

## Density-functional theory of Wigner crystallization

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(Received 10 April 1978)

We present a theory of the transition from a low-density electron crystal to a uniform electron gas based on the density-functional formalism. We find a first-order transition near  $r_s = 26$ ; for  $r_s$  slightly greater than the transition value the electrons must still be regarded as itinerant, but with inhomogeneous density. As a step in our calculation we find a new value for the low-density limit of the exchange-correlation energy to replace Wigner's well-known form.

In 1934 Wigner pointed out that, for sufficiently low densities, electrons in a uniform positive background will crystallize.<sup>1</sup> This remarkable electronic property has inspired many attempts to obtain estimates of the density at which the transition occurs.<sup>2</sup> These estimates have varied over a wide range, in terms of the dimensionless parameter  $r_s$ , from 5 to 700. (Here  $r_s$  is related to the mean density  $n_0$  and the Bohr radius  $a_B$  by  $\frac{4}{3}\pi r_s^3 = n_0^{-1}a_B^3$ .) In view of this uncertainty and, lacking an experimental verification of the transition to the crystalline state, we reconsider the problem in this paper and present yet another estimate. We hope to demonstrate that our method leads to new insights into this well-studied system and in particular, that this approach gives a unique qualitative picture of the nature of the transition. In the course of the calculation we will present a new value for the low-density limit of the exchange-correlation energy to replace Wigner's well-known estimate.<sup>1</sup>

The majority of previous papers have approached the problem from the extreme crystalline limit where well-known techniques in crystal physics can be used. The phase change to the uniform gas is usually located by extrapolating the crystalline energy to high densities and comparing it with the energy of the uniform phase or by using a Lindemann melting criterion. The uncertainty in this approach is illustrated by the widely varying estimates of the transition density. Clearly what it required is a theory which is capable of treating the uniform and nonuniform phases *on the same footing*. Such a theory is presently available in the density-functional (DF) formalism which has

enjoyed considerable success as a practical technique in inhomogeneous-electron-gas problems.<sup>3</sup> The DF method is ideally suited to the classic Wigner problem. In applying this method, our purpose is twofold: to clarify the fundamental question concerning the transition point and also to shed light on the application of DF theory to low-density situations.

We base our calculations on previous DF work for the cohesive energy of metals; we shall examine the ground-state energy of the electron gas allowing for arbitrary variations of the density. The gas is divided into lattice cells each containing one electron, which are then replaced by Wigner-Seitz spheres. (Thus we cannot distinguish between different crystal symmetries.) The ground-state energy per electron is given by DF theory as

$$E_0 = T + \frac{1}{2} \int \frac{[n(r) - n_0][n(r') - n_0]}{|r - r'|} + \int \epsilon_{xc}(n) n d^3r. \quad (1)$$

Here  $T$  is the kinetic energy (to be discussed below); the next term is the electrostatic self-energy of the electrons and their interactions with the positive background of density  $n_0$ ; and the last term is exchange and correlation, treated in the local approximation. The integrals extend over the Wigner-Seitz sphere (electrostatic interactions between cells are ignored).

An immediate problem arises in that the form of  $\epsilon_{xc}(n)$  at small densities is unknown, and is vital to our work. In this regard, we note that the famous low-density limit for the correlation

energy ( $\epsilon_w \rightarrow -0.88/r_s$  Ry) obtained by Wigner and subsequently widely used, is *not* the appropriate quantity to use in the context of Eq. (1). For, recall the derivation of  $\epsilon_w$ : the total crystalline energy is calculated from which is subtracted the electrostatic energy and the kinetic and exchange energy the gas would have were it *uniform*. The remainder is the correlation energy  $\epsilon_w$  for the inhomogeneous system. The correlation-energy contribution to  $\epsilon_{xc}(n)$  in Eq. (1) should, however, be the energy of a *uniform* electron gas of density  $n$ ; the quantity  $\epsilon_w$  then appears as a result of solving Eq. (1), rather than as input.

