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Note on the Electron Lattice*

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The question of the stability of Wigner's electron lattice, which is the ground state of a dilute electron gas, is considered. To determine the density range in which the electron lattice becomes unstable (coming from lower densities) a simple stability criterion is formulated. It is based on the notion that, in order for a solid structure to exist, the single particle potential should exhibit a localized well with at least one bound state. The disappearance of bound states with increasing density, marking the onset of melting in the model, is related to the possibility of defect formation. In this fashion an upper and a lower limit for the melting density can be established, which are found to occur at densities corresponding to $r_s \approx 47$ and $r_s \approx 100$, respectively (r_s is the radius of the unit sphere in Bohr units). Consequently, melting of the electron lattice is expected to take place at densities much lower than estimated previously.

I. INTRODUCTION

THE hypothetical electron gas consists of a large number N of electrons moving in a compensating uniform background of charge in a volume Ω. The electron density is usually expressed in terms of the dimensionless parameter r_s which is the radius (in Bohr units a_0) of the sphere representing the volume per particle, i.e., $\frac{4}{3}\pi(r_s a_0)^3=\Omega/N$.

Wigner[1,2] has argued that as the density tends to zero ($r_s \to \infty$) the Coulomb interactions will dominate the kinetic energy of the electrons, as a result of which these will arrange themselves in the configuration of lowest potential energy. This is a body-centered cubic (bcc) lattice.

In recent years there has been a renewed interest in the electron lattice and a number of authors[3–5] have given a detailed evaluation of the ground-state energy.

A question which has received little attention so far and which is the subject of this note is that of the range of densities for which the electron lattice represents the ground state of the electron gas. So far, two estimates have been given for the "melting density" at absolute zero, i.e., the density above which the lattice cannot exist and below which it forms the ground state. Both estimates lead to a melting density corresponding to $r_s \cong 20$. Nozières and Pines[6] arrive at this result by applying Lindemann's melting formula to the electron gas. Mott[7] finds the same number from a comparison of the energies of the lattice state and the metallic state. On the other hand, Carr[3] estimates the low-density region to extend up to densities corresponding to $r_s \cong 5$. The latter, however, is not claimed to be the melting density, but rather the density below which Carr's expression for the ground-state energy converges.

In this paper we introduce a simple stability criterion for the electron lattice. This stability criterion is related to the full problem of lattice stability and melting in somewhat the same fashion as the Einstein approximation is related to the full theory of lattice dynamics. The neglect of correlations is, of course, drastic if one wants to describe a phenomenon like melting, which can, in general, be characterized as the breaking down of long-range correlations. However, the situation in the electron lattice is peculiar in the following sense. As Wigner has pointed out, the fact that the lattice is the ground-state configuration at low densities is the result

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[1] E. P. Wigner, Phys. Rev. 46, 1002 (1934).

[2] E. P. Wigner, Trans. Faraday Soc. 34, 678 (1938).

[3] W. J. Carr, Jr., Phys. Rev. 122, 1437 (1961).

[4] R. A. Coldwell-Horsfall and A. A. Maradudin, J. Math. Phys. 1, 395 (1960).

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[6] P. Nozières and D. Pines, Phys. Rev. 111, 442 (1958).

[7] N. F. Mott, Phil. Mag. 6, 287 (1961).

of the long-range Coulomb interactions, which keep the electrons as far apart from each other as possible. But once the system is in the lattice configuration, the main part of the binding energy as well as of the force governing the electron motion, arise from the interaction of the electron with the background in its immediate vicinity. It can be shown (see the Appendix) that the spherical approximation, in which each electron is considered to reside in a spherical cell and in which all interactions between the cells are neglected, accounts for 99.5% of the electrostatic binding energy, while its result for the vibrational energy is too large by only 13% [viz. $3r_s^{-3/2}$ (Wigner) as compared to $2.65\ r_s^{-3/2}$ (Carr)]. It thus appears that an Einstein-type approximation, in which an electron moves in the average field of all the other electrons, as if these were at rest in their equilibrium positions, and of the background, is not at all a bad approximation at low densities. In the following it will be shown how such a model can be used to derive *limits* between which the real melting density should be expected to lie.

The stability criterion which is used for obtaining these limits relates melting to the disappearance of bound states for the individual electrons. A criterion which is in some repects similar has first been proposed by Mott[7] in connection with the transition between nonconducting and conducting states in metals and semiconductors.

The present stability criterion is based on the property of a solid, that the particles remain confined to small regions around fixed points in space. Thus, a solid arrangement may be characterized by the fact that the single-particle potential has a spatially localized well in which there exists at least one stable bound state. At densities where this condition is no longer fulfilled, i.e., when bound states disappear, no solid arrangement can exist.

The potential V which we have to consider for the stability of the electron lattice is, strictly speaking, not a single-particle potential. Although V depends explicitly on the position coordinate r of only one electron, it takes account of the formation of an interstitial-vacancy pair (crowdion-anticrowdion pair) for values of r outside the central cell ($r>r_s$). That is, through r, V implicitly depends on the coordinates of a number of other electrons.

