

Fourth-order gradient contributions in extended Thomas-Fermi theory for noninteracting fermions at finite temperature

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Nonlocal corrections to the free energy of a system of noninteracting fermions are considered within the framework of extended Thomas-Fermi theory. The density and temperature dependence of gradient corrections is given through fourth order in powers of the density gradient. The calculation is based on long-wavelength expansions of linear and nonlinear response functions of a nearly uniform system. Results are given in terms of Fermi-Dirac integrals and convenient forms are given which span the full density and temperature range from the degenerate limit to the classical limit.

I. INTRODUCTION

There have been many studies of the Thomas-Fermi or statistical theory, and of its various extensions, of matter under various conditions of temperature and pressure. In addition to atomic, molecular, and conventional condensed-matter problems, important applications have been made in nuclear physics and astrophysics. Discussions of this approach to inhomogeneous many-particle systems and extensive references to the original literature are given in recent review articles and conference proceedings.¹⁻⁶ The original form of Thomas-Fermi theory is purely local and, consequently, local physical quantities are determined only in terms of local particle densities.^{7,8} A number of suggestions can be made to improve upon this local-density approximation (LDA) by including nonlocal corrections which are inevitable in inhomogeneous systems. Perhaps the simplest way to include nonlocality is by means of gradient expansions.⁹ [Many other procedures, often with specific objectives within the universal framework of density-functional theory (DFT) can also be devised.^{4,9}] The general objective is the representation of both local and nonlocal contributions to the total energy, including the kinetic energy plus one-body and two-body interaction energies, as a reasonably convenient approximate functional of the particle density (or densities for multicomponent systems). The relevant energy functional is the ground-state energy $E[n]$ for zero-temperature systems or the thermodynamic free energy $F[n]$ for systems at finite temperature ($T \neq 0$).¹⁰ The particular version of DFT which is based on the Thomas-Fermi theory plus gradient corrections is known as the extended Thomas-Fermi (ETF) theory.

One major attractive feature of the ETF, as compared to methods based on self-consistent determination of single-particle orbitals, is its extreme simplicity. Consequently, ETF is well suited to exploratory work on systems having low symmetry particularly when finite-temperature effects are of interest. Thus, while ETF is typically less precise than self-consistency schemes such as that of Kohn and Sham¹¹ (KS), its accuracy may nevertheless be adequate in many situations of interest.

For example, although a truncated gradient expansion does not reproduce specific quantum effects such as shell structure or quantum density oscillations, these effects are smeared out at finite temperature in any case, eventually becoming unimportant, and there are situations where highly accurate and simple procedures based on ETF can be devised for the treatment of finite-temperature properties such as equations of state and related quantities.¹² In this context, we note that since ETF involves an expansion in powers of gradients (and higher derivatives) of the density and since quantum density oscillations are smeared out at finite temperature, we may well expect the convergence of finite-temperature gradient expansions to be superior in some respects to those at zero temperature. The question of convergence properties of gradient expansions in general and of their presumed asymptotic character (at least at $T \neq 0$) is still unsettled to some degree and further information is desirable.⁴

There are at least two distinct ways to view the free-energy functional $F[n]$ when considering this question. The variational principle for the free energy leads to the Euler-Lagrange equation $\delta F/\delta n(\mathbf{r})=0$ which is a differential equation to be solved for $n(\mathbf{r})$ thus yielding the required $F[n]$. This differential equation is nonlinear and potentially of high order, depending on the number of gradient corrections under consideration, but is generally numerically tractable. However, it may be that physical considerations suggest a particular form for the density which is not fully compatible with the Euler-Lagrange equation of the approximate free-energy functional. It is then often convenient to constrain the form of the density $n(\mathbf{r};\{\lambda\})$ and to introduce parameters $\{\lambda\}$ which are chosen by the variational principle to optimize the energy.

The form of the various nonlocal corrections to the LDA for the universal free energy can be determined, within ETF, by simple arguments. By symmetry the lowest-order nonlocal contribution to the ETF form of the free energy is

$$\int d\mathbf{r} B(n(\mathbf{r}))[\nabla n(\mathbf{r})]^2$$

with an obvious extension to multicomponent systems.

Higher-order terms involve $(\nabla n)^4, (\nabla^2 n)(\nabla n)^2, (\nabla^2 n)^2, (\nabla n)^6, \dots$, each with an appropriate coefficient, to be determined, which is implicitly temperature dependent. Each such coefficient has contributions arising from kinetic energy and both one-body and two-body interactions. For many-electron systems in their ground state ($T=0$), the kinetic-energy contributions to these coefficients are known up to sixth order in gradients,¹³⁻¹⁶ while the interaction contributions are known only to second order in powers of gradients both in the high-density limit¹⁷⁻²¹ and at metallic densities.^{22,23} At finite temperature, the contribution of the kinetic energy to the second-order gradient coefficient has previously been known²⁴⁻²⁶ and we give here details of a calculation of kinetic-energy contributions to the three fourth-order gradient contributions.²⁷ We consider the free-energy functional of a system of electrons (fermions) of density $n(\mathbf{r})$ at temperature T in an external potential $V(\mathbf{r})$ in the form

$$F[n] = F_k[n] + \int d\mathbf{r} n(\mathbf{r})V(\mathbf{r}) + F_H[n] + F_{xc}[n] \quad (1)$$

and our present objective is to give the full fourth-order gradient expansion (at $T \neq 0$) of $F_k[n]$. In this work, we shall refer to $F_k[n]$ as the kinetic free energy, for brevity, and we note that $F_k[n]$ contains the usual entropy contribution, $-TS$. The last two terms in Eq. (1) are the Hartree and the exchange-correlation free-energy contributions, respectively. The Hartree contribution is

$$\frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' n(\mathbf{r})v(\mathbf{r}-\mathbf{r}')n(\mathbf{r}'),$$

where $v(\mathbf{r}-\mathbf{r}')$ is the interparticle interaction, of course. To date, no results have been reported for the temperature dependence of gradient contributions to $F_{xc}[n]$ although work is in progress.

