FINITE-TEMPERATURE DENSITY-GRADIENT THEORY

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Abstract

The density-functional theory derivation of density-gradient corrections to the description of an inhomogeneous electron gas (extended Thomas-Fermi theory) at finite-temperatures is reviewed. Analytical partial summations of the full density-gradient expansion are then discussed with the aim of explaining how first-order density gradient theory can be extended to include higher-order gradient effects (including possibly interference). The ultimate goal is to develop improved engineering-oriented tools for the analysis of quantum transport phenomena in semiconductor devices.

1. Introduction

One early and well-known effort to improve on the understanding of the inhomogeneous electron gas provided by the Thomas-Fermi theory was via density-gradient corrections [1]. In succeeding years this approach received much attention both in the form of improved derivations [2-5] and in applications [6,7]. However, following the development of the Kohn-Sham equations [8] which allow direct inclusion of gradient effects to all orders, the density-gradient approaches lost favor. Only in the area of non-equilibrium problems where simplicity is at a premium have density-gradient approaches continued to be employed [9]. One example in a semiconductor context is the work of the present author in which a density-gradient theory with a more macroscopic flavor has been developed and explored [10]. This theory was shown to be useful in analyzing quantum confinement situations in heterostructures [11] and tunneling effects both in semiconductors [12] and metals [13]. Significantly, in many of these applications the first-order density-gradient approach can be made quantitatively accurate in regimes well beyond that in which it is strictly valid. In this paper, we provide partial justification for this empirical observation by partial summing the full gradient expansion and re-expressing the result as an effective density-gradient theory.

2. Density-Gradient Corrections to Semi-Classical Transport Theory

Apart from effects of Fermi-Dirac statistics, the lowest-order corrections to semi-classical electron transport theory arising from quantum mechanics may be expressed as density-gradient corrections to the equation of state of the electron gas. A transport theory containing these corrections may be deduced microscopically, e.g., via density-functional theory [3] or from the Wigner transport equation [14], or macroscopically using methods of classical field theory [10]. Which approach is to be preferred, of course, depends on motivation. For this paper, we wish to discuss the higher-order gradient effects engendered by quantum mechanics, a topic much more easily approached microscopically.

In generalization of the zero-temperature density-functional theory of Hohenberg and Kohn [3], Mermin [15] proved that at finite-temperatures there exists a functional of the density n(**r**), namely g[n(**r**)], which is independent of the potential v(**r**) and for which

$$\Omega[n(\mathbf{r})] = \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + \frac{e^2}{2}\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' + \int g[n(\mathbf{r})]d\mathbf{r}\,, \qquad (2.1)$$

is a minimum when n(**r**) is the equilibrium density. At this minimum, Ω is the grand potential of the system, the first integral is the potential energy associated with v(**r**), the second is the Coulomb energy and the g[n] term groups kinetic energy and exchange and correlation contributions. Now, if an electron gas is slowly-varying in density, g[n] may be given a gradient expansion [3]

$$g[n] = g_o(n) + g_2^{(2)}(n)\nabla n\cdot\nabla n + [g_4^{(2)}(n)\nabla^2 n\nabla^2 n + g_4^{(3)}(n)\nabla^2 n(\nabla n\cdot\nabla n) + g_4^{(4)}(n)(\nabla n\cdot\nabla n)^2] + \ldots . \quad (2.2)$$

Inserting this into (2.1), with the constraint that the average density is n_o, we find

$$v(\mathbf{r}) - \mu + e^2\int \frac{n(\mathbf{r})d\mathbf{r}}{|\mathbf{r} - \mathbf{r}'|} + g_o' - g_2^{(2)\prime}(\nabla n)^2 - 2g_2^{(2)}\nabla^2 n + \ldots = 0 \quad , \quad (2.3)$$

where μ is a Lagrange multiplier (chemical potential). In the limit of almost constant density, (2.3) yields an expression for the polarizability [3] which may be further specified in the random phase approximation for which the susceptibility is given by the Lindhard result [16]. When T=0, one finds [3] the density-gradient correction of Ref. 1 directly. At finite temperatures no closed-form expressions are possible, however, by expanding the susceptibility for small q, equations for the gradient coefficients in (2.3) can be obtained [13] as follows [the F_m are Fermi-Dirac integrals]

$$g_o'' = \frac{4}{\beta e^2}\left(\frac{\beta p h^2}{2m}\right)^{3/2}\left[F_{1/2}'\right]^{-1} , \quad g_2^{(2)} = \frac{h^2}{4me^2}\left(\frac{\beta p h^2}{2m}\right)^{3/2}\left(F_{1/2}'\right)^{-2}\left[F_{1/2}'' - \frac{2}{9}F_{3/2}'''\right] . \quad (2.4)$$