In the present considerations, the defect formation for values of $r>r_s$ is shown to determine the bound states in the central well of the potential, i.e., for r values smaller than r_s. It is shown that a determination of the bound states in this way leads to a melting density somewhere in the range $r_s\approx 47$ to $r_s\approx 100$. Such a melting density is considerably lower than the estimates quoted above.

II. DEFECTS IN THE ELECTRON LATTICE

The volume Ω, occupied by the electron lattice, can be divided into N unit cells (Wigner-Seitz cells), centered around the N lattice points. Each electron carries out vibrations around the center of its individual cell. In the lowest approximation (Wigner[2]) the cells are considered as spherical (Wigner cells) and the dipolar interaction between the cells is neglected.

At extremely low densities, for $r_s\gtrsim 1000$ say, all electrons are well localized inside their Wigner cells. As the density is increased (r_s decreased) the extension of the wave function outside the cell increases and so does the probability for an electron to escape from its cell. If an electron can escape and settle elsewhere without breaking up the surrounding lattice, the electron density in the region around the interstitial electron is increased and that in the region around the vacancy is decreased. We can get an idea about the distance over which the influence of such a defect is felt, by evaluating the static dielectric constant of the electron lattice. An elementary calculation gives that the polarizability of an isolated Wigner cell is equal to R^3, where R is the radius of the sphere. It then follows from the Clausius-Mossotti relation that $\epsilon_{\text{static}}=-\infty$.[8] This means that the influence of a static electric disturbance is shielded over a very short distance. As a consequence, the regions affected by the defects, which result when an electron is displaced from its lattice site, will be quite small and they will not interact.

To avoid going into the details of the deformation of the lattice around such defects, we assume, for the calculation of the defect formation energy, that these regions are spherical and that the electron density in each of them is constant. Such a pair of defects will be called a crowdion-anticrowdion pair[9] (c–ac pair). We further assume that, as a result of the strong shielding, only the immediate neighbors of the interstitial and the vacancy are included in the crowdion and the anticrowdion. In the bcc lattice, which is the structure with the lowest electrostatic binding energy, an interstitial site has six immediate neighbors and so we assume that seven electrons participate in the crowdion, namely the intruder plus its six neighbors: $n_c=7$. In the anticrowdion the eight neighbors of the empty cell divide the extra volume, i.e., $n_{ac}=8$.[10]

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[8] The same result is obtained by taking the limit $\omega\to 0$ of the frequency dependent dielectric constant $\epsilon(\omega)$. One finds for a cubic arrangement of Wigner spheres with dipolar interaction

$$\epsilon(\omega)=1-3(\omega_0^2/\omega^2),$$

where $\omega_0^2=(e^2/mR^3)$ $(=\frac{1}{3}\omega_{\text{plasma}}^2)$ is the frequency of oscillation of an electron in an isolated Wigner sphere. The fact that ϵ is negative for $\omega<\omega_{\text{plasma}}$ is a result of the large polarizability of the Wigner sphere.

[9] The word "crowdion" has a well-defined meaning in the theory of lattice defects, indicating an interstitial, located in a closest packed row of a lattice [H. Paneth, Phys. Rev. **80**, 708 (1950)]. Here we mean a small region of the crystal in which the density is higher than average. An anticrowdion is the opposite.

[10] This simplified model for lattice defects has also been applied to solid α-He^3 to account for the anomalous specific heat and the self-diffusion. [F. W. de Wette, Phys. Rev. **129**, 1160 (1963).]

III. THE ENERGIES OF CROWDION AND ANTICROWDION

The formation energy of the crowdion-anticrowdion pair can be evaluated from $\epsilon(r_s)$, the energy per electron in the undisturbed lattice. The main contributions to $\epsilon(r_s)$ are the electrostatic binding energy and zero-point energy (cf. Ref. 3)

$$\epsilon(r_s) = -(1.792/r_s) + (2.65/r_s^{3/2}). \qquad (1)$$

We first evaluate the crowdion energy. Inside the crowdion the electron density is higher than the average electron density, but the background density ρ_b is unchanged. Since the r_s dependence of the zero-point energy [second term in (1)] is due to the background density, this term remains unchanged. In other words, the crowdion energy is purely electrostatic. There are two contributions to this energy, the first one is due to the electrostatic interactions inside the crowdion, and the second one is due to the interactions with the rest of the lattice. As a result of the strong shielding, the latter contribution may be evaluated as arising from a positive surface charge $\Delta\sigma$ on the crowdion surface, which shields the net negative charge of the crowdion (one electron charge) from the outside.[11] The electrostatic energy arising inside the crowdion is obtained as follows. Let the electron density in the crowdion correspond to $r_s + \Delta r_s (\Delta r_s < 0)$, then