It may be noted that in many nuclear-physics applications it is possible to exploit the short range of the (Skyrme-like) internucleon interactions in such a way that two-body interactions, including their dependence on linear and angular momentum, are incorporated into the free-energy functional by nonlocal one-body interactions with a suitable choice of effective mass and spin-orbit coupling.⁶ (This inclusion of two-body interaction effects in a one-body form is in sharp contrast to the many-electron problem where explicit detailed treatment of F_{xc} is mandatory.) The contributions to the free energy due to this effective nuclear one-body Hamiltonian have been given by Jennings, Bhaduri, and Brack^{9(b)} and by Grammaticos and Voros²⁸ to second and fourth order in gradients, respectively, at $T=0$. Finally, we note that there is no immediate need for the temperature dependence of sixth- and higher-order gradient coefficients for the kinetic or noninteracting part of the free energy, at least when parametrized densities are used to characterize the free energy (see above). Best results are obtained in practice when the gradient expansion for the kinetic-energy contributions is truncated after the fourth-order terms. This applies to both many-electron problems²⁹⁻³¹ and nuclear problems.⁶

The outline of the remainder of this paper is as follows. In Sec. II we derive a consistent perturbation expansion in powers of the induced density variation for the free energy

of a system of noninteracting fermions in the presence of an external local potential. The expansion is valid through fourth order in powers of the potential. The required nonlinear response functions are then approximated by their long-wavelength forms and an expansion in powers of gradients of the density variation is obtained. In Sec. III, a partial resummation is carried out and the coefficients of the second- and four-order gradient corrections are exhibited in a compact form in terms of Fermi-Dirac integrals. Limiting cases of the strongly degenerate limit ($T \ll T_F$) and the classical limit ($T \gg T_F$) are discussed. Convenient dimensionless forms and parametrizations useful for numerical applications are given. Details of this work are provided in three appendixes. Finally, Sec. IV consists of a summary and discussion.

II. DERIVATION OF GRADIENT EXPANSION OF KINETIC FREE ENERGY

To generate a density-functional description of an inhomogeneous system of electrons in the presence of an external potential V , it is convenient to express the partition function $Z(\mu, T)$, which is a function of the chemical potential and temperature, as an explicit series expansion in powers of V by standard methods of finite-temperature perturbation theory.³² The expansion for the grand potential, $\Omega_v = -k_B T \ln Z$, then follows as

$$\Omega_v = \Omega^{(0)}(\mu, T) + \sum_{\alpha=1}^{\infty} \Omega^{(\alpha)}(\mu, T), \quad (2)$$

where $\Omega^{(0)}$ is the grand potential of a uniform system at the same μ and T and the perturbative corrections can be expressed in the form

$$\Omega^{(\alpha)}(\mu, T) = \sum_{\mathbf{q}_1 \dots \mathbf{q}_\alpha} C^{(\alpha)}(\mathbf{q}_1, \dots, \mathbf{q}_\alpha) \times V(\mathbf{q}_1), \dots, V(\mathbf{q}_\alpha) \quad (3)$$

with the coefficients $C^{(\alpha)}$ given by various (linear and nonlinear) response functions evaluated for the uniform system (see Appendix A). As usual, $\Omega_v = F - \mu N = -k_B T \ln Z$ and the well-known procedure of discarding all disconnected or unlinked clusters when evaluating the coefficients $C^{(\alpha)}(\{q\})$ by Wick's theorem corresponds to taking the logarithm of $Z(\mu, T)$ so that the free energy results directly. It is easy to verify that the appropriate zero-temperature limit of this result is consistent with results from the theory of the structure of simple metals where the electron energy is expanded in powers of the electron-ion potential (or pseudopotential).³³⁻³⁵

In order to convert F_v from the above to a functional of the density, or more precisely to a functional of the nonuniform part of the density $\tilde{n}(\mathbf{r}) = n(\mathbf{r}) - n_0$ where $n_0 = n_0(\mu, T)$, we proceed by expanding the Fourier components $\tilde{n}(\mathbf{q})$ as a perturbation expansion in powers of the potential. This yields $\tilde{n}(\mathbf{q}) = \sum_{\alpha} \tilde{n}_{\alpha}(\mathbf{q})$, where $\tilde{n}_{\alpha}(\mathbf{q})$ has the same general form as Eq. (3). By a straightforward iteration procedure precisely analogous to the Lagrange inversion of an ordinary power series, the series for $\tilde{n}(\mathbf{q})$ in powers of V can be inverted to give $V(\mathbf{q})$ as a series in

powers of \tilde{n} , $V(\mathbf{q}) = \sum_{\alpha} V^{(\alpha)}(\mathbf{q})$ where $V^{(\alpha)}(\mathbf{q})$ has α factors of \tilde{n} and a known coefficient determined from those of the \tilde{n} series (note that the $\mathbf{q} = \mathbf{0}$ point requires special treatment). This functional series for $V(\mathbf{q})$ in powers of \tilde{n} is now inserted into Eq. (3). Finally, we must remember that μ is dependent on the external potential so that fixing the chemical potential by the usual particle number conservation, $N(\mu, T) = N_0(\mu_0, T)$ causes $\mu - \mu_0 = \delta\mu$ to become expressed as a functional of \tilde{n} . Putting together all of these sources of \tilde{n} dependence yields, after lengthy but straightforward algebra, the desired form for the kinetic-free-energy functional (which we truncate at fourth order in \tilde{n}) as

$$F_k[\tilde{n}] = F_k^{(0)}(n_0) + \sum_{\alpha=2}^4 F_k^{(\alpha)}[\tilde{n}]. \quad (4)$$