Now in previous work [10], using methods of classical field theory we deduced the general equation obeyed by *any* gas whose internal energy depends only on the density of the gas and on the gradient of that density. In lowest-order linear form, the density-gradient effect was gauged by a coefficient b and it is not surprising that the general equation is identical to (2.3). The foregoing

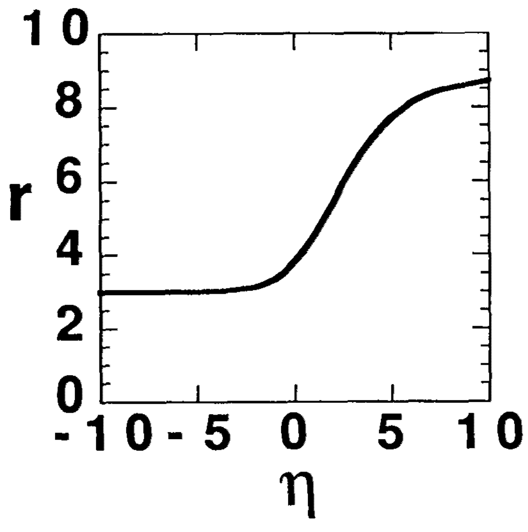

Fig. 1. DG parameter r versus normalized chemical potential.

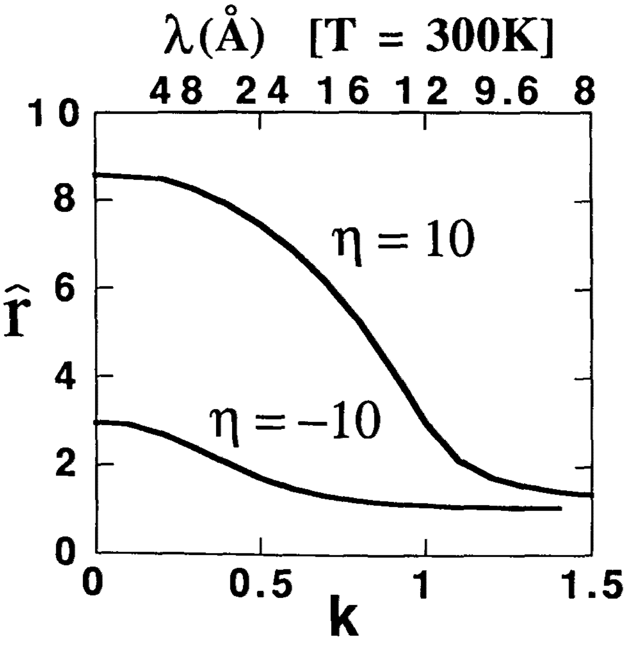

Fig. 2. Effective DG parameter r̂ versus normalized wavenumber and wavelength.

thus represents a microscopic derivation of b with the specific relation being $b=2n_o g_2^{(2)}=h^2/4mer$ where the second equality defines a numerical factor r. The numerical result for r as given by (2.4) (random-phase approximation) is plotted as a function of η (=μ/kT) in Fig. 1. Readily apparent in the Figure are the high temperature limit (η<<1) with r=3 [5,14], the low temperature limit (η>>1) with r approaching 9 [1] and a smooth transistion between these limits.

3. Partial Summation of the Density-Gradient Expansion

An electron transport theory in which the lowest-order effects of quantum mechanics are incorporated through a density-gradient term is useful for non-equilibrium calculations of scattering [9] and for understanding transport phenomena in semiconductors [10-12] and even in metals [13]. The density-gradient approach allows one to analyze "real" transport problems (i.e., ones with electromagnetic, geometric and/or other complications) in which tunneling and/or confinement effects are important. It cannot, however, describe interference effects as noted long ago [3]. In this Section, we outline an approach based on a partial summation of gradient terms (again following Ref. 3) which improves the description and which could, in principle, supply interference corrections. In this paper, however, we do not examine the latter issue; instead we use the summed theory merely to provide justification for using ordinary density-gradient theory with b treated as a phenomenological parameter. As previously noted, such an approach was followed in Refs. 11 and 13 and much improved agreements with quantum mechanical results were obtained in regimes in which higher-order gradients were undoubtedly non-negligible.