$$-1.792/(r_s + \Delta r_s) \qquad (2)$$

is the electrostatic energy per electron in a crowdion with compensating background. But this takes into account too much background and we have to add the energy resulting from a negative charge density $\Delta\rho$, which reduces the background density again to ρ_b, i.e., $\Delta\rho = \rho_b - \rho_b^n$ (ρ_b^n is the background density which neutralizes the electron density inside the crowdion). The total crowdion energy can thus be found by using (2) and adding the total effect of the extra background density $\Delta\sigma + \Delta\rho$ (see Fig. 1). Hence, there are three terms to be added to (2), namely, the interaction energy of $\Delta\sigma + \Delta\rho$ with [1] the crowdion electrons, [2] the neutralizing background ρ_b^n, and [3] itself. A straightforward calculation, assuming spherical Wigner cells, leads to:

$$\text{contributions } [1]+[2] = -\frac{3}{5}\frac{1}{r_s + \Delta r_s}\,\text{Ry}, \qquad (3)$$

$$\text{contribution } [3] = \frac{1}{5 n_c^{1/3}(r_s + \Delta r_s)}\,\text{Ry}, \qquad (4)$$

where n_c is the number of crowdion electrons. Δr_s is determined by n_c, namely

$$r_s + \Delta r_s \simeq (1 - 1/3n_c) r_s = 0.952 r_s \quad \text{for} \quad n_c = 7. \qquad (5)$$

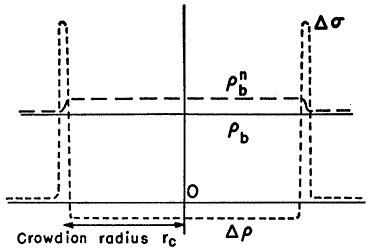

FIG. 1. Charge densities used in the calculation of the crowdion energy, plotted along a line through the center of the crowdion. The symbols are defined in the text.

The total crowdion energy E_c is the sum of n_c times (2), and (3)+(4). Finally, the crowdion formation energy ΔE_c is the difference between E_c and the energy of n_c electrons in the undisturbed lattice (which is $-1.792\, n_c r_s^{-1}$). Using $n_c = 7$, we find

$$\Delta E_c = \frac{0.108}{r_s}\,\text{Ry}. \qquad (6)$$

The energy of the anticrowdion is found by similar arguments. $\Delta\rho$ is then positive inside and $\Delta\sigma$ represents the surface density equal to one smeared-out electron charge. The formulas (2) and (4) remain unchanged but (3) has the opposite sign, due to the changed sign of $\Delta\rho$. Instead of (5) we have

$$r_s + \Delta r_s \simeq [1 + (1/3n_{ac})] r_s = 1.042 r_s \quad \text{for} \quad n_{ac} = 8. \qquad (7)$$

Using $n_{ac} = 8$, we find

$$\Delta E_{ac} = 0.094/r_s\ \text{Ry}. \qquad (8)$$

Since there is no interaction between crowdion and anticrowdion, the formation energy of the pair is simply the sum of the separate formation energies, i.e.,

$$\Delta E = \Delta E_c + \Delta E_{ac} \cong 0.2/r_s\ \text{Ry}. \qquad (9)$$

IV. THE STABILITY CRITERION

As mentioned in the Introduction, we will introduce a simple stability criterion, which will enable us to indicate an upper and a lower limit, between which the real melting density of the electron lattice should lie. This criterion relates the stability of the electron lattice to the existence of bound states for an electron in a single-particle potential $V(r)$, which is thought to be centered around a lattice point. A logical choice is to take for $V(r)$ the potential energy of the static lattice, expressed as a function of the position coordinate r of one electron. For $r < r_s$ (electron inside its cell) $V(r)$ coincides, for all practical purposes, with the potential energy of an electron in its isolated Wigner cell [i.e., $V(r)$ quadratic in r], while for $r > r_s$ (electron outside its cell) $V(r)$ contains the effect of the crowdion-anticrowdion formation. This means that through r, $V(r)$ implicitly depends on the rest-positions of those

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[11] This positive surface charge represents the effect of the slight outward shift of the lattice electrons surrounding the crowdion, which is caused by the negative crowdion charge.

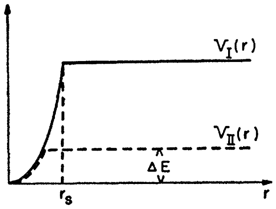

FIG. 2. Solid line: potential energy function $V_{\rm I}(r)$ for the determination of the absolute upper limit to the melting density. Dashed line: $V_{\rm II}(r)$ for the determination of the lower limit to the melting density.

other electrons, which are involved in the crowdion and the anticrowdion. Thus, $V(r)$ exhibits a central well, which is responsible for localizing the electron, and it has as yet an unspecified form for $r>r_s$. Obviously, the form of V for $r>r_s$ is of crucial importance for the lattice stability, because it is this form that determines the existence and the energies of the bound states inside the central part of $V(r)$. The estimates for the upper and lower limits for the melting density are now obtained by successively making two extreme assumptions for the shape of $V(r)$ in the range $r>r_s$.