The kinetic free energy of the noninteracting unperturbed (uniform) electron gas is $F_k^{(0)}(n_0)$. A term of first order in \tilde{n} is absent from Eq. (4) as it and appropriate higher-order terms already have been extracted to form the contribution $\int d\mathbf{r} n(\mathbf{r})V(\mathbf{r})$ to Eq. (1). The second-order (in \tilde{n}) contribution to the kinetic free energy is well known:²⁴

$$F_k^{(2)}[\tilde{n}] = (2v)^{-1} \sum_{\mathbf{q}} \tilde{n}(\mathbf{q})\tilde{n}(-\mathbf{q})[\pi_0^{(2)}(\mathbf{q})]^{-1}, \quad (5)$$

where v is the volume and $\pi_0^{(2)}$ is the Lindhard function. The third-order term is

$$F_k^{(3)}[\tilde{n}] = (3v^2)^{-1} \sum_{\mathbf{q}_1, \mathbf{q}_2} \tilde{n}(\mathbf{q}_2)\tilde{n}(\mathbf{q}_2)\tilde{n}(-\mathbf{q}_1-\mathbf{q}_2)\pi_0^{(3)}(\mathbf{q}_1+\mathbf{q}_2, \mathbf{q}_2)[\pi_0^{(2)}(\mathbf{q}_1)\pi_0^{(2)}(\mathbf{q}_2)\pi_0^{(2)}(-\mathbf{q}_1-\mathbf{q}_2)]^{-1}, \quad (6)$$

and the fourth-order term is

$$F_k^{(4)}[\tilde{n}] = -(4v^3)^{-1} \sum_{\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3} \tilde{n}(\mathbf{q}_1)\tilde{n}(\mathbf{q}_2)\tilde{n}(\mathbf{q}_3)\tilde{n}(-\mathbf{q}_1-\mathbf{q}_2-\mathbf{q}_3)[\pi_0^{(4)}(\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3, \mathbf{q}_2+\mathbf{q}_3, \mathbf{q}_3) \\ - 2\pi_0^{(3)}(-\mathbf{q}_1-\mathbf{q}_2, \mathbf{q}_3)\pi_0^{(3)}(\mathbf{q}_1+\mathbf{q}_2, \mathbf{q}_2)/\pi_0^{(2)}(-\mathbf{q}_1-\mathbf{q}_2)] \\ \times [\pi_0^{(2)}(\mathbf{q}_1)\pi_0^{(2)}(\mathbf{q}_2)\pi_0^{(2)}(\mathbf{q}_3)\pi_0^{(2)}(-\mathbf{q}_1-\mathbf{q}_2-\mathbf{q}_3)]^{-1}. \quad (7)$$

The primes on the sums denote the following restrictions: $\mathbf{q} \neq \mathbf{0}$ in Eq. (5); $\mathbf{q}_1 \neq \mathbf{0}$, $\mathbf{q}_2 \neq \mathbf{0}$, and $\mathbf{q}_1 + \mathbf{q}_2 \neq \mathbf{0}$ in Eq. (6); $\mathbf{q}_1 \neq \mathbf{0}$, $\mathbf{q}_2 \neq \mathbf{0}$, $\mathbf{q}_3 \neq \mathbf{0}$, and $\mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3 \neq \mathbf{0}$, in Eq. (7). The various linear ($\alpha=2$) and nonlinear ($\alpha=3,4$) response functions, $\pi_0^{(\alpha)}$, are specified in Appendix A. Thus far, Eqs. (4)–(7) are valid for either slowly or rapidly varying densities, $\tilde{n}(\mathbf{r})$, but are valid only to fourth order in powers of the perturbation. This fourth-order expansion in \tilde{n} is sufficient to yield all terms in the gradient expansion up to and including fourth order in gradients.

To generate a gradient expansion, we assume that the spatial variation of the density is slow so that only the

very-low-wave-number Fourier components $\tilde{n}(\mathbf{q})$ are appreciable. The structure of the restricted wave-number sums in Eqs. (5)–(7) then implies that all of the response functions can be expanded in powers of all of their wave-number arguments (k_{α} is small, for all α , and so are the appropriate linear combinations). After a further considerable amount of algebra, the small wave-number expansions can be put into standard forms which are then easily transformed from wave number to configuration space, as described in Appendix B.

The resulting expansion in powers of the density gradients of the kinetic free energy is

$$F_k[\tilde{n}] = \int d\mathbf{r} \left\{ \mathcal{L}_k(n_0) + \sum_{\alpha=2}^4 (\alpha!)^{-1} \int d\mathbf{r} \left[\frac{\partial^{\alpha} \mathcal{L}_k}{\partial n_0^{\alpha}} \right] [\tilde{n}(\mathbf{r})]^{\alpha} + \dots \right. \\ \left. + [\nabla \tilde{n}(\mathbf{r})]^2 \left[B(n_0) + \sum_{\alpha=1}^2 (\alpha!)^{-1} \left[\frac{\partial^{\alpha} B}{\partial n_0^{\alpha}} \right] [\tilde{n}(\mathbf{r})]^{\alpha} + \dots \right] \right. \\ \left. + (\nabla^2 \tilde{n}(\mathbf{r}))^2 \left[C(n_0) + \sum_{\alpha=1}^2 (\alpha!)^{-1} \left[\frac{\partial^{\alpha} C}{\partial n_0^{\alpha}} \right] [\tilde{n}(\mathbf{r})]^{\alpha} + \dots \right] \right. \\ \left. + [\nabla^2 \tilde{n}(\mathbf{r})][\nabla \tilde{n}(\mathbf{r})]^2 \left[D(n_0) + \left[\frac{\partial D}{\partial n_0} \right] \tilde{n}(\mathbf{r}) + \dots \right] + [\nabla \tilde{n}(\mathbf{r})]^4 [E(n_0) + \dots] + \dots \right\}. \quad (8)$$

In Eq. (8), $\mathcal{L}_k(n_0)$ is the kinetic-free-energy density of a uniform system and

$$B(n_0) = \frac{\hbar^2}{2m} [X_2 / 12X_1^2] \quad (9)$$

is the lowest-order expansion coefficient given by Perrot²⁴ and also by Brack.^{25,26} The new coefficients in the expansion are

$$C(n_0) = \left[\frac{\hbar^2}{2m} \right]^2 [X_2^2 / 72X_1^3 - X_3 / 120X_1^2], \quad (10)$$

$$D(n_0) = \left[\frac{\hbar^2}{2m} \right]^2 \{ -X_4 / 180X_1^3 + 11X_2X_3 / 360X_1^4 - X_2^3 / 36X_1^5 \}, \quad (11)$$

and

$$E[n_0] = \left[\frac{\hbar^2}{2m} \right]^2 [X_5 / 1440X_1^4 - X_2^2X_3 / 45X_1^6 + X_2^4 / 72X_1^7 + X_2X_4 / 180X_1^5 + X_3^2 / 288X_1^5]. \quad (12)$$

The quantities X_k are

$$X_k = (\partial / \partial \mu_0)^k n_0(\mu_0, T) \quad (13)$$

and can be expressed in terms of standard integrals over Fermi functions. Such integrals are readily calculable (see below), so we conclude that B , C , D , and E and their derivatives with respect to μ_0 may be regarded as known. This completes the formal derivation of the fourth-order gradient expansion for the kinetic free energy. Numerical results and further discussion are given in the following sections.

