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Energy, Specific Heat, and Magnetic Properties of the Low-Density Electron Gas

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A perturbation expansion in powers of $r_s^{-\frac{1}{2}}$ has been used to investigate the ground-state energy of a dilute electron gas, the result being, in rydberg units per particle, $E=-1.792/r_s+2.66/r_s^{\frac{3}{2}}+b/r_s^2+O(1/r_s^{5/2})$ +terms falling off exponentially with $r_s^{\frac{1}{2}}$. The dimensionless parameter r_s is the radius of the unit sphere in Bohr radii. The term in r_s^{-1} is the energy of a body-centered cubic lattice of electrons as calculated by Fuchs; the $r_s^{-\frac{3}{2}}$ term is the zero-point vibrational energy of the lattice, as obtained from a calculation of the normal modes, the result differing only by a small amount from the values estimated by Wigner; and br_s^{-2} is the first-order effect of anharmonicities in the vibration. The constant b has been estimated, its magnitude being smaller than unity.

The vibrational part of the specific heat has been calculated, and a first-order approximation has been obtained for the exponential terms in the energy. Part of this energy comes from exchange, which leads to the result that, except for very low densities ($r_s\gtrsim 270$), the electron spins are antiferromagnetically aligned. An order of magnitude for the Néel temperature has been calculated.

INTRODUCTION AND SUMMARY

An electron gas, as conceived by Wigner,[1] consists of a large number of electrons moving in a uniformly spread out positive charge having the density required to give the system charge neutrality. For many purposes the model is useful as an approximation to the solid state.

A convenient measure of the electron gas density is the dimensionless parameter r_s, defined as the radius of the unit sphere divided by the Bohr radius, the unit sphere enclosing a volume equal to the volume per electron of the gas.

Although properties may be calculated both for the high-density ($r_s\ll 1$) and low-density ($r_s\gg 1$) cases, the greatest attention has been given the high-density problem, and recently Gell-Mann and Brueckner[2] have given an exact treatment for the energy in this region. The direct applicability of this result to the study of solids is questionable since most frequently the intermediate range of r_s is of interest; for example, in the alkali metals r_s varies between 3 and 6, which might seem to correspond more closely with the low-density case to be considered here. In general, the intermediate case requires an interpolation between high- and low-density results, and the existence of an exact expression for the former indicates the need for a likewise exact formulation of the latter. Wigner[1] first considered the dilute electron gas problem and pointed out that in the limit $r_s\rightarrow\infty$ where the kinetic energy becomes negligible, the Coulomb interactions dominate in determining the wave function and the electrons tend to arrange themselves in a regular lattice with energy proportional to r_s^{-1}. Wigner also made an estimate of the correction to the energy due to the oscillatory motion of the electrons about their lattice points, the result being 3 $r_s^{-\frac{3}{2}}$ ry per particle. As Wigner's approximations suggest, the exact expression for the energy, E, involves an expansion in powers of $r_s^{-\frac{1}{2}}$. In the third section the lattice formation is discussed, and in the fourth section this expansion is carried out. The following is a summary of the present calculations and of the principal results obtained: The Hamiltonian, H, consists of the kinetic energy of the electrons and the Coulomb interactions of the system. If Ψ_n is a set of states for the N electrons and A is the operator which projects the antisymmetric part of Ψ_n ($A=\sum_\nu\pm P_\nu$, where P_ν is a permutation operator), the matrix elements of $H-E$ are $(N!)^{-1}\int(A\Psi_n^*)(H-E)A\Psi_m d\tau$, with the integral denoting an integration and summation over all space and spin coordinates of the N electrons. In the present case the antisymmetrized functions are not orthogonal. Since H is symmetric, the elements become $\int\Psi_n^*(H-E)A\Psi_m d\tau$, which can be written $\int\Psi_n^*(H_{\text{eff}}-E)\Psi_m d\tau$, with $H_{\text{eff}}=HA-E\times(A-1)$; i.e., in a formal sense the matrix representing $H-E$ in terms of the nonorthogonal antisymmetrized functions is the same as that representing $H_{\text{eff}}-E$ in terms of the orthogonal nonantisymmetrized functions. For a perturbation calculation the latter is somewhat more convenient. In the present problem the electrons are almost distinguishable and $A-1$ may be expected to affect the energy only in a perturbative way. If $(H-E)(A-1)$ is called the exchange Hamiltonian, then $H_{\text{eff}}=H+H_{\text{ex}}$. Next, let

$$H_{\text{eff}}=H_{\text{series}}+H',\tag{1}$$

where $H'=H-H_{\text{series}}+H_{\text{ex}}$, and H_{series} indicates the Hamiltonian obtained by expanding the potential energy in a Taylor series in powers of displacements of the electrons from a set of lattice points. An exact solution for the eigenvalues of H_{series} is obtained as a power series in $r_s^{-\frac{1}{2}}$ (assuming this series to possess some manner of convergence) and the H' is treated as a perturbation, it being understood that in each order the energy term in H' is replaced by an approximation from the previous order.

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[1] E. Wigner, Trans. Faraday Soc. **34**, 678 (1938).

[2] M. Gell-Mann and K. A. Brueckner, Phys. Rev. **106**, 364 (1957).