Upper Limit

The upper limit, i.e., the density above which the electron lattice will certainly not exist, is obtained when we estimate the density above which a bound state for an electron in its Wigner cell cannot exist, disregarding the crowdion-anticrowdion formation for $r>r_s$. For this estimate we use a potential $V_{\rm I}(r)$, which is the one-electron parabolic potential inside the cell ($r<r_s$), and which is cut off flat outside, i.e., $V_{\rm I}(r)=V_{\rm I}(r_s)$ for $r>r_s$ (see Fig. 2, solid line).

For a crude estimate of the condition for the existence of a bound state in this potential, we make a comparison with the square-well potential. A spherical well with radius ρ (in Bohr units a_0) and depth U (in Ry) has at least one bound state if

$$U\rho^2 \geqslant \tfrac{1}{4}\pi^2. \tag{10}$$

The quantity $U\rho^2$ is proportional to the volume of the cylinder with radius ρ and depth U. In a similar fashion, the criterion for the existence of a bound state in a truncated parabolic well can be expressed as

$$\text{Volume paraboloid} \geqslant \tfrac{1}{4}\pi^3 C, \tag{11}$$

where the constant C is nearly one.

The zero-point energy of 2.65 $r_s^{-3/2}$ per particle, given by (1), corresponds to an oscillatory well described by

$$V(r)=0.780r^2r_s^{-3}. \tag{12}$$

The radius at the top of the truncated paraboloid is r_s. Using these numbers in (11) (taking $C=1$) we find that the Wigner cell exhibits a bound state for

$$r_s \geqslant 6.33.$$

We notice that this limiting r_s is about the same as the one Carr estimates to limit the range of validity of his expression for the ground-state energy.

Lower Limit

A lower limit for the melting density may be estimated by making another extreme assumption about the form $V(r)$ for $r>r_s$. Let us suppose that the electron gives up all of its vibrational energy and moves freely through the lattice after is has left its cell and created a crowdion-anticrowdion pair. Then the potential $V(r)$ approaches the constant value $V(0)+\Delta E$ for values of r larger than the sum of the crowdion and the anticrowdion radii (r_c+r_{ac}). $V(0)$ is the value of V in the origin of the central well, and $\Delta E=0.2r_s^{-1}$ is the defect formation energy. The shape of $V(r)$ in the intermediate region $r_s<r<r_c+r_{ac}$ is not known. However, we will certainly obtain a *lower* limit to the melting density, if we evaluate the density at which a bound state ceases to exist, for a potential $V_{\rm II}(r)$, which consists of a parabolic well given by (12), which is cut off flat at the height $\Delta E=0.2r_s^{-1}$ (see Fig. 2, dashed line). The radius at the top of the well so obtained is $0.506r_s$. Using these numbers in (11), we find that the well will have a bound state if

$$r_s \geqslant 96.5.$$

A More Detailed Estimate of the Upper Limit

The upper and lower limits for the melting density which we have just estimated, are quite far apart. In particular, the high-density limit seems rather high, although the low-density expression for the ground-state energy seems to be valid up to such a density.[3] However, we will show that a more detailed consideration of the form of the effective single-particle potential $V(r)$ in the region $r>r_c+r_{ac}$ leads to a considerably lower estimate for the high-density limit.

The form of $V(r)$ for $r>r_c+r_{ac}$ is, of course, representative of the motion of the electron outside its cell, or rather, of the crowdion motion, since r is a configurational coordinate. In this connection there are two kinds of crowdion motion that have to be mentioned. First, the *interstitial* motion in which one and the same electron moves from one interstitial position to the other, and second, the *interstitialcy* motion, in which an interstitial electron occupies a lattice site while pushing the electron residing there into a different interstitial position. A mechanism similar to the latter is also responsible for the motion of the anticrowdion.

Since we are considering an effective single-particle potential, only the first kind of motion, the interstitial motion, can be treated. However, this limitation does not invalidate the ensuing estimate, because, since the activation energy for the interstitialcy motion is bound to be smaller than that for the interstitial motion, the effect of taking the former mechanism into account would be to further lower the upper limit. On the same grounds the anticrowdion motion can be left out of account.

In order to make a reasonable choice for $V(r)$ in the region $r>r_c+r_{ac}$, we notice that in contrast to what we assumed for deriving the lower limit, an electron does not give up all of its zero-point energy when it moves out of its cell. This is a result of the fact that even in an interstitial position, the electron has a certain amount of background to its own, which causes it to vibrate around the interstitial equilibrium position. In other words, the interstitial electron finds itself again in a parabolic potential, giving rise to the same vibration frequency (because the background density is unchanged), the minimum of which lies an amount ΔE higher than the minimum $V(0)$ of the central well.