III. NUMERICAL RESULTS FOR GRADIENT-EXPANSION COEFFICIENTS

In the preceding section, we derived perturbatively the fourth-order gradient expansion for the kinetic free energy

for a system of electrons having a density $n(\mathbf{r}) = n_0 + \tilde{n}(\mathbf{r})$ which is almost constant and slowly varying everywhere. The result, Eq. (8), is asymptotically valid to fourth order in the inhomogeneity $\tilde{n}(\mathbf{r})$, and is thus guaranteed to be accurate in practice only when higher-order terms are negligible. However, in such a case, Eq. (8) can equally well be replaced by

$$F_k[n] = \int d\mathbf{r} \{ \mathcal{L}_k(n(\mathbf{r})) + B(n(\mathbf{r}))[\nabla n(\mathbf{r})]^2 + C(n(\mathbf{r}))[\nabla^2 n(\mathbf{r})]^2 + D(n(\mathbf{r}))[\nabla^2 n(\mathbf{r})][\nabla n(\mathbf{r})]^2 + E(n(\mathbf{r}))[\nabla n(\mathbf{r})]^4 + \dots \} \quad (14)$$

which is clearly seen to be equivalent to Eq. (8), through fourth order, on making a Taylor expansion in powers of $\tilde{n}(\mathbf{r})$ of all $n(\mathbf{r})$ dependent functions. Further discussion of Eq. (14) will be given in Sec. IV, but for the present we note that in practice we will require only the quantities B , C , D , and E as functions of n_0 and do not explicitly need their derivatives with respect to n_0 [see Eq. (8)] since Eq. (14) has taken such terms into account implicitly by evaluating these coefficients at the exact local density $[n_0 \rightarrow n(\mathbf{r})]$. The basic elements in the specification of these coefficients, from Eqs. (9)–(13) are the quantities X_k .

For numerical work it is convenient to introduce dimensionless forms by measuring lengths in units of bohrs, $a_H = \hbar^2 / m_0 e^2$, where m_0 is the electron mass, and energies in units of hartrees, $\epsilon_H = e^2 / a_H$. The dimensionless mass, density, and "inverse temperature" are then $m^* = m / m_0$, $n^* = n a_H^3$, and $\beta^* = \beta \epsilon_H$. The dimensionless gradient coefficients are $B^* = B / (\epsilon_H a_H^5)$, $C^* = C / \epsilon_H a_H^7$, $D^* = D / \epsilon_H a_H^{10}$, and $E^* = E / \epsilon_H a_H^{13}$. The dimensionless form of Eqs. (9)–(12) are then

$$B^* = \frac{\pi^2}{24\sqrt{2}} (m^*)^{-5/2} (\beta^*)^{3/2} X_2^* / (X_1^*)^2, \quad (15)$$

$$C^* = \frac{\pi^2}{8\sqrt{2}} (m^*)^{-7/2} (\beta^*)^{5/2} [(X_2^*)^2 / 36(X_1^*)^3 - X_3^* / 60(X_1^*)^2], \quad (16)$$

$$D^* = \frac{\pi^4}{288} (m^*)^{-5} (\beta^*)^4 [-X_4^* / 5(X_1^*)^3 + 11X_2^*X_3^* / 10(X_1^*)^4 - (X_2^*)^3 / (X_1^*)^5], \quad (17)$$

and

$$E^* = \frac{\pi^6}{8\sqrt{2}} (m^*)^{-13/2} (\beta^*)^{11/2} [-X_5^* / 1440(X_1^*)^4 - (X_2^*)^2 X_3^* / 45(X_1^*)^6 + (X_2^*)^4 / 72(X_1^*)^7 + X_2^* X_4^* / 180(X_1^*)^5 + (X_3^*)^2 / 288(X_1^*)^5]. \quad (18)$$

The dimensionless quantities X_k^* in Eqs. (15)–(18) are given by

$$X_k^* = (\partial/\partial\eta)^k I_{1/2}(\eta), \quad (19)$$

where $\eta = \beta\mu_0 = \beta^*\mu_0^*$ with $\mu_0 = \mu_0(T)$ as usual and $I_{1/2}(\eta)$ is a special case of the Fermi-Dirac integral

$$I_p(\eta) = \int_0^\infty dx X^p / (e^{x-\eta} + 1). \quad (20)$$

Such integrals can be explicitly evaluated either by numerical integration or by making use of appropriate series expansions. The latter procedure is very convenient.³⁶

These Fermi-Dirac integrals are easily obtained analytically in the limit of either very strong degeneracy (quantum limit) or very weak degeneracy (classical limit). The results for very low temperature are

$$B^* = (72m^*n_0^*)^{-1} [1 + \pi^2/3(\beta^*\mu_0^*)^2], \quad (21)$$

$$C^* = [540(3\pi^2)^{2/3}m^*(n_0^*)^{5/3}]^{-1} \times [1 + 17\pi^2/24(\beta^*\mu_0^*)^2], \quad (22)$$

$$D^* = -[480(3\pi^2)^{2/3}m^*(n_0^*)^{8/3}]^{-1} \times [1 + 413\pi^2/324(\beta^*\mu_0^*)^2], \quad (23)$$

and

$$E^* = [1620(3\pi^2)^{2/3}m^*(n_0^*)^{11/3}]^{-1} \times [1 + 5\pi^2/3(\beta^*\mu_0^*)^2]. \quad (24)$$

Note that the Kirzhnits-Hodges values of the gradient coefficients for the ground-state kinetic energy are correctly reproduced as the $T \rightarrow 0$ limits of the above Eqs. (21)–(24).^{14,15} The corresponding limiting values of these coefficients in the high-temperature limit are

$$B^* = (24m^*n_0^*)^{-1}, \quad (25)$$

$$C^* = \beta^* [720(m^*)^2 n_0^*]^{-1}, \quad (26)$$

$$D^* = -\beta^* [1440(m^*)^2 (n_0^*)^2]^{-1}, \quad (27)$$

and

$$E^* = \pi^{3/2} (\beta^*)^{5/2} [5760(m^*)^{7/2} (n_0^*)^2]^{-1}. \quad (28)$$

The above limiting values provide useful checks on numerical work.

