term is obtained in that way, together with a new integral where appears the quantity ydf/dy, which can be extracted from Eq. (7). At this point, K is given by

$$\begin{aligned}K={}&\tfrac{3}{2}\beta^{-1}V\left(ny\frac{df}{dy}\right)_S-\tfrac{1}{2}W\\&+\frac{1}{2}\int_V rn\frac{d}{dr}\left(\frac{\partial\mathfrak{F}_{xc}}{\partial n}\right)d\vec{r}\\&+\frac{1}{2}\int_V\nabla\left(C\frac{\vec{r}}{r}\right)d\vec{r}\,,\end{aligned} \tag{39}$$

where C is the function

$$C=-2rh\left(n''-\frac{n'^2}{n}-\frac{n'}{r}\right)-rn'y'\frac{dh}{dy}. \tag{40}$$

Integrating the exchange term in (39) by parts and applying the Stokes theorem to the last integral, we arrive at

$$K=\tfrac{3}{2}\beta^{-1}V\left(ny\frac{df}{dy}\right)_S-\tfrac{1}{2}W+\tfrac{3}{2}V\left(n\frac{\partial\mathfrak{F}_{xc}}{\partial n}-\mathfrak{F}_{xc}\right)_S$$
$$-\frac{3}{2}\int_V\left(n\frac{\partial\mathfrak{F}_{xc}}{\partial n}-\mathfrak{F}_{xc}\right)d\vec{r}-3V(hn'')_S. \tag{41}$$

The boundary condition $(n')_S=0$ has been used in the last surface term.

The desired expression of the pressure results immediately from (38) and (41):

$$P=\left(n\frac{\partial\mathfrak{F}_0}{\partial n}-\mathfrak{F}_0\right)_S-2(hn'')_S+\left(n\frac{\partial\mathfrak{F}_{xc}}{\partial n}-\mathfrak{F}_{xc}\right)_S. \tag{42}$$

The first term is the homogeneous kinetic pressure P_0, the second is the kinetic gradient correction P_1, and the third is the exchange-and-correlation pressure P_{xc}.

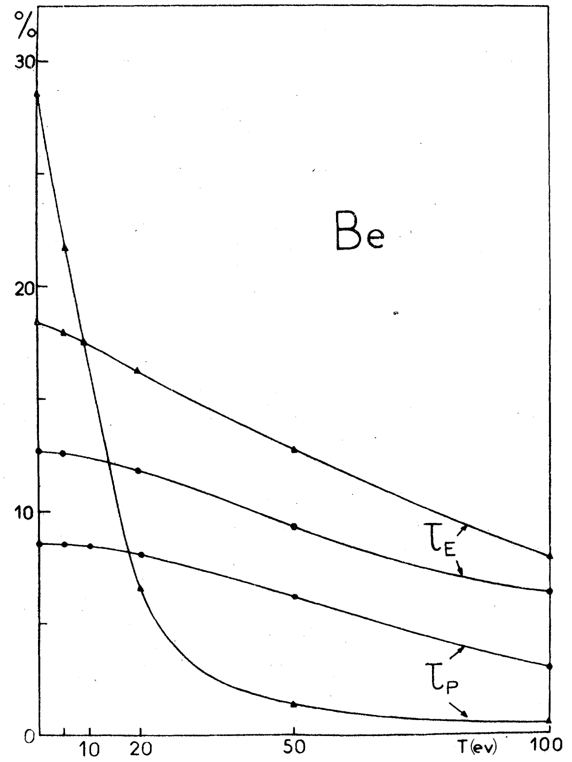

FIG. 2. Ratio τ_P of the inhomogeneous to homogeneous kinetic pressures, and similar ratio τ_E for kinetic energies, in beryllium. Triangles: $\rho/\rho_0=1$. Circles: $\rho/\rho_0=10$.