Next we have to consider the interstitial motion. The interstitial electron may move, with more or less ease, to neighboring interstitial positions. As a result, the interstitial electron "sees" a periodic potential of parabolic wells in the directions of the neighboring interstitial positions (see Fig. 5). This causes the zero-point energy of the interstitial electron to be broadened into a band, the width of which will be density dependent: the higher the density, the broader the band. Let us express the lowest energy in this band as $2.65r_s^{-3/2}\gamma(r_s)$. At a certain density the bottom of this band will become lower than the zero-point energy of the electron in the central well. At this density the localized state of the electron around its lattice position ceases to be a stable state. Thus, we may formulate our stability criterion as follows: the electron lattice is only stable for densities such that

$$\frac{2.65}{r_s^{3/2}} \leqslant \frac{2.65}{r_s^{3/2}}\gamma(r_s)+\Delta E(r_s). \tag{13}$$

At densities for which this condition is not fulfilled, the electron will eventually escape from its cell and diffuse through the lattice, moving from one interstitial position to another. Since this is true for all electrons in the system, the lattice will obviously not exist at such densities.

In order to determine the function $\gamma(r_s)$, we have to examine in some detail the interstitial potential field. An interstitial position in a bcc lattice has four first-neighbor interstitial positions located at a distance l in two mutually perpendicular directions, and eight second-neighbor interstitial positions at a distance $\sqrt{2}l$ in four directions which are perpendicular in pairs (directions in different pairs are at 60° angles), and which are at 45° angles with the first-neighbor directions (see Fig. 3). For the present estimate it is a reasonable approximation to assume that the three-dimensional interstitial field is additive in x, y, and z, and that as a function of each of these coordinates it is a periodic function of parabolic wells. If we take the x and y directions to point to the first-neighbor interstitial sites, then the positive z direction points to an occupied lattice site, but one that is surrounded by four second-neighbor interstitial sites. The approximation thus amounts to replacing these four interstitial sites at distance $\sqrt{2}l$ by a single one at distance l. This model, therefore, underestimates the mobility of the interstitial electron, which in turn leads to a calculated melting density which is higher than the real one. Consequently, we are again led to an *upper* limit for the melting density.

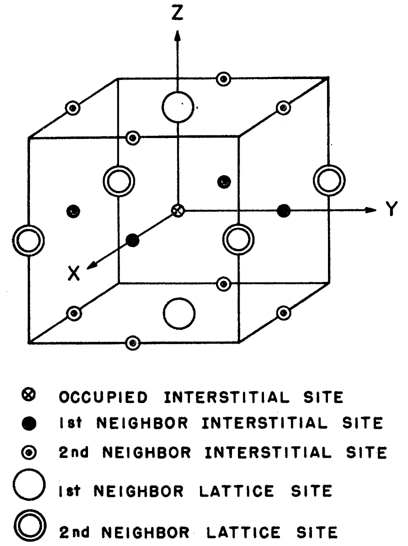

FIG. 3. Interstitial sites and lattice sites surrounding an occupied interstitial site in the bcc lattice.

Another question is whether the lattice electrons, surrounding the interstitial will move out of the way and thereby increase its mobility. Such displacements can be evaluated by direct computation of the polarization of the lattice around the interstitial. The result is that the two first lattice neighbors of the interstitial (in the z direction; cf. Fig. 3) will move out over a distance of about $0.4a$, while the four second lattice neighbors (in the x–y plane) will move out over a distance of about[12] $0.044a$ (a is the nearest neighbor distance in the bcc lattice). The outward displacement of the first lattice neighbors indicates that the lattice opens up around the interstitial as it moves along. Since this enhances its mobility, it further lowers the melting density of the real lattice. Therefore, neglecting this effect does not affect the upper limit derived from our model.

We can now proceed to determine the function $\gamma(r_s)$ appearing in (13). The assumption of additivity for the three-dimensional interstitial potential field reduces the problem to three one-dimensional ones. This enables us to use McColl and Simpson's[13] result for the one-dimensional periodic parabolic potential, to evaluate

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[12] This rapid decrease in the outward displacement from first to second neighbors is a result of the very effective shielding in the electron lattice, or, in other words, of its high dielectric constant. This is a direct justification for the assumption that the crowdion only extends to the six direct neighbors of the interstitial (cf. Sec. II).

[13] D. McColl and O. C. Simpson, Argonne National Laboratory Report ANL-6647 (unpublished).