The question arises, of course, whether any local form for  $\epsilon_{xc}$  exists as  $r_s \rightarrow \infty$ . In the low-density limit one is dealing with essentially isolated electrons: in the crystal they are bound to lattice sites by a harmonic potential due to the neutralizing positive background. But a single electron has no exchange-correlation energy, and no electrostatic self-energy, both of which occur in Eq. (1). A similar situation occurs in Hartree-Fock theory, although there the self-exchange and self-repulsion cancel exactly. Our problem is that a local  $\epsilon_{xc}$  cannot exactly compensate for nonlocal electrostatic energy.

This quandary has an interesting resolution. Suppose we take an  $\epsilon_{xc}$  of the form of  $\epsilon_w$ , namely,  $\epsilon_{xc} = -\alpha/r_s$ , and adjust  $\alpha$  until the electrostatic and exchange-correlation energies cancel, say for a Gaussian charge density; in this case,  $\alpha$  turns out to be  $2^{17/6} 3^{-7/6} \pi^{-1/3}$  Ry = 1.351 Ry. If the calculation is repeated for an exponential density, the answer for  $\alpha$  is  $2^{7/3} 3^{-8/35}$  Ry = 1.346 Ry; i.e., the same as the Gaussian case to three significant figures. Note that in both these cases  $\alpha$  is independent of the length scale in the charge density: the result holds for any Gaussian or exponential. Other profiles give almost the same result; for a large class of localized density profiles, we have

$$\epsilon_{xc} = -1.35/r_s \text{ Ry} \quad (2)$$

as the correct limit for  $\epsilon_{xc}$ . This should be compared to the conventional expression  $\epsilon_{xc} = -0.92/r_s + \epsilon_w = -1.80/r_s$  Ry, where the first term is exchange. We believe Eq. (2) to represent the best local form for  $\epsilon_{xc}$  as  $r_s \rightarrow \infty$ . For use in Eq. (1) we smoothly join the expression in Eq. (2) to the high-density results of Gunnarson and Lundquist.<sup>4</sup> The expression we use is, with  $x = r_s/11.4$ :

$$\epsilon_{xc} = -\frac{0.08038}{x} - 0.0666 \left[ (1+x^3) \ln \left( 1 + \frac{1}{x} \right) + \frac{x}{2} - x^2 - \frac{1}{3} \right] \quad \text{for } x < 1, \quad (3a)$$

$$\epsilon_{xc} = -x^{-1} \left( 0.117208 + \frac{0.000862(x-1)}{x-0.902245} \right) \quad \text{for } x > 1. \quad (3b)$$

The calculation of the kinetic energy in Eq. (1) is the heart of the DF method. The technique<sup>3,5</sup> is to solve the set of equations:

$$(-\frac{1}{2}\nabla^2 + v)\psi_i = \epsilon_i \psi_i, \quad (4a)$$

$$n(r) = \sum_i |\psi_i|^2, \quad (4b)$$

$$T = \sum_i \epsilon_i - \int n(r)v d^3r, \quad (4c)$$

$$v = \phi + \frac{d(n\epsilon_{xc})}{dn}. \quad (4d)$$

The first equation is to be solved with Bloch-wave boundary conditions at the edge of the Wigner-Seitz sphere. The energy levels are filled to generate the density according to Eq. (4b), and the kinetic energy according to Eq. (4c). Equation (4d) is the self-consistency condition on the potential  $v$ , where  $\phi$  is the electrostatic potential [cf. Eq. (1)]. In calculating the band structure we found it inconvenient to use the Kohn variational method<sup>6</sup> (as other workers have)<sup>5</sup> because spurious bands are generated, which are numerically difficult to separate from the correct bands. We used instead the method of Brooks.<sup>7</sup> Both methods involve numerical solution of the Schrödinger equation within the Wigner-Seitz sphere for several values of  $l$  (in our case for  $l=0$  to 6). They differ, however, in the way they determine the appropriate linear combination of the  $\psi_l(\vec{r})$  to approximately satisfy the Bloch condition on the surface of the sphere.

Equations (4a)–(4d) can be solved two different ways: a trial potential  $v$  can be chosen, the density generated, and a new potential obtained from Eq. (4d), and so on to self-consistency. Alternatively,  $v$  can be a variational function,<sup>8</sup>  $E_0$  being minimized when  $v$  satisfies Eq. (4d). For the Wigner problem it is evident that for any  $r_s$ ,  $n(r) \equiv n_0$  is a self-consistent solution. Of course, it does not necessarily give the absolute minimum energy.