A partial summation of the gradient expansion in (2.2) valid when the density is almost constant hinges on the fact that the integral [3]

$$-\frac{1}{2}\int K(\mathbf{r}')\left[n(\mathbf{r}+\tfrac{1}{2}\mathbf{r}') - n(\mathbf{r}-\tfrac{1}{2}\mathbf{r}')\right]^2 d\mathbf{r}' \quad \text{with} \quad K(\mathbf{r}) = -\frac{e^2}{2V}\sum_{\mathbf{q}}\frac{1}{\chi(\mathbf{q})}e^{-i\mathbf{q}\cdot\mathbf{r}} \ , \quad (3.1)$$

represents a summation of the $g_i^{(2)}$ terms in (2.2) as is readily shown [3]. Using (3.1), (2.1) leads to a new governing equation, analogous to (2.3), of the form [3,15]

$$v(\mathbf{r}) - \mu + e^2\int\frac{n(\mathbf{r})d\mathbf{r}}{|\mathbf{r}-\mathbf{r}'|} + g_o' - \frac{1}{2}\int\left[n(\mathbf{r}+\tfrac{1}{2}\mathbf{r}') - n(\mathbf{r}-\tfrac{1}{2}\mathbf{r}')\right]^2\frac{\delta K(\mathbf{r}')}{\delta n}d\mathbf{r}' - 2\int K(\mathbf{r}-\mathbf{r}')[n(\mathbf{r})-n(\mathbf{r}')]d\mathbf{r}' \ . \quad (3.2)$$

As noted, in principle, (3.2) should describe interference phenomena [3]. Now, to explore the extent to which higher-order gradient effects can be subsumed in ordinary density-gradient theory by taking b to be a phenomenological parameter, we define an effective b according to

$$\hat{b}(\mathbf{r}) \equiv -\frac{1}{2}\left(\frac{s}{\nabla^2 s}\right)\left\{\frac{1}{2}\int\left[n(\mathbf{r}+\tfrac{1}{2}\mathbf{r}')-n(\mathbf{r}-\tfrac{1}{2}\mathbf{r}')\right]^2\frac{dK(\mathbf{r}-\mathbf{r}')}{dn}d\mathbf{r}'+2\int K(\mathbf{r}-\mathbf{r}')[n(\mathbf{r})-n(\mathbf{r}')]d\mathbf{r}'\right\}, \quad (3.3)$$

where $s \equiv \sqrt{n}$. With (3.3), (3.2) takes the *form* of the density-gradient equation (2.3). Assuming almost-constant density together with (3.1), (3.3) can be re-written as

$$\hat{b}(\mathbf{r}) = -\frac{n_o}{\nabla^2\tilde{n}}\int\tilde{N}(\mathbf{p})\left[\frac{1}{\chi(0)}-\frac{1}{\chi(\mathbf{p})}\right]e^{i\mathbf{p}\cdot\mathbf{r}}d\mathbf{p} = \frac{1}{\nabla^2\tilde{n}}\int\tilde{N}(\mathbf{p})p^2\hat{b}_i(\mathbf{p})\,e^{i\mathbf{p}\cdot\mathbf{r}}\,d\mathbf{p} \ , \quad (3.4)$$

where $\tilde{N}(\mathbf{p})$ is the Fourier transform of the density-deviation $\tilde{n}(\mathbf{r})$, and $\hat{b}_i(\mathbf{p})$ is the "impulse" response of the almost-constant density gas. A plot of this impulse response, written as an equivalent $\hat{r}$, appears in Fig. 2 as a function of p in both the high ($\eta = -10$) and low ($\eta = 10$) temperature limits. On the top axis of the plot are given the wavelengths corresponding to p assuming T=300K. For small p, ordinary density-gradient theory is recovered with, as before, $\hat{r}\approx 3$ (high-temperature) or $\hat{r}\approx 9$ (low-temperature). Fig. 2 further shows that for density disturbances on scales larger than O(50Å), standard density gradient theory is appropriate (at 300K) in accord with Ref. 11. In addition, Fig. 2 demonstrates that as the wavelength of the disturbance decreases the value of $\hat{r}$ also decreases as a consequence of the increasing importance of the higher-order gradients. This qualitative behavior is identical to that reported previously in