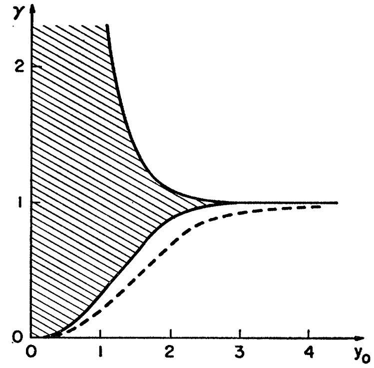

FIG. 4. Plot of the function $\gamma(y_0)$ for the periodic parabolic potential (lower solid line). For comparison, we have indicated the width of the zero-point band (shaded area), and the bottom of the zero-point band for the sinusoidal potential (dashed line). The symbols are defined in the text.

the lowest energy of the zero-point band as a function of the periodicity distance l. In Fig. 4 we have plotted $\gamma = E/\frac{3}{2}\hbar\omega$, i.e., the lowest energy in the zero-point band of an electron in the additive three-dimensional parabolic potential, divided by the unperturbed oscillator energy $\frac{3}{2}\hbar\omega$, as a function of the quantity $y_0 = \frac{1}{2}(m\omega/\hbar)^{1/2}l$ (lower solid line in Fig. 4). For comparison we have also plotted the same quantity (dashed line) for the periodic sinusoidal potential (Mathieu problem) which has the same curvature in the bottom of the well (i.e., the same ω). This problem was treated by Slater.[14] The r_s dependence of $\gamma(y_0)$ follows from that of y_0. The vibration energy of $2.65r_s^{-3/2}$ per electron leads to: $\omega = 0.883em^{-1/2}(a_0r_s)^{-3/2}$ (e and m are the electron charge and mass). Further, for the distance between the interstitial positions in the bcc lattice one finds $l = 1.02a_0r_s$.

All quantities in (13) can now be evaluated as functions of r_s. We then find that the inequality (13) is fulfilled for $r_s \gtrsim 47$. This should be, as we have argued, on upper limit for the melting density. Combining this with our result for the lower limit, our conclusion is that the electron lattice will not exist for densities for which $r_s \lesssim 47$, and that it will certainly exist for densities corresponding to $r_s \gtrsim 97$.

In Figs. 5(a) and (b) we have indicated how the zero-point band in the interstitial periodic parabolic potential is located with respect to the zero-point energy in the central well, for $r_s = 25$ and $r_s = 75$, respectively. We see that, according to our criterion, the lattice is not stable for $r_s = 25$, but that it can be stable for $r_s = 75$.

At this point we would like to re-emphasize the main point of this paper. Thanks to the fact that we used a simplified model for the solid, it has been possible to indicate *limits* for the real melting density. Of course, a reliable determination of this quantity itself would require a full-fledged many-body approach. That one can actually indicate these limits is a result of the fact that, whatever the real mechanism that is responsible for the melting, the criteria used here do pose a real limitation on the actual melting density. For instance, the states corresponding to single particles traveling through the lattice, which were used here for finding the upper limit, should be very close to possible states of the real system and as a result pose a limitation on the range of densities in which the real lattice is stable.

V. DISCUSSION

The electron gas has the rather peculiar property that at absolute zero it can occur in both the fluid and the solid phase, depending on the density.[15] In this paper, we have been concerned with determining the density range in which the solid phase is the ground state, i.e., the density range in which the electron lattice is stable. This we call the low-density region of the electron gas. As mentioned before this is not the same as the density region in which the expression for the energy of the lattice configuration (Carr[3]) converges and is a good approximation to the actual ground-state energy. While we find the low-density region to start for an r_s value somewhere between 47 and 100, the lattice expression

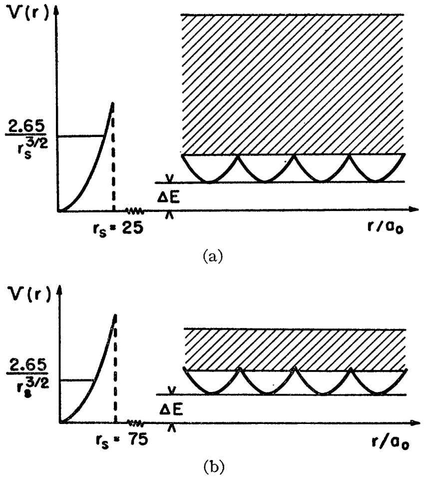

FIG. 5. Potential energy $V(r)$ for one electron in the static electron lattice (r is directed along the axis of one of the coordinates in which the potential is assumed to be separable). For $r<r_s, V(r)$ represents the central well (in this region r is strictly a one-electron coordinate). For $r \gg r_s, V(r)$ represents the periodic potential in the interstitial positions (in this region r is a configuration coordinate). The potential has not been drawn in the region immediately outside the central cell. Its form there is uncertain because of the overlap of the crowdion and the anticrowdion in that region. (a) Situation for $r_s = 25$. The bottom of the zero-point band lies below the zero-point level in the central well. The lattice is not stable. (b) Situation for $r_s = 75$. The bottom of the zero-point band lies above the zero-point level in the central well. The lattice can be stable [The scales along the abscissa and the ordinate are different in (a) and (b)].

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[14] J. C. Slater, Phys. Rev. **87**, 807 (1952). The curve for the sinusoidal potential lies below that for the periodic parabolic potential because in the latter potential the walls, separating neighboring wells, are higher.

