

phys. stat. sol. (b) **102**, 283 (1980)

Subject classification: 13; 21

*Department of Physics, Tulane University, New Orleans¹⁾**and Solid State Science Division, Argonne National Laboratory, Argonne²⁾ (a)**and Department of Physics and Astronomy, University of North Carolina, Chapel Hill³⁾ (b)*

Charge and Spin Density Waves in Jellium

By

J. P. PERDEW (a) and T. DATTA (b)

Is the uniform electron gas unstable against charge and spin density waves (CDW's and SDW's) of infinitesimal amplitude, which break the translational symmetry of the Hamiltonian? Within density functional theory, a CDW of wavevector $Q \approx 1.1(2k_F)$ appears at low densities. The local spin density approximation (LSDA) for exchange and correlation places the transition at $r_s \approx 30$, while inclusion of the next term in the gradient expansion suppresses the transition to densities as low as $r_s \approx 200$. The best estimate is that the CDW appears out of the uniform ferromagnetic phase of jellium at $r_s \approx 70$; this is also where Ceperley, in a recent calculation with correlated wave functions, found Wigner crystallization. Although no SDW in jellium is predicted within LSDA, the calculated uniform spin susceptibility diverges at $r_s \approx 35$, close to the highest density ($r_s \approx 26$) at which Ceperley found ferromagnetism.

Ist das gleichförmige Elektronengas instabil gegenüber Ladungs- und Spindichtewellen (CDW und SDW) von infinitesimaler Amplitude, die die Translationssymmetrie der Hamiltonfunktion aufheben? In der Dichtefunktions-Theorie taucht für geringe Dichten eine Ladungsdichtewelle (CDW) mit Wellenvektor $Q \approx 1,1(2k_F)$ auf. Die lokale Spindichte-Näherung (LSDA) für Austausch und Korrelation legt den Übergang auf $r_s \approx 30$, während Einbeziehung des nächsten Terms in der Gradientenentwicklung den Übergang bis zu Dichten von $r_s \approx 200$ unterdrückt. Der besten Schätzung nach erscheint die Ladungsdichtewelle aus der gleichförmig ferromagnetischen Phase im Jellium bei $r_s \approx 70$, wo auch Ceperley in einer neueren Rechnung mit korrelierten Wellenfunktionen Wigner-Kristallisation fand. Obwohl durch die lokale Spindichte-Näherung (LSDA) keine Spindichtewellen im Jellium vorhergesagt werden, divergiert die errechnete Suszeptibilität bei $r_s \approx 35$, nahe der höchsten Dichte ($r_s \approx 26$), wo Ceperley Ferromagnetismus fand.

1. Introduction

The ground state density of jellium, an electron gas neutralized by a rigid uniform positive background, need not be uniform [1]. Exchange and correlation may produce inhomogeneities in the up and down spin densities of the form [2]

$$n_{\uparrow}(\mathbf{r}) = \bar{n}_{\uparrow}[1 + A \cos(Qz + \varphi)], \quad (1)$$

$$n_{\downarrow}(\mathbf{r}) = \bar{n}_{\downarrow}[1 + A \cos(Qz - \varphi)], \quad (2)$$

where \bar{n}_{\uparrow} and \bar{n}_{\downarrow} are the average spin densities and $\bar{n} = \bar{n}_{\uparrow} + \bar{n}_{\downarrow} = k_F^3/3\pi^2 = (4\pi r_s^3/3)^{-1}$ is the average electron density. (We use atomic units $\hbar = m = e^2 = 1$). Here $\varphi = 0$ describes a charge density wave (CDW), and $\varphi = \pi/2$ a spin density wave (SDW) of wavevector Q , and dimensionless amplitude A .

Overhauser [1, 2] has shown that, in the Hartree-Fock approximation for jellium, there are SDW phases lower in energy than the uniform unpolarized phase, and that

¹⁾ New Orleans, Louisiana 70118, USA.

²⁾ Argonne, Illinois 60439, USA.

³⁾ Chapel Hill, North Carolina 27514, USA.

correlation, which tends to suppress ferromagnetic instabilities, may enhance CDW instabilities. Recently Shore et al. [3] have suggested that the CDW in jellium may be the first stage in the growth of the Wigner [4] crystal, which should be the ground state at very low densities where the long-range electrostatic interaction dominates the energy.

In this paper we will consider whether jellium is unstable against CDW's and SDW's of infinitesimal amplitude, and if so what are the critical densities and wavevectors. Since in a three-dimensional jellium these instabilities appear at unphysically low densities, the implications of our calculations will be more conceptual than experimental. We will point out some considerations which could be important in calculations for realistic systems which may exhibit CDW's or SDW's, such as alkali metals [5] (where the ionic lattice is deformable) and systems with fewer than three dimensions. The three-dimensional jellium is certainly the system in which the important effects of exchange and correlation on the energy and on the linear response functions have been most thoroughly studied. Recent results (Singwi et al. [6], Vashishta and Singwi [7], Geldart and Rasolt [8], Ceperley [9], Langreth and Perdew [10]) for metallic and low densities are probably reliable. In particular, Ceperley [9] has used trial wave functions to calculate and compare the energies of three phases of jellium. He finds an unpolarized uniform liquid for $r_s < 26$, a fully polarized or ferromagnetic uniform liquid for $26 < r_s < 67$, and a Wigner crystal for $r_s > 67$. His work both confirms and extends Wigner's [4] hypothesis about the low-density limit of the correlation energy. At low densities, the total energies of the three phases are so close that the calculated transition densities are much less certain than the energies themselves. At metallic densities ($2 < r_s < 6$), Ceperley's correlation energies for the unpolarized phase agree with the results of other calculations, especially those of Vashishta and Singwi [7].