In first-order perturbation the ground-state energy is

$$E=E_0+\langle H'\rangle=E_0+\langle H-H_{\text{series}}\rangle+\langle H_{\text{ex}}\rangle, \tag{2}$$

where E_0 is the ground state of H_{series}. The first term in E_0 is just the energy of a lattice of electrons in a background of positive charge, which according to Fuchs[3] is $-1.79186\ r_s^{-1}$ ry per particle for a body-centered cubic lattice. In agreement with Wigner, it is assumed that the bcc lattice has the lowest energy, although the difference between it and other simple lattices is extremely small. The next nonvanishing terms in H_{series} are quadratic in the electron coordinates. By means of a normal coordinate transformation, these terms together with the kinetic energy operators give a sum of oscillator Hamiltonians. The frequencies for these electronic lattice vibrations, or phonons, have been calculated for 512 points in the Brillouin zone, and by numerical integration $2.66\ r_s^{-\frac{3}{2}}$ ry is obtained for the zero-point energy.[4] The remaining terms in H_{series} are treated as a perturbation on the oscillator functions, giving energy terms proportional to r_s^{-2}, $r_s^{-\frac{5}{2}}$, etc.

As r_s approaches infinity, the matrix elements of H', calculated with eigenfunctions of H_{series} multiplied by a spin function, approach zero exponentially with $r_s^{\frac{1}{2}}$, giving some justification for treating H' as a perturbation. Thus the energy may be written

$$E=\frac{-1.792}{r_s}+\frac{2.66}{r_s^{\frac{3}{2}}}+\frac{b}{r_s^{2}}+O(1/r_s^{\frac{5}{2}})$$
$$+\text{terms falling off exponentially with } r_s^{\frac{1}{2}}. \tag{3}$$

The exact expression for the constant b is given in Appendix II. A rough numerical estimate shows it to be less than unity and therefore the term has only a small effect on the energy.

An estimate of the exponential terms in the energy may be obtained from the first-order term $\langle H'\rangle$. Since an exact evaluation of this integral is difficult the following approximation has been made. The unperturbed wave function, itself a perturbation series, is approximated by the first term in the series, which is a product of oscillator functions in the normal coordinates. This function in turn is approximated by setting all the frequencies equal. The resulting expression describes a set of electrons oscillating independently about their lattice points. (This "Einstein model" is in fact the wave function used by Wigner for the zeroth order $r_s^{-\frac{3}{2}}$ term, and gives for that case a coefficient only ten percent higher than the correct result.) The value of $\langle H-H_{\text{series}}\rangle$ per particle in this Einstein approximation is $\simeq 4.55 r_s^{-1}[P(1.25 r_s^{\frac{1}{4}})-1]+3.94 r_s^{-1}[P(1.44 r_s^{\frac{1}{4}})-1]$, with $P(x)$ the probability integral, which for large x differs from unity by a factor proportional to $\exp(-x^2)$. The quantity $\langle H-H_{\text{series}}\rangle$ is not zero because of the fact that the series expansion for the Hamiltonian does not converge for large displacements from the lattice points and gives only approximate values for the matrix elements.

The evaluation of $\langle H_{\text{ex}}\rangle$, still in the independent-oscillator approximation, may be given, for large r_s, in terms of exchange integrals,[5] the sign of which determines whether the lattice is ferromagnetic or antiferromagnetic. Although the result indicates ferromagnetism as $r_s \to \infty$, it occurs only for values so large that the Curie temperature (strength of the coupling) is infinitesimal. For values of r_s of physical interest, the above approximation gives an antiferromagnetic ground state. A rough estimate of the Néel temperature for large r_s is

$$\theta\sim 1.6\times 10^5[(13 r_s^{-1}-3.2 r_s^{-\frac{3}{4}})\exp(-1.55 r_s^{\frac{1}{2}})$$
$$-(10.5 r_s^{-1}-2.4 r_s^{-\frac{3}{4}})\exp(-2.06 r_s^{\frac{1}{2}})], \tag{4}$$

in degrees Kelvin.

With exponential terms included, the ground-state energy becomes

$$E\simeq\frac{-1.792}{r_s}+\frac{2.66}{r_s^{\frac{3}{2}}}+\frac{b}{r_s^{2}}+\cdots+\left(\frac{21}{r_s}-\frac{4.8}{r_s^{\frac{3}{4}}}-\frac{1.16}{r_s^{5/4}}\right)$$
$$\times\exp(-2.06 r_s^{\frac{1}{2}})-\left(\frac{2.06}{r_s^{5/4}}-\frac{0.66}{r_s^{7/4}}\right)\exp(-1.55 r_s^{\frac{1}{2}}). \tag{5}$$

It is difficult to estimate the accuracy of the exponential terms without investigating higher orders in the perturbation series; however, the above terms contribute relatively little to the energy for low density. They are ten percent of the total at $r_s=6$, and completely negligible in the range of $r_s>10$.