For convenient presentation of numerical results, it is useful to observe that although the quantities B^* , C^* , D^* , and E^* are functions of both temperature and density, the ratios $\tilde{B} = B^*/B^*(T=0)$, $\tilde{C} = C^*/C^*(T=0)$, $\tilde{D} = D^*/D^*(T=0)$, and $\tilde{E} = E^*/E^*(T=0)$ can all be expressed as functions of a single reduced variable y given by

$$I_{1/2}(\eta) = \pi^2 (m^*)^{-3/2} n_0^* (\beta^*)^{3/2} 2^{-1/2} \equiv y. \quad (29)$$

That is, elimination of η between Eqs. (29) and (15)–(18) determines all coefficients relative to their zero-temperature forms. Note that the classical limit ($\eta \rightarrow -\infty$) corresponds to $y \rightarrow 0$ and the quantum limit ($\eta \rightarrow \infty$) corresponds to $y \rightarrow \infty$.

In terms of this reduced variable y , the coefficients in the weakly degenerate limit are given by

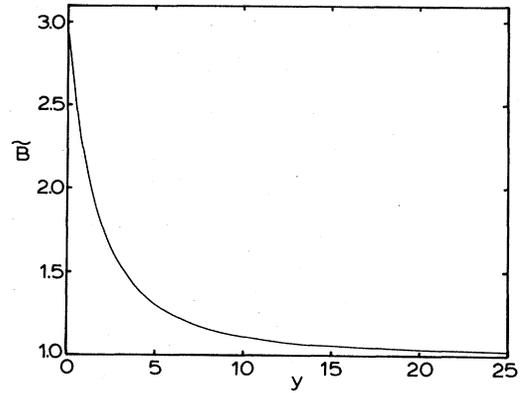


FIG. 1. Normalized second-order gradient coefficient $\tilde{B}(y)$ as a function of y as described in Sec. III.

$$\tilde{B}(y) = 3(1 - y/\sqrt{2\pi} + \dots), \quad (30)$$

$$\tilde{C}(y) = \frac{3}{4}(3\sqrt{2})^{2/3} y^{2/3} + \dots, \quad (31)$$

$$\tilde{D}(y) = \frac{1}{3}(3\sqrt{2})^{2/3} y^{2/3} + \dots, \quad (32)$$

and

$$\tilde{E}(y) = \frac{9}{16}(3\sqrt{2})^{2/3} (2\pi)^{-1/2} y^{5/3} + \dots, \quad (33)$$

while results for these coefficients in the strongly degenerate limit are given by omitting the prefactors (which give the $T=0$ normalizations) in Eqs. (21)–(24) and making the replacement $\beta^*\mu_0^* = (3y/2)^{2/3}$. These limiting values of the reduced coefficients are also useful for checking of numerical results.

We have plotted $\tilde{B}(y)$ in Fig. 1 as a function of y . Although we have not indicated the values given by Perrot's approximate analytical fit to his data (see the second equation of Appendix B in Ref. 24: note that the coefficient of u^{-12} is missing a factor of 10^3), the agreement

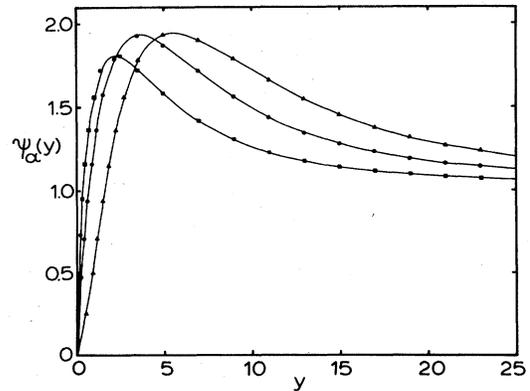


FIG. 2. Normalized fourth-order gradient coefficients $\psi_\alpha(y)$ as a function of y as described in Sec. III. $\tilde{C}(y)$, $\tilde{D}(y)$, and $\tilde{E}(y)$ correspond to $\alpha=1$ (squares), 2 (circles), and 3 (triangles), respectively.

TABLE I. Correspondence between long-wavelength terms of the gradient expansion and their corresponding forms in configuration space. See Appendix B.

i	Φ_i	I_i
1	1	$\int d^3r[\tilde{n}(\mathbf{r})]^\alpha$
2	\mathbf{q}_1^2	$3 \int d^3r[\tilde{n}(\mathbf{r})]^{\alpha-2}[\nabla\tilde{n}(\mathbf{r})]^2$
3	$\mathbf{q}_1 \cdot \mathbf{q}_2$	$-I_2/3$
4	$\mathbf{q}_1^2 \mathbf{q}_2^2$	$\int d^3r[\tilde{n}(\mathbf{r})]^{\alpha-2}[\nabla^2\tilde{n}(\mathbf{r})]^2$
5	$\mathbf{q}_1^2(\mathbf{q}_2 \cdot \mathbf{q}_3)$	$\int d^3r[\tilde{n}(\mathbf{r})]^{\alpha-3}[\nabla^2\tilde{n}(\mathbf{r})][\nabla\tilde{n}(\mathbf{r})]^2$
6	\mathbf{q}_1^4	$3I_4 + 6I_5$
7	$\mathbf{q}_1^2(\mathbf{q}_1 \cdot \mathbf{q}_2)$	$-I_4 - 2I_5$
8	$(\mathbf{q}_1 \cdot \mathbf{q}_2)(\mathbf{q}_1 \cdot \mathbf{q}_3)$	$-\{I_5 + \int d^3r[\tilde{n}(\mathbf{r})]^{\alpha-4}[\nabla\tilde{n}(\mathbf{r})]^4\}/2$
9	$(\mathbf{q}_1 \cdot \mathbf{q}_2)^2$	$I_4 + 3I_5 + \int d^3r[\tilde{n}(\mathbf{r})]^{\alpha-4}[\nabla\tilde{n}(\mathbf{r})]^4$

between the two calculations is excellent. (However, note that Fig. 1 of Ref. 24 appears to be different from our Fig. 1.) Finally, our numerical results for $\tilde{C}(y)$, $\tilde{D}(y)$, and $\tilde{E}(y)$ are plotted in Fig. 2 as a function of y . For applications it is useful to have simple analytical representations of these normalized gradient coefficients. These are given in Appendix C.