Consider now  $r_s = 50$  for which the ground state is crystalline in our theory. We first use a variational-potential approach, and put  $v = A r^2/r_s^3$ , where  $A$  is the variational parameter. We find a minimum energy of  $E_0 = -0.0274$  Ry as compared with the uniform-gas value  $-0.0260$  Ry; the charge density is Gaussian and is plotted in Fig. 1. The value of  $A$  for which the minimum occurs is  $A_{\min} = 0.98$  Ry. These results, of course, are to be expected in the Einstein phonon approximation to

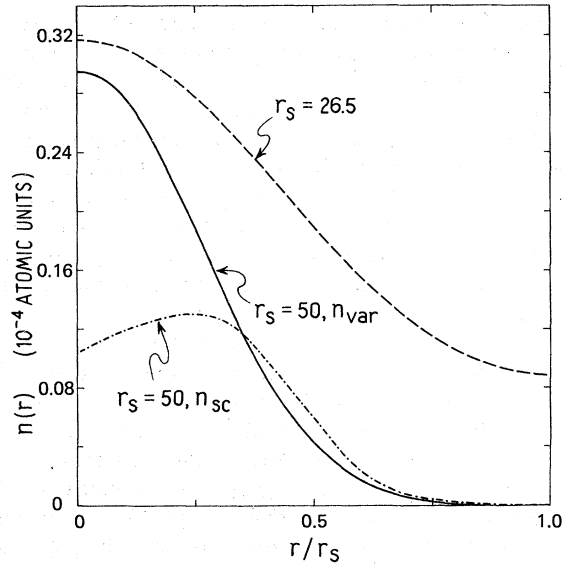


FIG. 1. Charge densities as a function of position in the Wigner-Seitz sphere. For  $r_s = 50$  both variational and self-consistent results are plotted. For  $r_s = 26.5$  the variational result is given.

which our method reduces by virtue of the cancellation of the electrostatic self-energy and the exchange-correlation energy. For comparison, the more realistic harmonic phonon approximation of Carr<sup>9</sup> gives  $-0.0283$  Ry for the ground-state energy at this density.

If we now iterate the calculation to self-consistency, we see both the virtues and vices of Eq. (2). The energy remains essentially the same, having a value of  $-0.0275$  Ry for the self-consistent solution. However, the charge density takes on the unphysical form plotted in Fig. 1. The reason

for this behavior can be traced to the local approximation for  $\epsilon_{xc}$ . Although the electrostatic self-energy and the exchange-correlation energy of the single electron cancel globally, the potentials due to these contributions do not cancel locally. This difficulty clearly illustrates the limitations of the local approximation and suggest the Wigner problem as a useful test for any proposed nonlocal corrections to  $\epsilon_{xc}$ .

Fortunately, these difficulties do not occur in the transition region where our chief interest lies. The location of the phase change can be investigated conveniently in terms of the parameter  $A_{\min}(r_s)$  at which an absolute energy minimum is found. These results are plotted in Fig. 2 where it is seen that a first-order transition occurs in the vicinity of  $r_s = 26$ . The electronic density in the nonuniform state near the transition point is shown in Fig. 1. Unlike the situation at  $r_s = 50$ , the self-consistent and variational charge densities differ by less than 10% near the transition, and are both monotonic.

The fact that the density at the edge of the Wigner-Seitz sphere in the nonuniform state is reasonably large suggests that the electrons are itinerant, i.e., a well-defined band structure exists. Thus, results based on a crystalline melting criterion would appear to be of doubtful validity. The picture of the transition that emerges is one of spontaneous growth of a charge-density wave.<sup>10</sup>

To examine this point in more detail, we consider the density response function of an electron gas whose energy is given by Eq. (1). It is straightforward to show that the static dielectric function for this case is