Finally, the specific heat per particle has been calculated in a zero-order approximation. The result for the vibrational part, which is extremely small except for large r_s and high temperatures, is

$$C_v=1.6\times 10^{-14} k T^3 r_s^{9/2}, \tag{6}$$

with k the Boltzmann constant and T the absolute temperature. For T small compared with θ a magnetic part should be added to (6), which part, according to the calculation of Kubo,[6] also should vary as T^3, with the order of magnitude $k(T/\theta)^3$.

RANGE OF THE "LOW-DENSITY" APPROXIMATION

It is of some interest to discuss the range of the "low-density" region for which the calculations given here apply. The low-density region will be defined as that region of r_s in which the probability density for a

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[3] K. Fuchs, Proc. Roy. Soc. (London) **A151**, 585 (1935).

[4] *Note added in proof.* Rosemary Coldwell-Horsfall and A. A. Maradudin, J. Math. Phys. **1**, 395 (1960), recently have published a value $2.638\ r_s^{-\frac{3}{2}}$, obtained by the method of moments. Their value for the specific heat per electron is $56.21\ k r_s^{9/2}\ (kT)^3$ ry.

[5] W. J. Carr, Jr., Phys. Rev. **92**, 28 (1953).

[6] R. Kubo, Phys. Rev. **87**, 568 (1952).

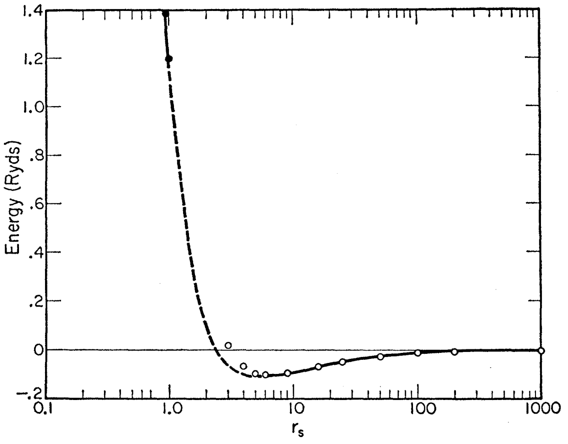

FIG. 1. Energy of the electron gas plotted against r_s. The open circles are points given by Eq. (5) with anharmonic terms neglected. The filled circles were calculated from the Gell-Mann and Brueckner[2] expression. In constructing the dashed curve connecting the two end regions, consideration was given to the fact that it must fall below the sum of the Fermi plus exchange energy for plane waves. The open circle points below $r_s=6$ have lower accuracy, even if the approximations apply to this region, since for these points the exponential terms in (5) are appreciable.

pair of electrons can be considered as that for a perturbed lattice arrangement (with its zero-point motion). The only point one can investigate here is whether the perturbation series seems to break down at some value of r_s. Insofar as the calculation has been carried, there is no evidence of a "breakdown" above r_s equal to 5 or 6. This statement is so because the exponential and anharmonic terms are small down to these intermediate densities. Since the low-density perturbation calculation is based on the premise that the Coulomb energy (C.E.) is larger in magnitude than the kinetic energy (K.E.), it is not unreasonable to speculate that the region of applicability is roughly that for $E<0$, inasmuch as $E=0$ corresponds to K.E.$=|$C.E.$|$. Thus according to Fig. 1, this rough estimate would indicate the low-density region extends down to an r_s of about 2.3. On the contrary, however, Nozières and Pines[7] estimate the low-density range to be above $r_s=20$.[8]

Of course, there is a more important point to consider: namely, at what value of r_s does another state become lower in energy than the perturbed lattice state considered here. There is little reason to doubt that, at some density, energy bands, formed, for example, from polar states of the lattice, will become lower. Then (5) will give the ground state only to the extent the states which cross over lie not much lower. A plot of Eq. (5), with anharmonic terms neglected, is shown in Fig. 1. This plot indicates that the density at which the electron gas is stable corresponds to an r_s in the neighborhood of 5.

DISCUSSION OF THE LATTICE FORMATION

The Hamiltonian for the system is $T+V$, where T is the kinetic energy operator for the electrons and the potential energy V is given by

$$V=\frac{e^2\rho^2}{2}\int\int\frac{d\mathbf{r}d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}+\frac{e^2}{2}\sum_{i\neq j}\sum\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}-e^2\rho\sum_j\int\frac{d\mathbf{r}}{|\mathbf{r}-\mathbf{r}_j|}. \qquad (7)$$

The first term on the right is the self-energy of the uniform positive charge, the second the Coulomb energy of the electrons, and the third term the interaction between electrons and positive charge, in a self-evident notation. ρ is the density, given in terms of Bohr radii by $(3/4\pi)r_s^{-3}$.

The argument that as $r_s\rightarrow\infty$ the electrons approach a lattice configuration is the following: If a wave function can be found which minimizes the potential energy and still leads only to a negligible higher-order result for the positive kinetic energy, then obviously, to first order, the energy has been minimized and the ground state obtained. With surface effects ignored, a regular lattice of electrons would seem to minimize the potential energy,[9] and of these, in accord with Wigner's hypothesis, the body-centered cubic is assumed to have lowest energy. If the electrons now are constrained, not to the lattice points, but to regions about the lattice points of radius proportional to a positive fractional power of r_s, say r_s^t, then the change in potential energy is found by a Taylor expansion to be proportional to higher order terms in r_s, and the kinetic energy, which is proportional to the inverse two-thirds power of the volume or r_s^{-2t}, is also a higher-order term if $t>\frac{1}{2}$.