IV. SUMMARY AND DISCUSSION

The Kirzhnits-Hodges^{14,15} calculation of the gradient expansion for the ground-state kinetic energy of a many-electron system has been generalized to the kinetic free energy at finite temperature. The density and temperature dependence of the resulting gradient-expansion coefficients, through fourth order, has been determined. The second-order coefficient agrees with the work of Perrot²⁴ and Brack,^{25,26} while our results for the third- and fourth-order gradient coefficients, which are required in many applications, are new. Numerical results are conveniently expressed as ratios of dimensionless forms (see Figs. 1 and 2) of a single dimensionless variable $y = I_{1/2}(\eta)$ for the full range of parameters from the extreme quantum limit to the classical limit.

Our derivation is based on a perturbation expansion,

TABLE II. Coefficients in polynomial fits to \tilde{B} , $L=1$.

k	$f_k^{(1)}$	$g_k^{(1)}$
1	1.377 014 990 521	2.989 610 661 57
2	-0.597 830 142 115 8	-1.100 736 924 804
3	0.409 039 674 1	0.370 362 490 267 7
4	-0.254 345 028 296 6	-0.804 944 000 891 2
5	0.149 264 271 152 7	0.011 224 085 473 65
6	-0.084 006 731 008 36	-0.001 001 521 905 861
7	0.046 612 624 721 19	0.000 056 589 648 206 29
8	-0.025 740 157 575 1	-0.000 001 952 787 048 821
9	0.013 848 461 132 5	$3.748 250 926 887 \times 10^{-8}$
10	-0.008 847 166 979 988	$-3.063 051 975 404 \times 10^{-10}$

TABLE III. Coefficients in polynomial fits to \tilde{C} , $L=2$.

k	$f_k^{(2)}$	$g_k^{(2)}$
1	1.216 184 735 933	0.086 577 453 348 53
2	-0.142 076 565 889 6	3.589 838 044 117
3	-0.114 374 453 830 9	-4.432 563 748 938
4	0.228 998 646 866 9	4.113 082 159 42
5	-0.235 112 179 912 7	-2.753 803 521 821
6	0.191 564 636 661 9	1.299 045 800 856
7	-0.139 244 249 037	-0.438 845 675 233 8
8	0.094 591 117 826 34	0.108 811 033 939 6
9	-0.062 342 127 825 19	-0.020 236 407 952 15
10	0.040 272 499 403 08	0.002 869 825 583 346
11	-0.026 662 787 681 7	-0.000 313 843 483 309
12	0.017 443 766 868 93	0.000 026 632 085 756 04
13	-0.012 468 047 497 73	-0.000 001 755 774 312 411
14	0.008 696 315 401 424	$8.955 589 538 879 \times 10^{-8}$
15	-0.007 145 677 149 003	$-3.496 498 321 287 \times 10^{-9}$
16	0.005 333 123 417 838	$1.024 642 717 325 \times 10^{-10}$
17	-0.004 361 494 971 388	$-2.179 839 165 022 \times 10^{-12}$
18	0.003 817 140 705 672	$3.176 919 706 681 \times 10^{-14}$
19	-0.002 400 734 847 834	$-2.835 832 367 703 \times 10^{-16}$
20	0.003 044 589 976 579	$1.168 814 995 943 \times 10^{-18}$

about a uniform electron gas, in powers of the density inhomogeneity ($|\tilde{n}(\mathbf{r})|/n_0 \ll 1$) and on the assumption that only long-wavelength components of the (slowly varying) density are significant. The form of Eq. (8) is consistent with, and suggests the hypothesis of, a partial resummation of higher-order terms in the $\tilde{n}(\mathbf{r})$ expansion which leads to Eq. (14) in which all functions are to be evaluated at the local density $n_0 + \tilde{n}(\mathbf{r}) = n(\mathbf{r})$ and there is no longer explicit reference to n_0 . Note that this partially resummed form of a local-density approximation plus gradient corrections is precisely what would have resulted had we done this calculation using the Kirzhnits¹⁴ method. Calculations of gradient coefficients by means of the Wigner-Kirkwood partition function and its semiclassical expansion also yield the "resummed" form, Eq. (14), directly whether at $T=0$ or at finite temperature.⁶ The present results show that there is no fundamental difference between any of these methods, within their domain of validity.

Finally, as indicated in the Introduction, work is

TABLE IV. Coefficients in polynomial fits to \tilde{D} , $L=3$.

k	$f_k^{(3)}$	$g_k^{(3)}$
1	1.279 905 380 539	0.038 333 363 040 31
2	-0.056 553 182 117 31	1.595 987 411 028
3	-0.293 332 593 736 5	-0.517 979 236 153 1
4	0.363 295 689 519 9	0.086 447 816 970 45
5	-0.282 834 868 478 4	-0.008 594 473 401 309
6	0.175 536 801 221 2	0.000 525 264 350 052 7
7	-0.092 705 985 751 67	-0.000 019 305 382 627 02
8	0.041 500 712 596 4	$3.908 463 846 586 \times 10^{-8}$
9	-0.015 473 013 091 52	$-3.345 325 284 891 \times 10^{-9}$

currently in progress to extend the calculations of the lowest-order exchange and correlation ground-state-energy gradient corrections so as to obtain a representation of $F_{xc}[n]$ of Eq. (1) at finite temperature in the form of a local-density approximation plus second-order gradient expansions. We plan to report these results as well as applications in the near future.

Note added. In a recent as yet unpublished manuscript, Bartel, Brack, and Durand³⁷ report that they have also evaluated the temperature-dependent fourth-order gradient coefficients. We have verified that their results, which were obtained by a different method, agree with ours. The work of Bartel *et al.*³⁷ also contains interesting discussions of applications to inhomogeneous nuclear matter.