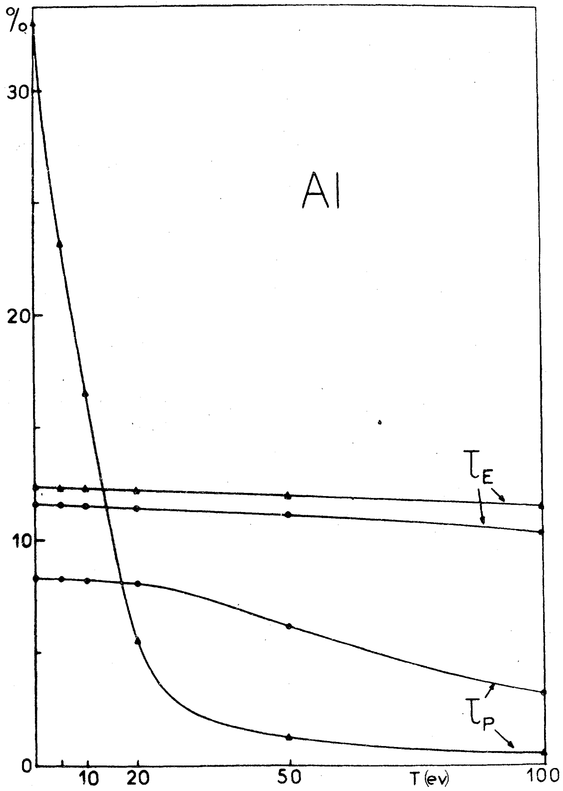

FIG. 3. Same as Fig. 2 in aluminum.

V. RESULTS AND DISCUSSION

Here we present the results obtained for the equation of state of beryllium, aluminum, and copper when applying Eq. (7) to the self-consis-

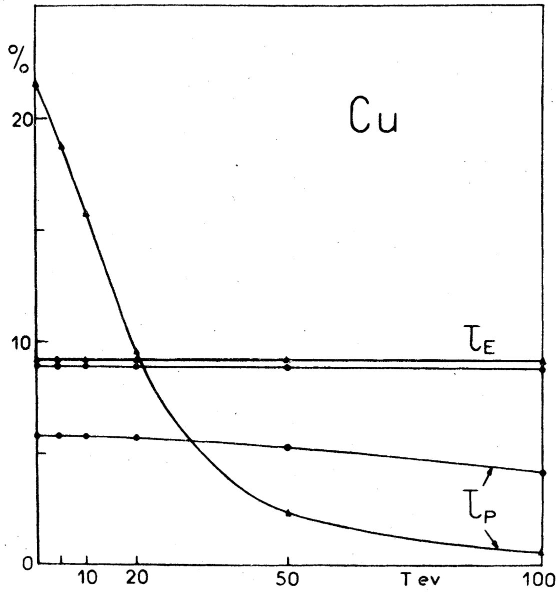

FIG. 4. Same as Fig. 2 in copper.

TABLE I. Beryllium: Total pressure P (Mbar) and energy E (a.u./atom).

	$\rho/\rho_0=0.1$						$\rho/\rho_0=1$						$\rho/\rho=10$					
	TFDW		TFD		TF		TFDW		TFD		TF		TFDW		TFD		TF	
T (eV)	P	E	P	E	P	E	P	E	P	E	P	E	P	E	P	E	P	E
0	−0.004	−0.11	⋯	⋯	0.007	−0.32	0.267	−0.12	0.508	−0.12	1.413	−0.12	109.4	1.40	117.3	1.61	153.7	2.49
5	0.072	0.38	0.082	0.33	0.122	0.20	0.658	0.08	0.986	0.09	2.311	0.17	112.1	1.48	120.1	1.69	156.5	2.57
10	0.257	1.39	0.270	1.33	0.325	1.15	1.899	0.62	2.335	0.64	4.090	0.78	119.7	1.70	127.9	1.92	164.7	2.81
20	0.792	4.12	0.804	4.00	0.873	3.64	6.447	2.39	6.873	2.39	8.725	2.45	145.0	2.49	154.2	2.72	194.3	3.68
50	2.960	13.86	2.952	13.52	3.019	12.57	25.05	9.60	25.33	9.45	27.06	9.08	258.8	6.29	270.6	6.55	337.8	8.02

TABLE II. Aluminum: Total pressure P (Mbar) and energy E (a.u./atom).