The principal question in the argument is whether the body-centered cubic lattice really is the configuration of lowest potential energy. By means of an Ewald-type calculation, Fuchs[3] obtained a value $-1.79186\ r_s^{-1}$ ry per particle for the bcc case and $-1.79172\ r_s^{-1}$ for the fcc case. A similar calculation by the author for the simple cubic structure gives $-1.760\ r_s^{-1}$. Kohn and Schechter[10] have obtained the value $-1.79168\ r_s^{-1}$ for the hexagonal close-packed lattice. Thus, at least for the simple structures, the body-centered cubic lattice does have the lowest energy although the difference is very slight. Possibly, when

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[7] P. Nozières and D. Pines, Phys. Rev. **111**, 442 (1958). The interesting observation is made that according to the Lindemann formula, the lattice would "melt" at $r_s\approx 20$. However, this formula is an empirical rule governing the thermal vibrations of nuclei, and its applicability to the zero-point motion of electrons in this problem is a matter which remains to be established.

[8] *Note added in proof.* Rosemary Coldwell-Horsfall and A. A. Maradudin, J. Math. Phys. **1**, 395 (1960), point out the difficulty in choice of Lindemann constant. An uncertainty of a factor of two in this constant means a factor of 16 uncertainty in the r_s for "melting."

[9] For a discussion of this point see R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, London, 1955), pp. 7–9.

[10] W. Kohn and D. Schechter (unpublished). These authors note a mistake in the calculations of C. Herring and A. G. Hill, Phys. Rev. **58**, 132 (1940). The latter reported the hexagonal close-packed lattice as having the lowest energy.

zero-point terms are included, another lattice will have slightly lower energy for finite r_s, but this question has not been considered.

It may be argued that a lattice configuration is not consistent with the translational symmetry in the Hamiltonian. This objection can be removed by forming a new wave function which is a linear combination of all translations of the original lattice; the resultant function will have uniform electronic charge density, as symmetry demands, but the energy will be unchanged.

SERIES EXPANSION FOR THE HAMILTONIAN

In this part of the problem the electrons are treated as distinguishable, with the jth electron close to the jth lattice point.

It is convenient to write the potential energy in the following form:

$$V=V_0-e^2\rho\sum_j\left[\int\frac{d\mathbf{r}}{|\mathbf{r}-\mathbf{r}_j|}-\int\frac{d\mathbf{r}}{|\mathbf{r}-\mathbf{R}_j|}\right]+\frac{e^2}{2}\sum\sum_{i\neq j}\left[\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}-\frac{1}{|\mathbf{R}_i-\mathbf{R}_j|}\right],\qquad(8)$$

where the $\mathbf{R}_j$ are the lattice points of a body-centered cubic lattice with the spacing adjusted so there are equal numbers of lattice points and electrons, and V_0 is given by

$$V_0=\frac{e^2\rho^2}{2}\int\int\frac{d\mathbf{r}d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}-e^2\rho\sum_j\int\frac{d\mathbf{r}}{|\mathbf{r}-\mathbf{R}_j|}+\frac{e^2}{2}\sum\sum_{i\neq j}\frac{1}{|\mathbf{R}_i-\mathbf{R}_j|},\qquad(9)$$

with numerical value $[(-1.79186)/r_s)]N$ ry.

Let $\mathbf{R}_j+\mathbf{u}_j$ be substituted for $\mathbf{r}_j$ and $(\pi/3)^{\frac{1}{3}}r_sa_B\mathbf{n}_j$ for $\mathbf{R}_j$ where the components of $\mathbf{n}_j$ are integers, all even or all odd, and a_B is the Bohr radius. After a Taylor expansion (see Appendix I) the potential energy in rydberg units becomes

$$V_{\text{ry}}=\frac{-1.792}{r_s}N+\frac{1}{r_s^3}\sum_j u_j^2+\left(\frac{3}{\pi}\right)^{\frac{1}{3}}\frac{1}{r_s}\sum\sum_{i\neq j}\left\{\left(\frac{3}{\pi}\right)^{\frac{2}{3}}\frac{1}{r_s^2}\frac{[(\mathbf{u}_i-\mathbf{u}_j)\cdot\boldsymbol{\nabla}_{ij}]^2}{2!}+\left(\frac{3}{\pi}\right)\frac{1}{r_s^3}\frac{[(\mathbf{u}_i-\mathbf{u}_j)\cdot\boldsymbol{\nabla}_{ij}]^3}{3!}+\cdots\right\}\frac{1}{|\mathbf{n}_i-\mathbf{n}_j|},\qquad(10)$$

where the $\mathbf{u}$'s are now measured in units of the Bohr radius.

Terms in (10) beyond the quadratic terms are to be treated as perturbations.