We consider only instabilities of the uniform phases against CDW's and SDW's of infinitesimal amplitude, which are heralded by divergences in the static dielectric response function or spin susceptibility at finite wavevector. Of course if the actual transitions are first order, there may be a range of densities in which the uniform phase is metastable: unstable against inhomogeneities of finite amplitude, but stable against those of infinitesimal amplitude. In fact Shore et al. [3], using a modified and spin-unpolarized version of the local spin density approximation (LSDA) [11, 12] for exchange and correlation, found that the uniform unpolarized phase undergoes a first-order Wigner crystallization at $r_s = 26$ and a divergence of the dielectric function for $Q \approx 2k_F$ at $r_s = 27$.

As we will see, the LSDA and the density gradient expansion (GE) [8, 11] can give very different results for the transition densities, which are sensitive to small errors in the treatment of exchange and correlation. It is perhaps only in linear response that we can presently hope to treat exchange and correlation accurately enough to estimate the transition density, and even then our estimate will be rather rough. At least the existence or non-existence of divergences in the linear response functions, and the corresponding wavevectors, can be established with some confidence.

2. Instability Conditions in Linear Response

Here we derive some formal results for the ground-state instability of a uniform jellium against infinitesimal perturbation. The main conclusions are not surprising and have been summarized at the beginning of Section 4.

As an unperturbed system, we consider a jellium of volume Ω , subject to periodic boundary conditions. The ground state energy as a functional of the spin densities

is [11, 12]

$$E_0[n_\uparrow, n_\downarrow] = T_s[n_\uparrow, n_\downarrow] + E_{xc}[n_\uparrow, n_\downarrow] + \frac{1}{2} \int d^3r \int d^3r' \frac{[n(\mathbf{r}) - \bar{n}][n(\mathbf{r}') - \bar{n}]}{|\mathbf{r} - \mathbf{r}'|}, \quad (3)$$

where T_s is the kinetic energy of a system of non-interacting electrons with spin densities $n_\sigma(\mathbf{r})$, E_{xc} is the exchange-correlation energy (Section 3), and $n = n_\uparrow + n_\downarrow$.

First suppose that the ground state spin densities are uniform, so that the last term in (3) is zero, while the kinetic energy per electron is

$$\frac{T_s}{N} = \frac{3}{10} k_F^2 \frac{(1 + \zeta)^{5/3} + (1 - \zeta)^{5/3}}{2}, \quad (4)$$

where $\zeta = (\bar{n}_\uparrow - \bar{n}_\downarrow)/\bar{n}$. We assume that the correlation energy depends on ζ in the same way that the exchange energy does [12, 13], so that

$$\frac{E_{xc}}{N} = \left[-\frac{3k_F}{4\pi} + h_c(\bar{n}) \right] \frac{(1 + \zeta)^{4/3} + (1 - \zeta)^{4/3}}{2} + \varepsilon_c^{(U)}(\bar{n}) - h_c(\bar{n}), \quad (5)$$

where

$$h_c(\bar{n}) = \frac{\varepsilon_c^{(P)}(\bar{n}) - \varepsilon_c^{(U)}(\bar{n})}{2^{1/3} - 1} \quad (6)$$

and $\varepsilon_c(\bar{n})$ is the correlation energy per electron in a fully polarized (P) or unpolarized (U) electron gas of density \bar{n} . Now the total energy given by (4) and (5) has a rapidly convergent expansion in powers of ζ^2 , and it is not hard to see from this expansion that minimization of E_0 gives $\zeta^2 = 0$ or 1; the uniform phase is either unpolarized or fully polarized in the absence of external fields (see Appendix A).

Now we apply a spin-dependent external perturbation $\delta v_\sigma(\mathbf{r})$ (with zero volume average). The energy becomes

$$E[n_\uparrow, n_\downarrow] = E_0[n_\uparrow, n_\downarrow] + \delta V[n_\uparrow, n_\downarrow], \quad (7)$$

$$\delta V[n_\uparrow, n_\downarrow] = \sum_\sigma \int d^3r \delta n_\sigma(\mathbf{r}) \delta v_\sigma(\mathbf{r}), \quad (8)$$

where $\delta n_\sigma(\mathbf{r}) = n_\sigma(\mathbf{r}) - \bar{n}_\sigma$ is the change in ground-state density. Since the perturbation does not change the number of electrons with spin σ , and $\delta E_0/\delta n_\sigma(\mathbf{r})|_{\bar{n}_\uparrow, \bar{n}_\downarrow} = \mu_0 =$ unperturbed chemical potential, the change in E_0 is