	$\rho/\rho_0=0.1$						$\rho/\rho_0=1$						$\rho/\rho_0=10$					
	TFDW		TFD		TF		TFDW		TFD		TF		TFDW		TFD		TF	
T (eV)	P	E	P	E	P	E	P	E	P	E	P	E	P	E	P	E	P	E
0	−0.001	−0.09	⋯	⋯	0.003	−0.37	0.106	−0.12	0.293	−0.12	1.030	−0.12	124.9	2.83	135.9	3.29	183.2	5.24
5	0.054	0.77	0.061	0.72	0.090	0.59	0.396	0.28	0.676	0.30	1.853	0.45	127.7	3.00	138.7	3.47	186.1	5.42
10	0.198	2.72	0.209	2.66	0.255	2.55	1.612	1.42	1.968	1.46	3.475	1.73	135.7	3.50	147.0	3.98	194.8	5.94
20	0.654	8.53	0.670	8.44	0.744	8.23	5.617	5.13	6.035	5.17	7.860	5.46	163.1	5.28	175.5	5.80	226.7	7.89
50	2.874	34.63	2.896	34.32	3.025	33.38	23.99	28.43	24.51	22.36	26.90	22.27	288.5	14.40	304.9	15.03	388.7	18.34

tent determination of the electron density. In the following, this model will be referred to as TFDW (we keep the denomination used in[23] at zero temperature, where the letter W referred to Von Weizsäcker for the gradient correction, although the magnitude of the correction suggested by this author is nine times larger). We shall compare the results with the TF and TFD equations of state. The effect of temperature has been studied up to 50 eV for the compressions $\rho/\rho_0 = 0.1$, 1, and 10. The normal densities are ρ_0 (g/cm^3) $= 1.8450$, 2.7847, and 8.9382 for Be, Al, and Cu, respectively.

In Figs. 2–4 are shown the variations of the quantities

$$\tau_P = P_1/P_0\,,$$

ratio of the inhomogeneous to homogeneous kinetic pressures, and

$$\tau_E = K_1/K_0$$

similar ratio for the kinetic energies. At normal density, τ_P is large [(20–30)%] at $T=0$ and decreases very fast with rising temperature; at $\rho/\rho_0 = 10$, τ_P is smaller at low temperature but decreases much slower. It can be shown that τ_P varies approximately as

$$\tau_P = a\mu^{-1/2}\,, \quad T \to 0 \tag{43}$$

and

$$\tau_P = b\beta^{1/2}e^{\beta\mu}\,, \quad T \to \infty \tag{44}$$

where a and b are numerical constants and μ is the chemical potential. According to (43), τ_P tends to zero with increasing density at $T=0$. The temperature behavior is determined by the quantity $\beta\mu$, and τ_P begins to decrease when $\beta\mu$ becomes negative. The larger the density, the higher the temperature where $\beta\mu$ vanishes, so that the τ_P curves become increasingly flat. The curves representing τ_E show much less structure; they are quasilinear in temperature in the region of interest, and their sensitivity to density is weak. As the energies entering τ_E are integrated quantities (instead of quantities calculated on the boundary $r = S$ for τ_P), τ_E is driven by $\beta(\mu - \overline{U})$, where $\overline{U}$ is an average potential. The temperature where $\beta(\mu - \overline{U})$ becomes negative is very high, so that the behavior of τ_E changes very slowly.

The numerical values of total pressure P [Eq. (42)] and energy [Eqs. (33)–(36)] are given in Tables I–III. The origin of energies has been fixed, for each material, in order to reproduce the experimental cohesive energy at $T=0$, $\rho/\rho_0 = 1$. It is not possible to choose the free-atom energy as origin since there is no solution in the TFD model for very low densities at $T \to 0$. The

TABLE III. Copper: Total pressure P (Mbar) and energy E (a.u./atom).

	$\rho/\rho_0 = 0.1$						$\rho/\rho_0 = 1$						$\rho/\rho_0 = 10$					
	TFDW		TFD		TF		TFDW		TFD		TF		TFDW		TFD		TF	
T (eV)	P	E	P	E	P	E	P	E	P	E	P	E	P	E	P	E	P	E
0	−0.005	−0.20	⋯	⋯	0.011	−0.91	1.320	−0.13	1.940	−0.13	4.520	−0.13	706.8	12.52	747.3	13.74	928.0	19.01
5	0.081	0.82	0.096	0.70	0.159	0.19	2.159	0.41	2.901	0.44	5.822	0.52	710.8	12.70	751.4	13.93	932.1	19.19
10	0.314	3.27	0.338	3.14	0.438	2.82	3.557	1.64	4.511	1.72	8.802	2.16	722.5	13.23	763.3	14.47	944.3	19.74
20	1.070	10.82	1.108	10.73	1.270	10.47	10.49	6.37	11.68	6.49	17.12	7.23	767.7	15.32	809.6	16.58	992.3	21.89
50	4.962	48.05	5.038	47.77	5.351	47.20	44.81	30.60	46.38	30.70	53.47	31.48	1024.0	27.83	1073.0	29.29	1286.0	35.45