In rydberg units the kinetic energy operator is $-\sum_j\nabla_j^2$ and the unperturbed Hamiltonian, apart from the constant $-1.792N/r_s$, becomes

$$H_{\text{ry}}=-\sum_j\nabla_j^2+\frac{1}{r_s^3}\sum_j u_j^2-\frac{3}{2\pi r_s^3}\sum\sum_{i\neq j}\left\{\frac{(\mathbf{u}_i-\mathbf{u}_j)\cdot(\mathbf{u}_i-\mathbf{u}_j)}{|\mathbf{n}_i-\mathbf{n}_j|^3}-\frac{3[(\mathbf{u}_i-\mathbf{u}_j)\cdot(\mathbf{n}_i-\mathbf{n}_j)]^2}{|\mathbf{n}_i-\mathbf{n}_j|^5}\right\}.\qquad(11)$$

When placed in the form

$$H_{\text{ry}}=-\textstyle\sum_j\nabla_j^2+\sum_i\sum_j\mathbf{C}(\mathbf{n}_i-\mathbf{n}_j)\mathbf{u}_i\mathbf{u}_j,\qquad(12)$$

the components of the tensor $\mathbf{C}(\mathbf{n}_i-\mathbf{n}_j)$ are

$$C_{xx}(0)=\frac{1}{r_s^3},\qquad(13)$$

$$C_{xy}(0)=C_{yx}(0)=0,\qquad(14)$$

and for $i\neq j$

$$C_{xx}(\mathbf{n}_i-\mathbf{n}_j)=\frac{3}{\pi r_s^3}\left[\frac{1}{|\mathbf{n}_i-\mathbf{n}_j|^3}-\frac{3(n_{ix}-n_{jx})^2}{|\mathbf{n}_i-\mathbf{n}_j|^5}\right],\qquad(15)$$

$$C_{xy}(\mathbf{n}_i-\mathbf{n}_j)=C_{yx}(\mathbf{n}_i-\mathbf{n}_j)=\frac{-9}{\pi r_s^3}\frac{(n_{ix}-n_{jx})(n_{iy}-n_{jy})}{|\mathbf{n}_i-\mathbf{n}_j|^5}.\qquad(16)$$

The remaining components are determined by symmetry.

Thus the problem to be solved is the well-known problem of vibrational waves in a lattice; however, the "phonons" in this case are electrons vibrating in the fixed field of the positive charge, in addition to their mutual fields.

The solution of (12) is obtained by transforming to a set of $3N$ variables q_k which reduce (12) to the oscillator form,

$$H=\sum_k\left[-\frac{\partial^2}{\partial q_k^2}+\omega^2(k)q_k^2\right].\qquad(17)$$

The required transformation, which is given for notational purposes, is obtained by setting

$$\mathbf{u}_j=\frac{1}{(2N)^{\frac{1}{2}}}\sum_{\mathbf{f}}\sum_s\exp(i\mathbf{f}\cdot\mathbf{n}_j)\mathbf{v}(\mathbf{f},s)Q_{\mathbf{f}s},\qquad(18)$$

where the subscript k has been replaced by a double subscript $\mathbf{f}$, s, with s taking the values 1, 2, and 3, and $\mathbf{f}$ being a vector in the basic cell of reciprocal space. An arbitrary $\mathbf{f}$ can be written as $\pm\mathbf{f}^+$, where $\mathbf{f}^+$ is in the upper half-zone, and the variables Q are defined by $Q_{\mathbf{f}^+s}=q_{\mathbf{f}^+s}+iq_{-\mathbf{f}^+s}$ and $Q_{-\mathbf{f}^+s}=q_{\mathbf{f}^+s}-iq_{-\mathbf{f}^+s}$. The vectors

TABLE I. Values for $\omega(\mathbf{f}s)$ and $\mathbf{v}(\mathbf{f}s)$ at particular points in $\mathbf{f}$ space [2ω is the value of $h\nu$ in rydbergs where ν is the frequency]. The numbers given for ω are multiplied by $r_s^{\frac{3}{2}}$. For certain directions $\omega(1)\equiv\omega(\mathbf{f}1)$ is a longitudinal branch and $\omega(2)$ and $\omega(3)$ are transverse. In degenerate cases the $\mathbf{v}$'s are not specified because of the arbitrariness. The values for [000] refer to the limit as $\mathbf{f}$ approaches zero along a particular direction. The frequency of the $\mathbf{f}=0$ longitudinal mode is the "plasma" frequency. In some of the principal symmetry directions more accurate values for the frequencies have been given by Clark (reference 12). If

$$\mathbf{v}(f_x,f_y,f_z,s)=\begin{pmatrix}a\\b\\c\end{pmatrix},$$

then

$$\mathbf{v}(f_y,f_x,f_z,s)=\begin{pmatrix}b\\a\\c\end{pmatrix},\quad \mathbf{v}(-f_x,f_y,f_z,s)=\begin{pmatrix}-a\\b\\c\end{pmatrix},$$

etc.; while the ω's are unchanged by cubic symmetry operations. Since the $\mathbf{v}$'s are arbitrary in sign, it also is possible to take $\mathbf{v}(\mathbf{f}s)=\mathbf{v}(-\mathbf{f}s)$ instead of $\mathbf{v}(\mathbf{f}s)=-\mathbf{v}(-\mathbf{f},s)$.