$$\delta E_0 = \frac{1}{2} \sum_{\sigma, \sigma'} \int d^3r \int d^3r' \frac{\delta^2 E_0}{\delta n_\sigma(\mathbf{r}) \delta n_{\sigma'}(\mathbf{r}')} \bigg|_{\bar{n}_\uparrow, \bar{n}_\downarrow} \delta n_\sigma(\mathbf{r}) \delta n_{\sigma'}(\mathbf{r}') \quad (9)$$

to second order in δn_σ . We show in Appendix B that (for the self-consistent $\delta n_\sigma(\mathbf{r})$)

$$\delta E_0 = -\frac{1}{2} \delta V = -\delta E,$$

so that

$$\delta E_0 = -\frac{1}{2} \sum_\sigma \frac{1}{\Omega} \sum_{\mathbf{q} \neq 0} \delta n_\sigma(\mathbf{q}) \delta v_\sigma(-\mathbf{q}), \quad (10)$$

where

$$f(\mathbf{q}) = \int d^3r e^{-i\mathbf{q} \cdot \mathbf{r}} f(\mathbf{r}). \quad (11)$$

In spin density functional theory [11, 12], the $n_\sigma(\mathbf{r})$ are constructed from orbitals

which experience the effective potential

$$v_{\sigma}^{\text{eff}}(\mathbf{r}) = v_{\sigma}(\mathbf{r}) + v_H([n]; \mathbf{r}) + v_{\text{xc}}^{\sigma}([n_{\uparrow}, n_{\downarrow}]; \mathbf{r}), \quad (12)$$

where

$$v_H([n]; \mathbf{r}) = \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (13)$$

$$v_{\text{xc}}^{\sigma}([n_{\uparrow}, n_{\downarrow}]; \mathbf{r}) = \frac{\delta E_{\text{xc}}}{\delta n_{\sigma}(\mathbf{r})}. \quad (14)$$

Now to first order in δv_{σ} ,

$$\delta v_{\sigma}^{\text{eff}} = \delta v_{\sigma} + \delta v_H + \delta v_{\text{xc}}^{\sigma}. \quad (15)$$

But

$$\delta n_{\sigma}(\mathbf{q}) = \frac{1}{2} \Pi_0(2\bar{n}_{\sigma}, q) \delta v_{\sigma}^{\text{eff}}(\mathbf{q}); \quad (16)$$

where $\Pi_0(\bar{n}, q)$ is the usual Lindhard or non-interacting density response function of an unpolarized electron gas of density \bar{n} :

$$\Pi_0(\bar{n}, q) = -\frac{k_F}{\pi^2} F(x), \quad (17)$$

$$F(x) = \frac{1}{2} + \frac{1-x^2}{4x} \ln \left| \frac{1+x}{1-x} \right|, \quad (18)$$

where $x = q/2k_F$. Defining the local field correction $G_{\sigma\sigma'}(q)$ by the equation

$$\delta v_{\text{xc}}^{\sigma}(\mathbf{q}) = -\frac{4\pi}{q^2} \sum_{\sigma'} G_{\sigma\sigma'}(q) \delta n_{\sigma'}(\mathbf{q}), \quad (19)$$

we find

$$\delta v_{\sigma}(\mathbf{q}) = \sum_{\sigma'} \tilde{\epsilon}_{\sigma\sigma'}(q) \delta v_{\sigma'}^{\text{eff}}(\mathbf{q}), \quad (20)$$

where

$$\tilde{\epsilon}_{\sigma\sigma'}(q) = \delta_{\sigma\sigma'} - \frac{4\pi}{q^2} [1 - G_{\sigma\sigma'}(q)] \frac{1}{2} \Pi_0(2\bar{n}_{\sigma'}, q). \quad (21)$$

These equations can be used to express δE_0 in terms of δn_{σ} :

$$\delta E_0 = \frac{1}{2} \sum_{\sigma, \sigma'} \frac{1}{\Omega} \sum_{\mathbf{q} \neq 0} \frac{\delta n_{\sigma}(\mathbf{q}) \tilde{\epsilon}_{\sigma\sigma'}(q) \delta n_{\sigma'}(-\mathbf{q})}{-\frac{1}{2} \Pi_0(2\bar{n}_{\sigma'}, q)}. \quad (22)$$

Now the condition for instability of the uniform phase against an infinitesimal inhomogeneity can be obtained in two different but equivalent ways: The first is to seek a non-zero solution for $\delta v_{\sigma}^{\text{eff}}(\mathbf{q})$ from (20) when the external potential $\delta v_{\sigma}(\mathbf{r})$ is zero. Such a solution can be found if and only if the determinant of $\tilde{\epsilon}_{\sigma\sigma'}(q)$ vanishes. The second way is to ask for the condition under which the quadratic form (22) ceases to be positive, which again turns out to require the vanishing of the determinant of $\tilde{\epsilon}_{\sigma\sigma'}(q)$.