numerical values of the energy shifts may be deduced from Table 1 of Ref. 23. For all materials, and at all densities, the exchange and correlation effects are more important than the gradient correction: the TFDW and TFD results are closer than the TFD and TF ones. At the temperature of 50 eV, the TFDW and TFD pressures in Be agree within 0.3%, 1.2%, and 4.8% at $\rho/\rho_0 = 0.1$, 1, and 10, respectively. The corresponding percentages are 0.8%, 2.1%, 5.7% in Al and 1.5%, 3.5%, 4.8% in Cu. For energy, the three models give thermal components in very close agreement: the gradient correction to kinetic energy does not influence appreciably the specific heat.

In conclusion, I have presented a generalization of the gradient correction to nonzero temperatures. The functional $h(n)$ which describes this correction has been defined and computed. Application has been made to the calculation of equation of state, showing (i) the relative importance of the gradient correction to kinetic pressure, which decreases at $T=0$ when the density increases, goes to zero slower at high densities; (ii) the relative part of kinetic energy due to the gradient correction varies very smoothly with temperature and density.

APPENDIX A

An analytic representation of the function $\mathcal{F}_0(n)$, density of free-energy of the noninteracting electron gas, has been determined from Eqs. (5a) and (5b). It is clear that the correct variable is

$$y = (\pi^2/\sqrt{2})\beta^{3/2} n .$$

From the asymptotic forms of the Fermi functions, it is straightforward to show that

$$f(y) = \beta n^{-1}\mathcal{F}_0 = \begin{cases} \ln y + (\text{const}) + O(y) , & y \to 0 , \\ y^{2/3}[\tfrac{3}{10}(3\sqrt{2})^{2/3} + O(y^{-4/3})] , & y \to \infty . \end{cases}$$

The relation between $\mathcal{F}_0$ and n is obtained by tabulating (5a) and (5b) for values of η in the range $-10 \leqslant \eta \leqslant 20$. Owing to the change of behavior of the Fermi functions when η passes through zero, it was convenient to consider two regions $y \leqslant y_0$ and $y \geqslant y_0$ ($y_0 = 3\pi/4\sqrt{2}$). In both of them, a least-squares fit with Chebyshev polynomials has been performed, requiring the continuity of $f(y)$ and its first and second derivatives at $y = y_0$. The following approximation was found:

$$\begin{aligned} f(y) = {} & \ln y - 0.879\,188\,021\,5 + 0.198\,971\,874\,2 y + 0.106\,869\,704\,3 \times 10^{-2} y^2 - 0.881\,268\,572\,6 \times 10^{-2} y^3 \\ & + 0.127\,218\,302\,7 \times 10^{-1} y^4 - 0.977\,275\,858\,3 \times 10^{-2} y^5 + 0.382\,063\,047\,7 \times 10^{-2} y^6 - 0.597\,121\,704\,1 \times 10^{-3} y^7 \\ & \text{for } y \leqslant y_0 = 1.666\,081\,101 , \\ f(y) = {} & 0.786\,222\,418\,3 u - 0.188\,297\,945\,4 \times 10^1 u^{-1} + 0.532\,195\,268\,1 u^{-3} + 0.230\,445\,795\,5 \times 10^1 u^{-5} \\ & - 0.161\,428\,077\,2 \times 10^2 u^{-7} + 0.522\,843\,138\,6 \times 10^2 y^{-9} - 0.959\,264\,561\,9 \times 10^2 y^{-11} \\ & + 0.946\,223\,017\,2 \times 10^2 y^{-13} - 0.389\,375\,393\,7 \times 10^2 u^{-15} \quad \text{for } y \geqslant y_0 \text{ with } u = y^{2/3} . \end{aligned}$$

The relative accuracy is always better than 1.2×10^{-4} on $f(y)$ and df/dy, and better than 1×10^{-3} on d^2f/dy^2. When the exact value of df/dy is exactly 0, the approximation gives -0.39×10^{-5}.