$(8/\pi)\mathbf{f}$	$\omega(1)$	$\omega(2)$	$\omega(3)$	$\mathbf{v}(1)$	$\pm$ $\mathbf{v}(2)$	$\mathbf{v}(3)$
[110]	1.715	0.085	0.228	$\frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\\0\end{pmatrix}$	$\frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\\0\end{pmatrix}$	$\begin{pmatrix}0\\0\\1\end{pmatrix}$
[200]	1.668	0.330	0.330	$\begin{pmatrix}1\\0\\0\end{pmatrix}$	Trans.	Trans.
[211]	1.676	0.244	0.365	$\begin{pmatrix}0.806\\0.419\\0.419\end{pmatrix}$	$\begin{pmatrix}-0.593\\0.570\\0.570\end{pmatrix}$	$\frac{1}{\sqrt{2}}\begin{pmatrix}0\\-1\\1\end{pmatrix}$
[220]	1.672	0.157	0.423		See [110]	
[222]	1.617	0.440	0.440	$\frac{1}{\sqrt{3}}\begin{pmatrix}1\\1\\1\end{pmatrix}$	Trans.	Trans.
[310]	1.603	0.427	0.499	$\begin{pmatrix}0.930\\0.367\\0\end{pmatrix}$	$\begin{pmatrix}-0.367\\0.930\\0\end{pmatrix}$	$\begin{pmatrix}0\\0\\1\end{pmatrix}$
[321]	1.606	0.312	0.569	$\begin{pmatrix}0.781\\0.570\\0.257\end{pmatrix}$	$\begin{pmatrix}-0.625\\0.705\\0.335\end{pmatrix}$	$\begin{pmatrix}0.0036\\-0.415\\0.910\end{pmatrix}$
[330]	1.627	0.210	0.554		See [110]	
[332]	1.499	0.507	0.705	$\begin{pmatrix}0.657\\0.657\\0.370\end{pmatrix}$	$\frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\\0\end{pmatrix}$	$\begin{pmatrix}0.262\\0.262\\-0.929\end{pmatrix}$
[400]	1.468	0.650	0.650		See [100]	
[411]	1.500	0.502	0.707	$\begin{pmatrix}0.907\\0.299\\0.299\end{pmatrix}$	$\begin{pmatrix}-0.423\\0.641\\0.641\end{pmatrix}$	$\frac{1}{\sqrt{2}}\begin{pmatrix}0\\-1\\1\end{pmatrix}$
[420]	1.546	0.466	0.626	$\begin{pmatrix}0.827\\0.563\\0\end{pmatrix}$	$\begin{pmatrix}-0.563\\0.827\\0\end{pmatrix}$	$\begin{pmatrix}0\\0\\1\end{pmatrix}$
[422]	1.467	0.393	0.835	$\begin{pmatrix}0.795\\0.429\\0.429\end{pmatrix}$	$\begin{pmatrix}-0.607\\0.562\\0.562\end{pmatrix}$	$\frac{1}{\sqrt{2}}\begin{pmatrix}0\\-1\\1\end{pmatrix}$
[431]	1.548	0.342	0.697	$\begin{pmatrix}0.739\\0.667\\0.095\end{pmatrix}$	$\begin{pmatrix}0.662\\-0.691\\-0.289\end{pmatrix}$	$\begin{pmatrix}0.128\\-0.277\\0.953\end{pmatrix}$
[433]	1.291	0.651	0.953	$\begin{pmatrix}0.736\\0.478\\0.478\end{pmatrix}$	$\begin{pmatrix}-0.677\\0.521\\0.521\end{pmatrix}$	$\frac{1}{\sqrt{2}}\begin{pmatrix}0\\-1\\1\end{pmatrix}$
[440]	1.608	0.228	0.601		See [110]	
[442]	1.424	0.533	0.830		See [110]	
[444]	1	1	1			
[510]	1.357	0.748	0.774	$\begin{pmatrix}0.931\\0.366\\0\end{pmatrix}$	$\begin{pmatrix}-0.366\\0.931\\0\end{pmatrix}$	$\begin{pmatrix}0\\0\\1\end{pmatrix}$
[521]	1.403	0.511	0.877	$\begin{pmatrix}0.810\\0.569\\0.143\end{pmatrix}$	$\begin{pmatrix}0.540\\-0.625\\-0.564\end{pmatrix}$	$\begin{pmatrix}0.231\\-0.534\\0.813\end{pmatrix}$
[530]	1.522	0.481	0.672		See [110]	
[532]	1.351	0.414	1.001	$\frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\\0\end{pmatrix}$	$\begin{pmatrix}0.602\\-0.602\\-0.525\end{pmatrix}$	$\begin{pmatrix}0.371\\-0.371\\0.851\end{pmatrix}$
[600]	1.173	0.901	0.901		See [100]	
[611]	1.211	0.751	0.985	$\begin{pmatrix}0.877\\0.340\\0.340\end{pmatrix}$	$\begin{pmatrix}-0.481\\0.620\\0.620\end{pmatrix}$	$\frac{1}{\sqrt{2}}\begin{pmatrix}0\\-1\\1\end{pmatrix}$
[620]	1.313	0.777	0.820		See [110]	
[622]	1.172	0.501	1.172	Trans. to $\mathbf{v}(2)$	$\frac{1}{\sqrt{3}}\begin{pmatrix}-1\\1\\1\end{pmatrix}$	Trans. to $\mathbf{v}(2)$
[710]	1.095	0.948	0.950		See [110]	
[800]	1	1	1			
[000]	$\sqrt{3}$	0	0	Long.	Trans.	Trans.