In the unpolarized ($\zeta = 0$) uniform electron gas, the symmetry between \uparrow and \downarrow implies that

$$\det \tilde{\epsilon}_{\sigma\sigma'}(q) = \tilde{\epsilon}(q) [\tilde{\epsilon}_{\uparrow\uparrow}(q) - \tilde{\epsilon}_{\uparrow\downarrow}(q)], \quad (23)$$

where

$$\tilde{\varepsilon}(q) = \tilde{\varepsilon}_{\uparrow\uparrow}(q) + \tilde{\varepsilon}_{\uparrow\downarrow}(q) = 1 - \frac{4\pi}{q^2} [1 - G(q)] \Pi_0(\bar{n}, q) \quad (24)$$

and

$$G(q) = \frac{1}{2} [G_{\uparrow\uparrow}(q) + G_{\uparrow\downarrow}(q)] . \quad (25)$$

The conventional dielectric function $\varepsilon(q)$, defined by $\delta v = \varepsilon(\delta v + \delta v_H)$, is

$$\varepsilon(q) = \frac{\tilde{\varepsilon}(q)}{1 + \frac{4\pi}{q^2} G(q) \Pi_0(\bar{n}, q)} . \quad (26)$$

The spin susceptibility $\chi(q)$, which relates the spin magnetization δm to the external magnetic field δH through $\delta m(\mathbf{q}) = \chi(q) \delta H(\mathbf{q})$, is easily shown to be

$$\chi(q) = \left(\frac{\mu}{2} \right)^2 \frac{-\Pi_0(\bar{n}, q)}{\tilde{\varepsilon}_{\uparrow\uparrow}(q) - \tilde{\varepsilon}_{\uparrow\downarrow}(q)} , \quad (27)$$

where $\mu/2$ is the magnetic moment of an electron. Thus the instability condition is equivalent to $\tilde{\varepsilon}(q) = 0$ (a pure CDW) or $\chi(q) = \infty$ (a pure SDW); instabilities of the “mixed” CDW-SDW type of (1) and (2) are not found. In the polarized ($\zeta = 1$) electron gas,

$$\det \tilde{\varepsilon}_{\sigma\sigma'}(q) = \tilde{\varepsilon}_{\uparrow\uparrow}(q) , \quad (28)$$

and the instability condition is $\tilde{\varepsilon}_{\uparrow\uparrow}(q) = 0$ (a pure CDW).

3. Approximations for Exchange and Correlation

Exchange and correlation enter the linear response theory through the local field corrections $G_{\sigma\sigma'}(q)$ of (19) and (21), which can be found from (14) or (22) when the functional $E_{xc}[n_\uparrow, n_\downarrow]$ is known. There are two conventional approximations for this functional, which are valid when $n_\sigma(\mathbf{r})$ varies slowly over space.

In the local spin density approximation (LSDA),

$$E_{xc}^{\text{LSDA}} = \int d^3r n(\mathbf{r}) \varepsilon_{xc}(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r})) , \quad (29)$$

where $\varepsilon_{xc}(n_\uparrow, n_\downarrow)$ is just the left-hand side of (5). The corresponding local field correction is

$$G_{\sigma\sigma'}^{\text{LSDA}}(q) = -\frac{q^2}{4\pi} \frac{\partial^2}{\partial n_\sigma \partial n_{\sigma'}} (n \varepsilon_{xc}(n_\uparrow, n_\downarrow))|_{\bar{n}_\uparrow, \bar{n}_\downarrow} . \quad (30)$$

In exchange-only calculations, the correlation energies $\varepsilon_c^{(U)}(n)$ and $\varepsilon_c^{(P)}(n)$ in (5) would be set to zero; in our calculations, which include correlation, we have used Ceperley's [9] parametrizations $\varepsilon_c = (a + b \sqrt{r_s} + cr_s)^{-1}$.

In what we shall call the first gradient expansion (GE) [11, 14], one adds to E_{xc}^{LSDA} the gradient correction

$$\Delta E_{xc} = \int d^3r \sum_{\sigma, \sigma'} B_{\sigma, \sigma'}^{xc}(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r})) \nabla n_\sigma(\mathbf{r}) \cdot \nabla n_{\sigma'}(\mathbf{r}) , \quad (31)$$

which produces an additional local field correction

$$\Delta G_{\sigma\sigma'}(q) = -\frac{q^4}{2\pi} B_{\sigma\sigma'}^{xc}(\bar{n}_\uparrow, \bar{n}_\downarrow) . \quad (32)$$

For exchange alone, the gradient expansion is known for the spin-unpolarized system:

$$\Delta E_x = \int d^3r \frac{C_x}{n^{4/3}} |\nabla n|^2, \quad (33)$$

where $C_x = -1.67 \times 10^{-3}$ [15]. (In density functional theory, the exchange energy is the Hartree-Fock exchange integral evaluated with Kohn-Sham [11] orbitals; its gradient expansion exists and is well-known. Other definitions of the exchange energy can lead to different conclusions about its gradient expansion.) For arbitrary spin polarization one could use the trivial identity [16]

$$E_x[n_\uparrow, n_\downarrow] = \frac{1}{2} E_x[2n_\uparrow] + \frac{1}{2} E_x[2n_\downarrow], \quad (34)$$

where $E_x[n]$ is the exchange energy of an unpolarized system, to find

$$B_{\sigma\sigma'}^x(n_\uparrow, n_\downarrow) = \delta_{\sigma,\sigma'} \frac{C_x}{2^{1/3}} \frac{1}{n^{4/3}}. \quad (35)$$