APPENDIX B

The same technique of approximation has been used for the function $h(y)$ defined by Eq. (14). The expression below is continuous at $y = y_0$, and also its first and second derivatives:

$$\begin{aligned} 12h(y) = {} & 0.5 - 0.199\,917\,631\,6 y + 0.976\,561\,570\,9 \times 10^{-1} y^2 - 0.623\,760\,992\,4 \times 10^{-1} y^3 + 0.580\,146\,632\,2 \times 10^{-1} y^4 \\ & - 0.444\,928\,777\,4 \times 10^{-1} y^5 + 0.190\,321\,169\,7 \times 10^{-1} y^6 - 0.328\,409\,692\,6 \times 10^{-2} y^7 \quad \text{for } y \leqslant y_0 , \\ 12h(y) = {} & \tfrac{1}{6} + 0.311\,590\,799\,0 u^{-2} + 0.329\,566\,243\,9 \times 10^1 u^{-4} - 0.292\,203\,832\,6 \times 10^2 u^{-6} + 0.116\,108\,453\,1 \times 10^3 u^{-8} \\ & - 0.250\,454\,314\,7 \times 10^3 u^{-10} + 0.281\,433\,688\,0 u^{-12} - 0.128\,878\,480\,6 \times 10^3 u^{-14} \quad \text{for } y \geqslant y_0 . \end{aligned}$$

The accuracy on $h(y)$ is better than 10^{-3}; the maximum error occurs at $y \simeq 2$.

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[1] C. F. Von Weizsäcker, Z. Phys. 96, 431 (1935).

[2] P. L. Gombas, *Handbuch der Physik* (Springer, Berlin, 1956), Vol. 36, part 2.

[3] D. A. Kirshnits, Sov. Phys. JETP 5, 64 (1957).

[4] A. S. Kompaneets and E. S. Pavlowskii, Sov. Phys. JETP 4, 328 (1957).

[5] N. H. March, Adv. Phys. 6, 1 (1957).

[6] S. Golden, Phys. Rev. 105, 604 (1957).

[7] N. H. March and W. H. Young, Proc. Phys. Soc. (London) 72, 182 (1958).

[8] K. L. Le Couteur, Proc. Phys. Soc. (London) 84, 837 (1964).

[9] H. M. Schey and J. L. Schwartz, Phys. Rev. 137, A709 (1965).

[10] P. L. Gombas, Phys. Lett. 28A, 585 (1969).

[11] A. M. K. Müller, R. Baltin and P. Schroth, Phys. Lett. 32A, 515 (1970).

[12] J. C. Stoddart, A. M. Beattie and N. H. March, Int. J. Quantum Chem. Suppl. 4, 35 (1970).

[13] J. Goodisman, Phys. Rev. A 1, 1574 (1970).

[14] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).

[15] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

[16] Chia. C. Shih, Phys. Rev. A 14, 919 (1976).

[17] K. Yonei and Y. Tomishima, J. Phys. Soc. Jpn. 20, 1051 (1965).

[18] Y. Tomishima and K. Yonei, J. Phys. Soc. Jpn. 21, 142 (1966).

[19] C. Q. Ma and V. Sahni, Phys. Rev. B 16, 4249 (1977).

[20] L. M. Kahn and M. Rasolt, J. Phys. F 7, 1993 (1977).

[21] L. M. Kahn and M. Rasolt, Solid State Commun. 27, 33 (1978).

[22] F. Perrot, Phys. Status Solidi B 87, 707 (1978).

[23] F. Perrot, Phys. Status Solidi B (to be published).

[24] R. Latter, Phys. Rev. 99, 1854 (1955).

[25] L. Hedin and S. Lundqvist, in *Solid State Physics*, edited by F. Seitz, E. Turnbull, and H. Ehrenreich (Academic, New York, 1969), Vol. 23, p. 1.

[26] B. Horovitz and R. Thieberger, Physica (Utr.) 71, 99 (1974).

[27] A. Isihara and D. Y. Kojima, Physica (Utr.) 77, 469 (1974), and references therein.

[28] L. G. Caron, Phys. Rev. B 9, 1388 (1974).