[15] The only real substance showing this property is helium. In contrast to the electron gas, helium is solid at high densities and liquid at low densities.

for the ground-state energy is probably an excellent approximation for r_s values from 10 up. The reason for this is that the existence of long-range order, which is characteristic for a lattice configuration, does not affect the energy too much. This can easily be shown to be the case for the electrostatic binding energy, which gives the largest contribution to the ground-state energy. The exact value of this quantity in the bcc lattice is $-1.792r_s^{-1}$ Ry per particle. In the Appendix we show that by taking an isolated spherical cell, thus completely neglecting long-range order, one finds $-1.800r_s^{-1}$ for this quantity. It should be emphasized that the difference between these numbers represents the influence of the long-range order only. The use of a spherical cell is justified only when the immediate surrounding of the actual cell is highly symmetric, and this is only the case when there is complete local order. The fact that both numbers differ so little shows how insensitive the electrostatic binding energy is to long-range order. In a similar fashion it may be possible to show that local coupling of the vibrational motions (thus again neglecting long-range order) will lead to a value for the vibrational energy per particle, which is closer to $2.65r_s^{-3/2}$ [cf. (1)] than the value $3r_s^{-3/2}$, which is obtained by Wigner's method in which all dipole coupling between the cells is neglected.

One conclusion to be drawn here, which is already implied in the foregoing, is that it will be very difficult to make any prediction about the density at which the electron lattice becomes the ground-state configuration, from a consideration of the ground-state energy. A second, closely related conclusion is, that it will be impossible to derive the lattice ground state from first principles by using a variation procedure in which the density is varied.

At this point the method and the results of the present work should be compared with the two other estimates of the melting density of the electron lattice, which are available in the literature. With regards to Nozières and Pines' estimate, it has been pointed out (Ref. 3) that the applicability of the empirical Lindemann melting formula to the electron lattice remains something to be established, and that an estimate based on it is subject to rather large uncertainties. On the other hand, Mott's estimate is based on a comparison of the lattice energy with the Hartree energy, in a range of densities ($r_s \cong 20$) in which the Hartree approximation is not at all valid. Moreover, as we have argued, the ground-state energy is not a good quantity to consider, for the purpose of determining the melting density.

The main assumption underlying the present considerations is that a meaningful limitation of the actual melting density can be obtained from a model in which melting is pictured as a single-particle process, whereas the real melting process is, of course, probably a cooperative effect. We believe that the single-particle picture is in this particular case justified by the fact that in the lattice configuration at low densities, the main force on an electron arises, not from the other electrons, but from the positive background in its immediate vicinity.

Finally, it should be remarked that the neglect of particle statistics implies that these considerations are equally valid for a system of charged bosons (see Foldy[16]). The question arises whether the inclusion of statistics would invalidate the present results. Carr[3] has shown that the effects of statistics enter the energy expression in overlap terms proportional to exp $(cr_s^{1/2})$, which are found to be completely negligible for $r_s > 10$. This suggests that at $r_s \approx 50$ the effects of overlap and exchange are much too small to alter the effective single-particle potential in such a way as to invalidate the results obtained from it.

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APPENDIX

The Binding Energy of the Static Electron Lattice

The total potential energy of the static electron lattice is

$$\mathcal{V}^{(1)}=\frac{e^2}{2}\sum_i\sum_{j\neq i}\frac{1}{|\mathbf{R}_i-\mathbf{R}_j|}-e^2\rho\sum_i\int\frac{d\mathbf{r}}{|\mathbf{r}-\mathbf{R}_i|}+\frac{e^2\rho^2}{2}\int\int\frac{d\mathbf{r}d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}. \qquad \text{(A1)}$$

e is the electronic charge, ρ is the number density and $\mathbf{R}_i$ and $\mathbf{R}_j$ are electron coordinates. The first term is the electron-electron interaction, the second term is the electron-background interaction, and the third term is the background-background interaction. For an infinite system, the background-background interaction cancels half of the electron-background interaction, so that $\mathcal{V}$ may also be written as

$$\mathcal{V}^{(2)}=\frac{e^2}{2}\sum_i\sum_{j\neq i}\frac{1}{|\mathbf{R}_i-\mathbf{R}_j|}-\frac{e^2\rho}{2}\sum_i\int\frac{d\mathbf{r}}{|\mathbf{r}-\mathbf{R}_i|}. \qquad \text{(A2)}$$

The energy which is gained by adding the last electron to the lattice is

$$e^2\sum_{j\neq i}\frac{1}{|\mathbf{R}_i-\mathbf{R}_j|}-e^2\rho\int\frac{d\mathbf{r}}{|\mathbf{r}-\mathbf{R}_i|}=\frac{2\mathcal{V}^{(2)}}{N}. \qquad \text{(A3)}$$

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[16] L. L. Foldy, Phys. Rev. 124. 649 (1961).