The gradient expansion for exchange and correlation is also known for the unpolarized case:

$$\Delta E_{xc} = \int d^3r \frac{C_{xc}(n)}{n^{4/3}} |\nabla n|^2, \quad (36)$$

where $C_{xc}(n) = 2.57 \times 10^{-3}$ in the high-density limit. In the range of metallic densities, $C_{xc}(n)$ is a slowly-varying function of n . Depending on how higher-order RPA terms are approximated, $C_{xc}(n)$ at low densities appears to be either somewhat less than [8] or approximately equal to [10] its high-density limit; we prefer the latter estimate and take $C_{xc}(n) = 2.57 \times 10^{-3}$ for all n .

The functions $B_{\sigma\sigma'}^{xc}(n_\uparrow, n_\downarrow)$ for exchange and correlation are known for arbitrary spin polarization only in the high-density limit [14], where they show a strong spin-dependence. We are more concerned here with low densities. In the low-density limit, electrostatic arguments show that $\epsilon_{xc}(n_\uparrow, n_\downarrow) \rightarrow \epsilon_{xc}(n) \approx (\text{const}) n^{1/3}$ (as confirmed by Ceperley's [9] calculation at very low densities), and

$$B_{\sigma\sigma'}^{xc}(n_\uparrow, n_\downarrow) \rightarrow B^{xc}(n) = \frac{C_{xc}(0)}{n^{4/3}}, \quad (37)$$

where $C_{xc}(0)$ is an imperfectly-known constant which we take to be 2.57×10^{-3} . Although we do not know how low the density must be before this spin-independent limit is reached, we have assumed, in the absence of any firmer knowledge, that (37) can be used at the low densities where we find instabilities of the uniform phase. As partial justification for our use of (37), we note that when (37) is used the gradient corrections cancel out of the spin susceptibility $\chi(q)$, which should then be given accurately by LSDA. Thus if we write the exchange-correlation enhancement of $\chi(q)$ as

$$\frac{\chi(q)}{\chi_0(q)} = \frac{1}{1 + I(\bar{n}, q) I_0(\bar{n}, q)}, \quad (38)$$

where $\chi_0(q)$ is the spin susceptibility for non-interacting electrons, we should find $I(\bar{n}, q)$ independent of q , a result obtained by Singwi et al. [6] even at low metallic densities.

The local field correction which enters $\tilde{\epsilon}(q)$ is $G(q)$, equation (25). (30) and (32) give the first two terms in the expansion of $G(q)$ in powers of q^2 . $G(q)$ is known at inter-

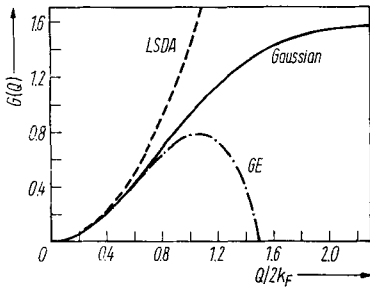


Fig. 1. Local field correction $G(Q)$ for exchange and correlation in an unpolarized jellium at a typical low density ($r_s = 30$). Dashed curve: local spin density approximation. Dash-dotted curve: first gradient expansion. Solid curve: Gaussian approximation of equation (39)

mediate and large q for exchange only [17 to 19], but when correlation is included there are only estimates of $G(q)$ which differ widely [17, 6]. Singwi et al. [6] found that $G(q)$ at metallic densities for $q \lesssim 2k_F$ could be approximated with a Gaussian

$$G(q) \approx \alpha [1 - e^{-\beta(q/2k_F)^2}], \quad (39)$$

where α and β depend on \bar{n} . Here we will fix α and β by requiring that (39) to order q^4 must be consistent with (30) and (32). In Fig. 1 we compare the Gaussian $G(q)$ with the LSDA and GE approximations for a typical low density $r_s = 30$.

The large q limit of $G(q)$ is known [20]

$$\lim_{q \rightarrow \infty} G(q) = \frac{2}{3} [1 - g(0)], \quad (40)$$

where $g(0)$ is the pair correlation function at the origin, which should be close to zero at low densities. While none of the three approximations for $G(q)$ shown in Fig. 1 is correct at large q , the Gaussian approximation is least objectionable in this limit.

4. Results and Conclusions

In Section 2 we reached the following conclusions about the ground-state instability of a uniform jellium against infinitesimal perturbations: The uniform phase of lowest energy is either spin-unpolarized or else *fully* polarized. The uniform unpolarized phase can be unstable against either CDW's (if the dielectric function $\epsilon(Q)$ vanishes) or SDW's (if the spin susceptibility $\chi(Q)$ diverges), but *not* against mixed CDW-SDW's (unless $\epsilon(Q) \rightarrow 0$ and $\chi(Q) \rightarrow \infty$ simultaneously). The uniform polarized phase can be unstable against CDW's.