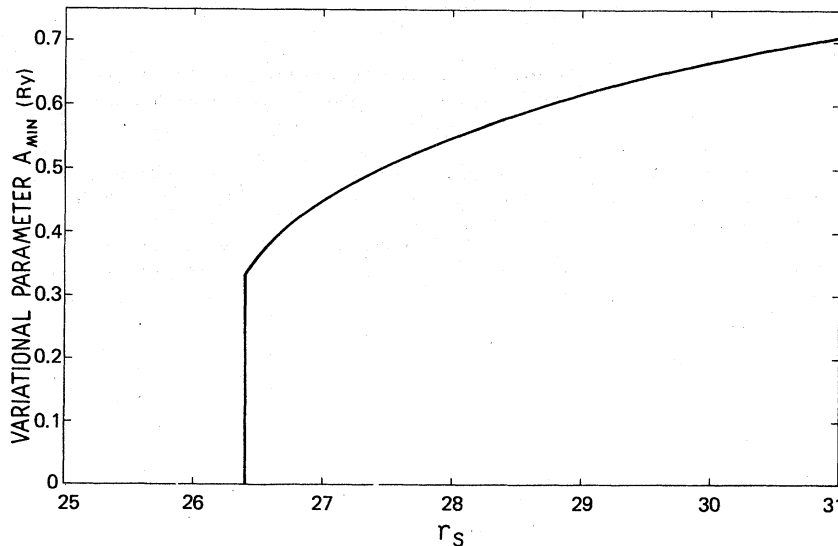


FIG. 2. Variational parameter as a function of  $r_s$ .

$$\epsilon(q) = 1 - \left( \frac{4\pi}{q^2} + \frac{d^2(n\epsilon_{xc})}{dn^2} \right) \chi_0(q), \quad (5)$$

where  $\chi_0(q)$  is the free-electron polarizability. Excluding the second term in the parentheses one recovers the random-phase approximation. The gas becomes unstable against small amplitude density fluctuations if  $\epsilon(q)$  has a zero for finite  $q$ . For our model this first occurs at  $r_s \approx 27$  which is close to the critical  $r_s$  found above. The  $q$  for this critical value of  $r_s$  is very close to  $q = 2k_F$ . One can imagine forming a periodic three-dimensional structure from intersecting planes of wave vector  $q$ . However, a primitive cell of this structure can contain a nonintegral number of electrons. For example, a simple cubic lattice with lattice wave vector  $2k_F$  contains  $\frac{1}{3}\pi$  electrons per unit cell. In our spherical-cell calculation, the number of electrons in the cell was restricted to unity; it is possible that the first-order character of the transition is a consequence of this restriction. A true band-structure calculation allowing arbitrary periodicity would enable one to investigate this possibility and, furthermore, to investigate the possibility of several incommensurate phases occurring near  $r_s = 26$ . In any event, we believe the location of the transition to be fairly reliable.

We should also point out the possibility of magnetic transitions in this system which could be studied similarly using the spin-density-functional formalism.<sup>11</sup> Since the low-density limit consists of one electron localized in each cell, the effect of local spin polarization should in principle be taken into account.

Our calculation indicated that the transition to the inhomogeneous state is of first order. It should be pointed out that this conclusion was

reached by using a mean-field approach to evaluate the parameter  $A_{\min}(r_s)$ ; the order of the transition may be changed if fluctuations are included. Furthermore, the low-density limit for  $\epsilon_{xc}$  was determined entirely by the requirement that the self-interaction terms for a single electron cancel. A calculation of  $\epsilon_{xc}(n)$  for an artificial homogeneous electron gas need not have the same low-density limit. Thus one cannot rule out the possibility that the order of the transition or the value of  $r_s$  at which it occurs, may be a consequence of the use of a *local* approximation for  $\epsilon_{xc}$ .

The system we have been discussing in this work is, unfortunately, mainly of academic interest, although there are said to be astrophysical occurrences of Wigner solids<sup>12</sup> and two-dimensional classical electron gases may crystallize.<sup>13</sup> In spite of this, we feel that this problem is worth solving for the insight it provides into the physics of the electron gas. Furthermore, it appears that an improved DF theory will undoubtedly play a role in finally resolving the details of the transition. The present calculation using this theory provides for the first time some interesting information about the nature of the ground state in the vicinity of the transition and suggests the possibility of studying other electronic transitions, such as the metal-insulator transition, using similar techniques.

#### ACKNOWLEDGMENTS

Two of us (H. B. S. and L. S.) would like to acknowledge partial support by the NSF under Grant No. DMR 77-11532 and No. DMR 74-12003, respectively.

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