APPENDIX A

The coefficients $C^{(\alpha)}$ entering Eq. (3) are essentially the various response functions of a noninteracting gas of fermions of uniform density n_0 and temperature T and have the general structure

$$\begin{aligned} \Pi_0^{(\alpha)}(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_{\alpha-1}) \\ = -\frac{2}{\beta v} \sum_n \sum_k g_k(i\omega_n) g_{\mathbf{k}+\mathbf{q}}(i\omega_n) \cdots g_{\mathbf{k}+\mathbf{q}_{\alpha-1}}(i\omega_n), \end{aligned} \quad (\text{A1})$$

where $\omega_n = (2n+1)\pi/\beta$ are Matsubara energies,

$$g_{\mathbf{k}}(i\omega_n) = (i\omega_n + \mu - \epsilon_{\mathbf{k}})^{-1}$$

$$\begin{aligned} \Pi^{(3)}(\mathbf{q}_1, \mathbf{q}_2) = -\frac{2}{v} \sum_{\mathbf{k}} \left[\frac{f(\epsilon_{\mathbf{k}} - \mu)}{(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}_1})(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}_2})} + \frac{f(\epsilon_{\mathbf{k}+\mathbf{q}_1} - \mu)}{(\epsilon_{\mathbf{k}+\mathbf{q}_1} - \epsilon_{\mathbf{k}})(\epsilon_{\mathbf{k}+\mathbf{q}_1} - \epsilon_{\mathbf{k}+\mathbf{q}_2})} \right. \\ \left. + \frac{f(\epsilon_{\mathbf{k}+\mathbf{q}_2} - \mu)}{(\epsilon_{\mathbf{k}+\mathbf{q}_2} - \epsilon_{\mathbf{k}})(\epsilon_{\mathbf{k}+\mathbf{q}_2} - \epsilon_{\mathbf{k}+\mathbf{q}_1})} \right] \end{aligned} \quad (\text{A3})$$

and

$$\begin{aligned} \Pi^{(4)}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3) = -\frac{2}{v} \sum_{\mathbf{k}} \frac{f(\epsilon_{\mathbf{k}} - \mu)}{(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}_1})(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}_2})(\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}_3})} + \frac{f(\epsilon_{\mathbf{k}+\mathbf{q}_1} - \mu)}{(\epsilon_{\mathbf{k}+\mathbf{q}_1} - \epsilon_{\mathbf{k}})(\epsilon_{\mathbf{k}+\mathbf{q}_1} - \epsilon_{\mathbf{k}+\mathbf{q}_2})(\epsilon_{\mathbf{k}+\mathbf{q}_1} - \epsilon_{\mathbf{k}+\mathbf{q}_3})} \\ + \frac{f(\epsilon_{\mathbf{k}+\mathbf{q}_2} - \mu)}{(\epsilon_{\mathbf{k}+\mathbf{q}_2} - \epsilon_{\mathbf{k}})(\epsilon_{\mathbf{k}+\mathbf{q}_2} - \epsilon_{\mathbf{k}+\mathbf{q}_1})(\epsilon_{\mathbf{k}+\mathbf{q}_2} - \epsilon_{\mathbf{k}+\mathbf{q}_3})} + \frac{f(\epsilon_{\mathbf{k}+\mathbf{q}_3} - \mu)}{(\epsilon_{\mathbf{k}+\mathbf{q}_3} - \epsilon_{\mathbf{k}})(\epsilon_{\mathbf{k}+\mathbf{q}_3} - \epsilon_{\mathbf{k}+\mathbf{q}_1})(\epsilon_{\mathbf{k}+\mathbf{q}_3} - \epsilon_{\mathbf{k}+\mathbf{q}_2})}, \end{aligned} \quad (\text{A4})$$

and the nonlinear-response functions of higher order are not required. Various transformations of these sums can be carried out to facilitate long-wavelength expansions or other objectives. These response functions also enter the perturbation expansion of $\tilde{n}(\mathbf{q})$ in powers of V and the relevant inversion which expresses $V(\mathbf{q})$ in powers of \tilde{n} . Keeping track of these expansions as well as that for the chemical potential in the presence of the external potential yields Eqs. (5)–(7) of the text.

APPENDIX B

In order to convert Eqs. (5), (6), and (7) to gradient expansions in configuration space, we first require the long-wavelength expansions of the response functions in Appendix A. The expansions of Eqs. (A2)–(A4) for small \mathbf{q}_α are obtained in a straightforward way and the particular combinations of long-wavelength response functions required in the text can be generated. Their forms are

TABLE V. Coefficients in polynomial fits to \tilde{E} , $L=4$.

k	$f_k^{(4)}$	$g_k^{(4)}$
1	1.275 554 253 356	−0.000 516 712 415 289
2	0.174 347 887 805 1	0.051 513 169 320 95
3	−0.514 780 082 319 1	0.860 497 975 362 5
4	0.431 767 201 479 3	−0.503 773 796 106 5
5	−0.226 934 917 933	0.151 429 450 375 5
6	0.071 366 892 030 07	−0.029 123 139 213 45
7	0.007 763 819 853 599	0.003 845 219 639 374
8	−0.034 513 441 614 98	0.000 358 661 214 284 2
9	0.035 712 355 785 06	0.000 023 840 118 954 43
10	−0.027 659 202 946 07	−0.000 001 121 998 780 923
11	0.018 510 242 584 87	3.651 242 790 938 $\times 10^{-8}$
12	−0.010 888 174 830 25	−7.810 790 733 214 $\times 10^{-10}$
13	0.005 594 395 462 207	9.878 131 545 68 $\times 10^{-12}$
14	−0.002 484 382 717 864	−5.594 332 541 208 $\times 10^{-14}$

are the usual propagators for free particles, $\epsilon_{\mathbf{k}} = \hbar^2 k^2 / 2m$, and v denotes the volume. The Matsubara sum is easily performed.