Numerical values for the exchange-correlation enhancement of the uniform spin susceptibility ((38) in the limit $q \rightarrow 0$) are presented in Table 1. Since the LSDA is exact for $q \rightarrow 0$, the only approximations are the use of (5) and of Ceperley's [9] correlation energies. The calculated enhancements for $r_s \lesssim 4$ agree well with accepted theoretical values [12, 21]. At very low densities, the Keiser-Wu [21] theoretical enhancement saturates, while the von Barth-Hedin [12] enhancement diverges at $r_s \approx 11$. The enhancement calculated here has an intermediate behavior at low densities, diverging at $r_s \approx 35$, which is consistent with Ceperley's [9] calculation of a first-order ferromagnetic transition at $r_s = 26$.

To make the instabilities most transparent, we write the effect of an inhomogeneity of type (1) to (2) on the energy per electron as

$$\frac{\delta E_0}{N} = eA^2 + O(A^4). \quad (41)$$

Table 1

Exchange-correlation enhancement of the uniform spin susceptibility of jellium as a function of density parameter r_s . (Based on equation (5) with correlation energies from Ceperley [9])

r_s	$\chi(0)/\chi_0(0)$
1	1.14
2	1.27
3	1.40
4	1.52
5	1.65
6	1.78
10	2.39
20	5.15
30	19.11

Now we find e for the three relevant cases (SDW and CDW in unpolarized (U) jellium, CDW in polarized (P) jellium) from (22), using (5) for the LSDA and (37) for the gradient correction:

$$e^{\text{SDW(U)}} = \frac{k_F^2}{12F(x)} - \frac{k_F}{12\pi} + \frac{1}{9} h_c(\bar{n}), \quad (42)$$

$$e^{\text{CDW(U)}} = \frac{k_F^2}{12F(x)} + \frac{k_F}{12\pi x^2} [1 - G_U(Q)], \quad (43)$$

$$e^{\text{CDW(P)}} = \frac{2^{2/3}k_F^2}{12F(x/2^{1/3})} + \frac{k_F}{12\pi x^2} [1 - G_P(Q)], \quad (44)$$

where $x = Q/2k_F$ and

$$G_i(Q) = \gamma_i x^2 - \frac{3}{5} x^4 + \dots, \quad (45)$$

$$\gamma_U = 1 - \frac{k_F^2}{\pi} g'_U(\bar{n}), \quad (46)$$

$$\gamma_P = 2^{1/3} - \frac{k_F^2}{\pi} g'_P(\bar{n}), \quad (47)$$

$$g_i(\bar{n}) = \bar{n} \varepsilon_c^{(i)}(\bar{n}). \quad (48)$$

The density dependence of γ_U and γ_P is shown in Fig. 2.

Fig. 3 to 5 show phase diagrams for jellium. The instability curves were generated by searching, at each value of $x = Q/2k_F$, for the value of \bar{n} (or k_F) at which e vanishes. The calculations were performed in the LSDA, the GE, and the Gaussian approximation, corresponding respectively to (45) to order x^2 , x^4 , or to all orders according to (39).

We see in Fig. 3 that there is no true SDW. As the density is lowered, the jellium first becomes unstable against an infinitesimal SDW with $Q = 0$; this is just the divergence of the uniform spin susceptibility at $r_s = 35$. Equation (42) shows that our conclusion about the non-existence of the SDW is independent of the choice of correlation energies $\varepsilon_c^{(U)}(\bar{n})$ and $\varepsilon_c^{(P)}(\bar{n})$ or of the gradient coefficient $C_{xc}(n)$; it does however depend on our assumption in (37) that the gradient coefficient $B_{\sigma\sigma}^{xc}$ is independent of σ and σ' , which is really justified only in the low-density limit.

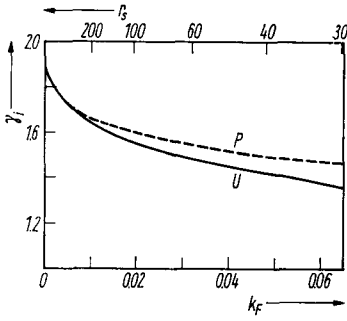


Fig. 2

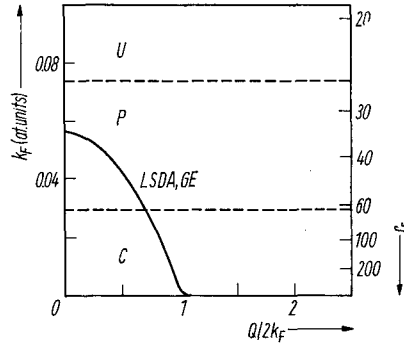


Fig. 3

Fig. 2. Coefficients γ_i of the $(Q/2k_F)^2$ term in the expansion of the local field correction $G(Q)$. U: unpolarized jellium, P: spin-polarized jellium