$\mathbf{v}$ which in the present case are real are defined by $\mathbf{v}(-\mathbf{f}s)=\mathbf{v}^*(\mathbf{f}s)$ in addition to

$$\mathbf{v}(\mathbf{f},s)\cdot\mathbf{v}^*(\mathbf{f}s')=\delta_{ss'}, \tag{19}$$

and

$$\mathbf{G}(\mathbf{f})\mathbf{v}(\mathbf{f}s)-\omega^2(\mathbf{f}s)\mathbf{v}(\mathbf{f}s)=0, \tag{20}$$

where the components of the tensor $\mathbf{G}$ are given by

$$G_{\alpha\beta}(\mathbf{f})=\sum_j C_{\alpha\beta}(\mathbf{n}_j)\exp(i\mathbf{f}\cdot\mathbf{n}_j)=\frac{\delta_{\alpha\beta}}{r_s^3}+G_{\alpha\beta}'(\mathbf{f}), \tag{21}$$

with $G_{\alpha\beta}'(\mathbf{f})=\sum_{j\neq0}C_{\alpha\beta}(\mathbf{n}_j)\exp(i\mathbf{f}\cdot\mathbf{n}_j)$; and finally the frequencies, which are proportional to ω, are given by

$$\det[G_{\alpha\beta}(\mathbf{f})-\omega^2(\mathbf{f},s)\delta_{\alpha\beta}]=0. \tag{22}$$

It is to be noted from (15) that $G_{xx}'+G_{yy}'+G_{zz}'=0$.

CALCULATION OF THE OSCILLATOR FREQUENCIES

The three-by-three determinant (22) gives a cubic equation in ω^2, with three positive roots.

The G's may be obtained from the calculations of Cohen and Keffer[11] and the frequencies for various values of $\mathbf{f}$, corresponding to 512 points in the basic cell, are given in Table I. Some of these points have

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[11] M. H. Cohen and F. Keffer, Phys. Rev. **99**, 1128 (1955).

been obtained previously by Clark[12] who used an Ewald-type calculation. Due to the presence of the fixed positive charge, one of the branches is observed to behave like an optical mode, as explained by Clark.

Because of the long-range nature of the Coulomb interaction, the frequency versus f curve appears to be discontinuous at $\mathbf{f}=0$ (see reference 11), since from (15), (16), and (21) $\mathbf{G}'$ goes to zero, at least at the center of the crystal, and therefore from (22) all three ω's equal $r_s^{-\frac{3}{2}}$. This is not the limit one obtains by letting $\mathbf{f}\rightarrow 0$, which is the physically interesting case.

The unperturbed energies in rydberg units are given by $\sum_k (2n_k+1)\omega(k)$. The ground-state or zero-point energy, for which all the quantum numbers n_k are zero, has been obtained according to the method of numerical integration used by Cohen and Keffer.[11] The result is $2.66\ r_s^{-\frac{3}{2}}$ rydbergs per particle, which compares with the value $3\ r_s^{-\frac{3}{2}}$ obtained by Wigner.[13]

PERTURBATIONS ON THE OSCILLATOR FUNCTIONS

The third and higher order terms in the expansion (10) may be transformed to the q coordinates and treated as a perturbation, the unperturbed states being

$$\Psi_{n_1\cdots n_{3N}}=\psi_{n_1}(q_1)\cdots\psi_{n_{3N}}(q_{3N}), \tag{23}$$

where $\psi_n(q)$ is the nth excited oscillator function. More explicitly, ψ is a function of $(\omega)^{\frac{1}{2}}q$ or $qr_s^{-\frac{3}{4}}$. An mth order term in the expansion (10) will contain terms of the type $q^m r_s^{-(m+1)}$, which contributes a factor proportional to $r_s^{(\frac{3}{4})m-m-1}$ or $r_s^{-(m/4+1)}$ to a matrix element. This contribution to the matrix element, divided by the difference between two unperturbed energies, is proportional to $r_s^{-m/4+\frac{1}{2}}$. It would appear from this result that the perturbation series is an expansion in powers of $r_s^{-\frac{1}{4}}$; however, parity considerations of the perturbation series[14] show that the coefficients of odd powers of $r_s^{-\frac{1}{4}}$ are all zero, so the series is really an expansion in powers of $r_s^{-\frac{1}{2}}$.

Since the unperturbed energies contain a factor $r_s^{-\frac{3}{2}}$, the next term in the series expansion of the energy is proportional to r_s^{-2}. Contributions of this power come from the fourth-order part of the expansion (10) ($m=4$) in first-order perturbation, and the third-order part ($m=3$) in second-order perturbation. These terms are calculated in Appendix II.