$$\Pi_0^{(1)} = n_0$$

with the appropriate limiting procedure and

$$\Pi^{(2)}(\mathbf{q}) = -\frac{2}{v} \sum_{\mathbf{k}} \frac{f(\epsilon_{\mathbf{k}} - \mu) - f(\epsilon_{\mathbf{k}+\mathbf{q}} - \mu)}{\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}}} \quad (\text{A2})$$

is the Lindhard function or linear-response function. The higher-order terms correspond to nonlinear-response functions. These are given by

$$F_k^{(2)}[\tilde{n}] = \frac{1}{v} \sum'_{\mathbf{q}} \tilde{n}(\mathbf{q})\tilde{n}(-\mathbf{q})(a_1 + a_2 q^2 + a_3 q^4 + \dots) \quad (\text{B1})$$

and

$$F_k^{(3)}[\tilde{n}] = \frac{1}{v^2} \sum'_{\mathbf{q}_1, \mathbf{q}_2} \tilde{n}(\mathbf{q}_1)\tilde{n}(\mathbf{q}_2)\tilde{n}(-\mathbf{q}_1 - \mathbf{q}_2)[b_1 + b_2(\mathbf{q}_1^2 + \mathbf{q}_2^2) + b_3(\mathbf{q}_1 \cdot \mathbf{q}_2) + b_4(\mathbf{q}_1^4 + \mathbf{q}_2^4) + b_5(\mathbf{q}_1^2 \mathbf{q}_2^2) + b_6(\mathbf{q}_1^2 + \mathbf{q}_2^2)(\mathbf{q}_1 \cdot \mathbf{q}_2) + b_7(\mathbf{q}_1 \cdot \mathbf{q}_2)^2 + \dots] \quad (\text{B2})$$

and

$$F_k^{(4)}[\tilde{n}] = \frac{1}{v^3} \sum'_{\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3} \tilde{n}(\mathbf{q}_1)\tilde{n}(\mathbf{q}_2)\tilde{n}(\mathbf{q}_3)\tilde{n}(-\mathbf{q}_1 - \mathbf{q}_2 - \mathbf{q}_3) \times \{C_1 + C_2(\mathbf{q}_1^2 + \mathbf{q}_2^2 + \mathbf{q}_3^2) + C_3(\mathbf{q}_1 \cdot \mathbf{q}_2 + \mathbf{q}_1 \cdot \mathbf{q}_3 + \mathbf{q}_2 \cdot \mathbf{q}_3) + C_4(\mathbf{q}_1^4 + \mathbf{q}_2^4 + \mathbf{q}_3^4) + C_5(\mathbf{q}_1^2 \mathbf{q}_2^2 + \text{permutations}) + C_6[(\mathbf{q}_1^2(\mathbf{q}_2 \cdot \mathbf{q}_3) + \text{permutations})] + C_7[(\mathbf{q}_1^2 + \mathbf{q}_2^2)(\mathbf{q}_1 \cdot \mathbf{q}_2) + \text{permutations}] + C_8[(\mathbf{q}_1 \cdot \mathbf{q}_2)^2 + (\mathbf{q}_1 \cdot \mathbf{q}_2)(\mathbf{q}_1 \cdot \mathbf{q}_3) + \text{permutations}]\} . \quad (\text{B3})$$

The primes on the summations indicate, as in the text, that $\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3, \mathbf{q}_1 + \mathbf{q}_2$, and $\mathbf{q}_1 + \mathbf{q}_3 + \mathbf{q}_3$ are not zero.

The various coefficients a_i, b_i , and c_i are all known from the corresponding expansions of the response functions and are explicitly density, temperature, and mass dependent. The above are converted into configuration space by inverse Fourier transformation of $\tilde{n}(\mathbf{q}_\alpha)$. The general structure is

$$I_i = \frac{1}{v^{\alpha-1}} \sum'_{\mathbf{q}_1, \dots, \mathbf{q}_{\alpha-1}} \tilde{n}(\mathbf{q}_1) \cdots \tilde{n}(\mathbf{q}_{\alpha-1}) \times \tilde{n}(-\mathbf{q}_1 - \cdots - \mathbf{q}_{\alpha-1}) \times \Phi_i(\mathbf{q}_1, \dots, \mathbf{q}_{\alpha-1}),$$

and a list of (I_i, Φ_i) pairs is given in Table I. Note that the various functions in this table can be symmetrized as required.

APPENDIX C

For convenience in applications we give approximate analytical representations of the normalized gradient coefficients $\tilde{B}(y), \tilde{C}(y), \tilde{D}(y)$, and $\tilde{E}(y)$ introduced in Sec. III. These coefficients are computed for a discrete set of points $\{y_i: i=1, \dots, n\}$. Denote by $\{G^{[L]}(y_i): i=1, \dots, n\}$ the corresponding sets of values for the gra-

dent coefficients where $L=1, 2, 3$, and 4 for $\tilde{B}, \tilde{C}, \tilde{D}$, and \tilde{E} , respectively. A polynomial least-squares fit is made to the given discrete data sets for y in the range $0.02=y_L \leq y \leq y_R=25$. The best-fitting polynomial $P_N^{[L]}(y)$ is computed in terms of Chebyshev polynomials on the basis of the requirement

$$\sum_{i=1}^n [G^{[L]}(y_i) - P_N^{[L]}(y_i)]^2 < \eta \sum_{i=1}^n [G^{[L]}(y_i)]^2, \quad (\text{C1})$$

where $\eta=10^{-5}$ was chosen to set the error limits on the fits. The resulting $P_N^{[L]}(y)$ can be expressed either in terms of the Chebyshev polynomials

$$P_N^{[L]}(y) = \sum_{k=1}^N \not\ell_k^{[L]} T_{k-1}(t(y)) \quad (\text{C2})$$

or as the rearranged polynomial

$$P_N^{[L]}(y) = \sum_{k=1}^N g_k^{[L]} y^{k-1}. \quad (\text{C3})$$

In Eq. (C2), $T_l(t)$ is a Chebyshev polynomial of degree l and $t(y)=ay+b$ lies in the interval $-1 \leq t \leq 1$ due to $a=2/(y_R-y_L)$ and $b=-(y_R+y_L)/(y_R-y_L)$. The coefficients $\not\ell_k^{[L]}$ and $g_k^{[L]}$ are given in Tables II–V. Results for $\tilde{B}(y), \tilde{C}(y), \tilde{D}(y)$, and $\tilde{E}(y)$ for values of y outside the range $y_L \leq y \leq y_R$ are conveniently obtained using the series expansions given in Sec. III.

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