Fig. 3. Critical k_F for the instability of a uniform unpolarized jellium against an infinitesimal spin density wave of wavevector Q vs. $Q/2k_F$. Solid curve: local spin density approximation (or first gradient expansion employing (37)). Horizontal lines separate the three phases studied by Ceperley [9]: uniform unpolarized (U), uniform polarized (P), and Wigner crystal (C)

Fig. 4 and 5 show the CDW instabilities of the unpolarized and polarized uniform electron gas, respectively. Except at very low densities, where spin polarization has no effect on the energy, the polarized electron gas is more susceptible to CDW's, because of its greater exchange. The transition densities predicted by LSDA and GE ($r_s \approx 30$ and 190 respectively for the unpolarized jellium) are very different, while the Gaussian approximation gives an intermediate result. This is reminiscent of the situation for the metal surface energy, which is underestimated by LSDA and overestimated by GE [10, 22] although for the surface energy the differences are not really large. Reliable calculations of CDW transition densities will require approximations

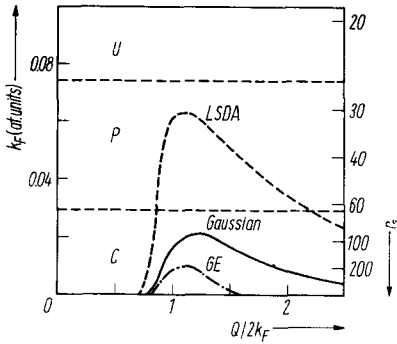


Fig. 4

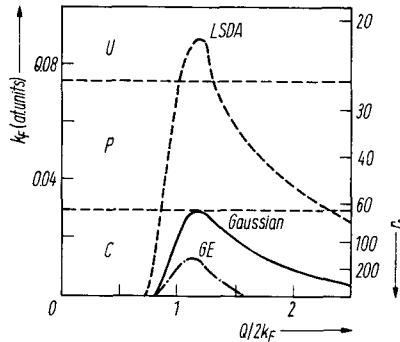


Fig. 5

Fig. 4. Critical k_F for the instability of a uniform unpolarized jellium against infinitesimal charge density waves of wavevector Q vs. $Q/2k_F$. Dashed curve: local spin density approximation. Dash-dotted curve: first gradient expansion. Solid curve: Gaussian approximation of equation (39). (See also caption of Fig. 3)

Fig. 5. Critical k_F for the instability of a uniform spin-polarized jellium against infinitesimal charge density waves of wavevector Q vs. $Q/2k_F$. (See also caption of Fig. 4)

more accurate than LSDA or GE, and less arbitrary than the Gaussian approximation; such approximations are being developed [10].

If Ceperley's [9] values for the transition densities from unpolarized to polarized uniform phase ($r_s = 26$), and from polarized uniform phase to Wigner crystal ($r_s = 67$), are correct, then only Fig. 5 is relevant. Within LSDA, the electron gas forms a CDW as soon as it goes ferromagnetic, while within GE the instability never has a chance to occur. The Gaussian approximation for exchange-correlation, which is probably our best estimate, gives an interesting result: the uniform polarized phase becomes unstable against infinitesimal CDW's of wave vector $Q \approx 1.14$ ($2k_F$) at $r_s = 67$. This is just the density at which Ceperley found Wigner crystallization, and the critical wavevector is close to the lowest reciprocal lattice vector of a b.c.c. solid with one electron per unit cell. In spite of huge uncertainties in our estimate of the transition density, this result lends some support to Shore et al.'s [3] identification of the charge density wave in jellium with the Wigner crystal.

Acknowledgements and Addenda

One of us (J.P.P.) gratefully acknowledges the support of the National Science Foundation (Grant No. DMR 78-12398), the hospitality of Argonne National Laboratory, and discussions with J. H. Rose.

A preliminary account of this work was given at the March 1979 American Physical Society meeting [23], where we also heard about an exchange-only calculation of charge density waves in jellium by J. T. Devreese and co-workers, and a local density calculation in two- and three-dimensional jellium by L. M. Sander et al. After our paper was written, we received a preprint of the latter work [24]. A.P.S. meeting we learned of a generalized RPA calculation of the spin susceptibility $\chi(q)$ for jellium at metallic densities by M. S. Jay et al. [25], which shows that correlation does indeed suppress the spin density wave.

Appendix A

Energy of the uniform jellium as a function of spin polarization ζ

With an error of about 1%, (4) and (5) can be expanded to fourth order in ζ for $|\zeta| \leq 1$. Thus the total energy per electron is approximately

$$\frac{E}{N} = a + b\zeta^2 + c\zeta^4, \quad (\text{A1})$$

where

$$b = \frac{5}{9} \left(\frac{3}{10} k_F^2 + \frac{2}{5} g \right), \quad (\text{A2})$$

$$c = \frac{5}{243} \left(\frac{3}{10} k_F^2 + g \right), \quad (\text{A3})$$

and $g = -3k_F/4\pi + h_c$. A minimum of E/N can lie in $0 < \zeta^2 < 1$ only if $b < 0$ and $c > 0$, which is clearly impossible.