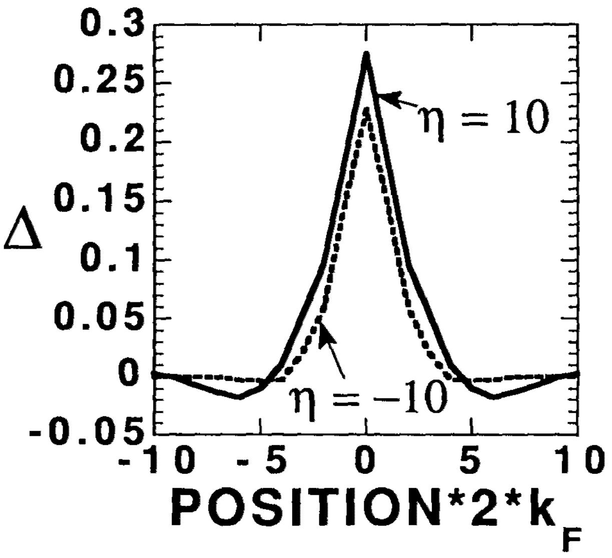

Fig. 3. Quantum response function Δ versus normalized position.

Refs. 11 and 13. Quantitatively, of course, the relation between Fig. 2 and the earlier work is less certain because, for real problems such as those of Refs. 11 and 13, the electron gas is *not* typically of almost constant density. Furthermore, for many cases [13] the electron density n_o is sufficiently large that exchange and correlation effects cannot be neglected. Nevertheless, we conclude that the results of Fig. 2 suggest a solid basis for our earlier phenomenological approach. Finally, for very rapid disturbances (large p), $\hat{r}$ decreases still further approaching the result of Ref. 4 (r=1) at any temperature. In this regime, the space scales are such that quantum statistical effects are insignificant. One final point related to (3.4) is of interest. Inserting (3.4) into (3.2) and switching to the spatial domain we can readily obtain

$$v(\mathbf{r}) - \mu + e^2 \int \frac{n(\mathbf{r})d\mathbf{r}}{|\mathbf{r} - \mathbf{r}'|} + g_o' + \frac{h^2}{4emn}\nabla^2\left[n(\mathbf{r}) - \int n(\mathbf{r}-\lambda)\Delta(\lambda)\, d\lambda\right] = 0, \qquad (3.5)$$

The quantity $\Delta(\lambda)$ is a new "impulse" response function which has resulted from separating out the "quantum potential" and thus characterizes the deviation from ideal pure-state behavior. In Fig. 3 we plot $\Delta(\lambda)$ as a function of position (normalized by $2{*}k_F$; at 300K, one unit equals 1.37Å; at 4.2K, one unit equals 11.6Å) for the cases of Fig. 2. The results for these two cases are in good agreement with one another suggesting that Δ is largely independent of η in the case of almost constant density. The fact that this function is nearly a delta-function in space is the "reason" that, for long wavelengths, first-order density-gradient theory is appropriate at all temperatures. Finally, we remark that the most general linear version of macroscopic theory of Ref. 10 takes precisely the same form as (3.5). It is thus conceivable that a theory of this form might also be adequate for real device situations well outside the realm of almost constant densities.

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References:

1. C. v. Weizsacker, Z. Phys. *96*, 431 (1935).
2. A.S. Kompaneets and E.S. Pavlovskii, Sov. Phys.-JETP *4*, 328 (1957).
3. P. Hohenberg and W. Kohn, Phys. Rev. *136*, 864 (1964);
4. W. Jones, Phys. Lett *34A*, 351 (1971).
5. F. Perrot, Phys. Rev. *A20*, 586 (1979).
6. J. Bardeen, Phys. Rev. *49*, 653 (1936); R. Smoluchowski, Phys. Rev. *60*, 661 (1941).
7. J.R. Smith, Phys. Rev. *181*, 522 (1969); J. Rudnick, Phys. Rev. *B5*, 2863 (1972).
8. W. Kohn and L. Sham, Phys. Rev. *A40*, 1133 (1965); E. Runge et al, PRL *52*, 997 (1984).
9. D.M. Deb, P.K. Chattaraj and S. Mishra, Phys. Rev. *A43*, 1248 (1991).
10. M.G. Ancona and H.F. Tiersten, Phys. Rev. *B35-II*, 7959 (1987).
11. M.G. Ancona, Superlatt. Microstruct. *7*, 119 (1990).
12. M.G. Ancona, Phys. Rev. *B42*, 1222 (1990).
13. M.G. Ancona, accepted for publication, Phys. Rev *B* (1992).
14. M.G. Ancona and G.J. Iafrate, Phys. Rev. *B39*, 9536 (1989).
15. N.D. Mermin, Phys. Rev. *137*, A1441 (1965).
16. J. Lindhard, Kgl. Danske Videnskab. Selskab Mat.-Fys. Medd. *28* (1954).