This is the expression that is summed over the lattice (bcc) to obtain an accurate value for $\mathcal{V}/N$, the electrostatic binding energy per electron.

Wigner's Approximation for Obtaining $\mathcal{V}/N$

Wigner[2] uses the expression (A2) as a starting point for his approximation. The entire volume Ω is divided into N unit cells, which are centered around the N lattice points. The integral in (A2) can then be written as a sum of integrals over the cells j. We have

$$\mathcal{V}^{(2)}=\sum_i \mathcal{V}_i^{(2)}=N\mathcal{V}_i^{(2)}, \tag{A4}$$

where

$$\mathcal{V}_i^{(2)}=\frac{e^2}{2}\sum_{j\neq i}\left(\frac{1}{|\mathbf{R}_i-\mathbf{R}|}-\rho\int_{\text{cell}\,j}\frac{d\mathbf{r}}{|\mathbf{r}-\mathbf{R}_i|}\right)-\frac{e^2\rho}{2}\int_{\text{cell}\,i}\frac{d\mathbf{r}}{|\mathbf{r}-\mathbf{R}_i|}. \tag{A5}$$

The first term in (A5) is small. It is the difference between the interaction of the central electron i with the other electrons j and the interaction of electron i with the positive background in the cells j. If the cells were spherical, this contribution would vanish. For nonspherical cells the field at electron i due to the background in cell j can be considered to result from an infinite series of higher multipoles in the center of cell j. The net background charge of cell j is cancelled by the charge of the electron j. The first term of (A5) thus represents one-half of the binding energy of electron i in a lattice which has at each site a series of higher multipoles. In a cubic lattice like the bcc lattice, the lowest multipoles that are compatible with the cubic symmetry are the hexadecapoles. Hence, in the first approximation going beyond the spherical approximation, the first term of (A5) is half the energy of an electron in a lattice of hexadecapoles.

In Wigner's approximation of spherical cells, the first term of (A5) is neglected and the second term is a simple integral over a sphere. The result is

$$\mathcal{V}_i^{(2)}(\text{spher. cells})=-1.5r_s^{-1}\ \text{Ry}. \tag{A6}$$

The exact result, obtained by direct summation of (A5) over a bcc lattice, is

$$\mathcal{V}_i=-1.79186r_s^{-1}\ \text{Ry}. \tag{A7}$$

Improved Spherical Approximation for Obtaining $\mathcal{V}/N$

The starting point for this approximation is (A1) instead of (A2). Again we write the integrals in (A1) as sums of integrals over the cells. We have as in (A4)

$$\mathcal{V}^{(1)}=\sum_i \mathcal{V}_i^{(1)}=N\mathcal{V}_i^{(1)}, \tag{A8}$$

where now

$$\mathcal{V}_i^{(1)}=\frac{e^2}{2}\sum_{j\neq i}\left(\frac{1}{|\mathbf{R}_i-\mathbf{R}_j|}+\rho^2\int_{\text{cell}\,i}\int_{\text{cell}\,j}\frac{d\mathbf{r}_i d\mathbf{r}_j}{|\mathbf{r}_i-\mathbf{r}_j|}-2\rho\int_{\text{cell}\,j}\frac{d\mathbf{r}_j}{|\mathbf{r}_j-\mathbf{R}_i|}\right)-e^2\rho\int_{\text{cell}\,i}\frac{d\mathbf{r}_i}{|\mathbf{r}_i-\mathbf{R}_i|}+\frac{e^2\rho^2}{2}\iint_{\text{cell}\,i}\frac{d\mathbf{r}_i d\mathbf{r}_i'}{|\mathbf{r}_i-\mathbf{r}_i'|}. \tag{A9}$$

The first term in (A9) is small. By arguments similar to those above, it can be shown that in a cubic crystal this term represents, in the first approximation beyond the spherical approximation, half the binding energy of a hexadecapole in a hexadecapole lattice. For spherical cells this contribution vanishes. The second and third term in (A9) give for spherical cells the contribution

$$\mathcal{V}_i^{(1)}(\text{spher. cells})=-1.8r_s^{-1}\ \text{Ry}. \tag{A10}$$

Although this result is also obtained with a spherical approximation, as was (A6), it comes surprisingly close (within 0.45%) to the exact result (A7). Wigner's result (A6) is off by 17%. The reason for this improvement is, that the term that is neglected in the spherical approximation, namely the first term in the expression for $\mathcal{V}_i$, is much smaller in (A9) than in (A5).

Summarizing this result, we can say that the electrostatic binding energy is mainly the result of the fact that the electrons are localized, which makes that each electron is bound by the positive background in its individual cell. The existence of long range order in the lattice is seen to have only a very minute influence on this binding energy. One therefore expects the contribution $-1.792r_s^{-1}$ to be a very good approximation to the electrostatic binding energy, also at those densities for which the ground state is no longer a lattice but a fluid in which the electrons are still localized and in which local order is still present.