Appendix B

The energy to second order

The energy E in the presence of a perturbation $\lambda \delta v_o(\mathbf{r})$ is

$$E_\lambda = E_0 + \varepsilon_1 \lambda + \varepsilon_2 \lambda^2 + \dots \quad (\text{B1})$$

By the Pauli-Hellman-Feynman theorem,

$$\frac{d}{d\lambda} E_\lambda = \langle \Psi_\lambda | \frac{\partial H_\lambda}{\partial \lambda} | \Psi_\lambda \rangle, \quad (\text{B2})$$

i.e.

$$\varepsilon_1 + 2\varepsilon_2\lambda + \dots = \sum_\sigma \int d^3r \delta v_\sigma(\mathbf{r}) [\bar{n}_\sigma + \lambda \delta n_\sigma(\mathbf{r}) + \dots], \quad (\text{B3})$$

where \bar{n} is the unperturbed density. Equating the coefficients of the linear terms gives

$$\varepsilon_2 = \frac{1}{2} \sum_\sigma \int d^3r \delta v_\sigma(\mathbf{r}) \delta n_\sigma(\mathbf{r}) \quad (\text{B4})$$

or $\delta E = \frac{1}{2} \delta V$. Since $\delta E = \delta E_0 + \delta V$, $\delta E_0 = -\frac{1}{2} \delta V$.

References

- [1] A. W. OVERHAUSER, Phys. Rev. **128**, 1437 (1962).
- [2] A. W. OVERHAUSER, Phys. Rev. **167**, 691 (1968).
- [3] H. B. SHORE, E. ZAREMBA, J. H. ROSE, and L. SANDER, Phys. Rev. B **18**, 6506 (1978).
- [4] E. P. WIGNER, Phys. Rev. **46**, 1002 (1934); Trans. Faraday Soc. **34**, 678 (1938).
- [5] M. L. BORLACK and A. W. OVERHAUSER, Phys. Rev. Letters **41**, 1066 (1978).
- [6] K. S. SINGWI, A. SJÖLANDER, M. P. TOSI, and R. H. LAND, Phys. Rev. B **1**, 1044 (1970).
- [7] P. VASHISHTA and K. S. SINGWI, Phys. Rev. B **6**, 875 (1972).
- [8] D. J. W. GELDART and M. RASOLT, Phys. Rev. B **13**, 1477 (1976).
- [9] D. CEPERLEY, Phys. Rev. B **18**, 3126 (1978).
- [10] D. C. LANGRETH and J. P. PERDEW, Solid State Commun. **31**, 567 (1979); Phys. Rev. B **21**, 5469 (1980).
- [11] W. KOHN and L. J. SHAM, Phys. Rev. **140**, A1133 (1965).
- [12] U. VON BARTH and L. HEDIN, J. Phys. C **5**, 1629 (1972).
- [13] O. GUNNARSSON and B. I. LUNDQVIST, Phys. Rev. B **13**, 4274 (1976).
- [14] M. RASOLT, Phys. Rev. B **7**, 4357 (1973).
- [15] L. J. SHAM, in: Computational Methods in Band Theory, Ed. P. M. MARCUS, J. F. JANAK, and A. R. WILLIAMS, Plenum Press, New York 1971 (p. 458).
- [16] G. L. OLIVER and J. P. PERDEW, Phys. Rev. A **20**, 397 (1979).
- [17] D. J. W. GELDART and R. TAYLOR, Canad. J. Phys. **48**, 155, 167 (1970).
- [18] L. J. SHAM, Phys. Rev. B **7**, 4357 (1973).
- [19] F. BROSENS, L. F. LEMMENS, and J. T. DEVREESE, phys. stat. sol. (b) **81**, 551 (1977).
- [20] G. NIKLASSON, Phys. Rev. B **10**, 3052 (1974).
- [21] G. KEISER and F. Y. WU, Phys. Rev. A **6**, 2369 (1972).
- [22] J. P. PERDEW, D. C. LANGRETH, and V. SAHNI, Phys. Rev. Letters **38**, 1030 (1977).
- [23] T. DATTA and J. P. PERDEW, Bull. Amer. Phys. Soc. **24**, 236 (1979).
- [24] L. M. SANDER, J. H. ROSE, and H. B. SHORE, Phys. Rev. B **21**, 2739 (1980).
- [25] M. S. JAY, N. E. BRENER, and J. L. FRY, Bull. Amer. Phys. Soc. **25**, 208 (1980).

(Received May 2, 1980)

Note added in proof:

Very recently Ceperley and Alder (unpublished) have performed an "exact" stochastic simulation of the Schrödinger equation for jellium. Their results for the correlation energy are very close to Ceperley's, but the transition densities are shifted: They find an unpolarized uniform liquid for $r_s < 75 \pm 5$, a fully polarized uniform liquid for $75 \pm 5 < r_s < 100 \pm 20$, and a Wigner crystal for $r_s < 100 \pm 20$. We have repeated our calculations using Ceperley-Alder's correlation, and find that the divergence of the uniform spin susceptibility now appears at $r_s = 100$, while the zeroes of the dielectric function occur at essentially the same Q and r_s as we found with Ceperley's correlation.