EXPONENTIAL TERMS DECREASING WITH $r_s^{\frac{1}{2}}$

In the approximation of distinguishable electrons, the different spin states are all degenerate. To determine the separation among spin states, it is necessary to introduce an antisymmetric wave function; the degenerate levels will then be split according to the exchange energy, which, as will be shown, decreases exponentially with $r_s^{\frac{1}{2}}$. For this calculation the Hamiltonian must be taken in closed form, since one is interested in the overlap of the "tails" of the wave functions, and in this region of large displacement, $\mathbf{u}$, the Taylor expansion (10), does not converge. In fact, the use of closed form for the Hamiltonian leads to exponential terms even without exchange.

An antisymmetric wave function might be formed as discussed in the introduction, by starting with the wave functions (23), transforming the q_k's to the displacements $\mathbf{u}_j=\mathbf{r}_j-\mathbf{R}_j$, multiplying by a spin function $\xi(\boldsymbol{\sigma}_1,\cdots\boldsymbol{\sigma}_N)$, and operating on the result with $\sum_\nu \pm P_\nu$ which permutes the electronic space and spin coordinates $\mathbf{r}_j$ and $\boldsymbol{\sigma}_j$. Such functions, however, make the calculation of matrix elements difficult. Another set which is nearly as good for the problem may be constructed by forming determinants from the complete basic set

$$\Phi_{m_1\cdots m_N}=\phi_{m_1}(\mathbf{r}_1-\mathbf{R}_1)\cdots\phi_{m_N}(\mathbf{r}_N-\mathbf{R}_N)\xi(\boldsymbol{\sigma}_1\cdots\boldsymbol{\sigma}_N), \tag{24}$$

where $\phi_m(\mathbf{r}-\mathbf{R})$ is a three-dimensional oscillator function centered about $\mathbf{R}$. The ϕ's are eigenfunctions of the first two groups of terms on the right-hand side of (11); i.e., the ground state differs from the ground state of (23) by the effect of correlation introduced by the electron interaction in the last group of terms in (11).[15] Since the above set is complete, a solution of the secular determinant formed from the antisymmetrized Φ's also should give the exact energy levels.

Matrix elements between antisymmetrized Φ's readily may be calculated (Appendix III). These exact matrix elements are just the values that would be obtained from the Taylor expansion (10) for the Hamiltonian, plus additional terms proportional to $\exp(-cr_s^{\frac{1}{2}})$, plus the exchange terms which also fall off exponentially with $r_s^{\frac{1}{2}}$. The result confirms that with exponential terms neglected, the solution is that obtained by neglecting exchange and by expanding the interaction in a Taylor series; therefore, it is the series solution, E_0, calculated in the previous sections. An improved solution is obtained by treating the first term of a perturbation expansion exactly, but neglecting the exponential part in all the higher terms. The result obtained in this way is simply E_0 plus the difference between the exact and the approximate diagonal elements. The ground-

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[12] C. B. Clark, Phys. Rev. **109**, 1133 (1958).

[13] Actually Wigner states in a footnote that a more accurate calculation leads to the value $2.7\ r_s^{-\frac{3}{2}}$, in agreement with the present result.

[14] The wave functions have a definite parity. Thus in a product of matrix elements,

$$\int\Psi_n F(q_k)\Psi_m d\tau \int\Psi_m F'(q_k)\Psi_j d\tau\cdots\int\Psi_s F''(q_k)\Psi_n d\tau,$$

where each wave function appears twice, the result is zero if the product $FF'\cdots F''$ changes sign when the sign of all the q's is reversed.

[15] The function Ψ_g is given by $\exp(-\frac{1}{2}\sum_k \omega_k q_k^2)$, whereas Φ_g is $\exp(-\frac{1}{2}r_s^{-\frac{3}{2}}\sum_j u_j^2)$. Since $\sum_k q_k^2=\sum_j u_j^2$, the two are equal in the approximation for which all the frequencies are the same and equal to $r_s^{-\frac{3}{2}}$.

state energy becomes

$$E=E_0+\frac{\int (A\Phi_g)H(A\Phi_g)d\tau}{\int (A\Phi_g)^2 d\tau}-\int \Phi_g H_{\text{series}}\Phi_g d\tau. \quad (25)$$

This result, although obtained in a slightly different way, is equivalent to the first-order perturbation result discussed in the Introduction.

The problem of calculating the mean value of a Hamiltonian in terms of exchange integrals between nonorthogonal wave functions has been considered in a previous publication.[5] For small overlap, or large r_s,

$$\frac{\int (A\Phi_g)H(A\Phi_g)d\tau}{\int (A\Phi_g)^2 d\tau}\approx\int \Phi_g H\Phi_g d\tau-\tfrac{1}{2}\sum_{i\neq j}\sum J_{ij}\langle P_{ij}\rangle, \quad (26)$$

where $\langle P_{ij}\rangle$ is the average over the spin function ξ of the permutation operator P_{ij}, and J_{ij} is the two-body "exchange integral."

From Appendix III, in units of rydbergs and Bohr radii,

$$\int \Phi_g H\Phi_g d\tau-\int \Phi_g H_{\text{series}}\Phi_g d\tau =\sum_{i\neq j}\sum \frac{1}{R_{ij}}[\mathcal{P}(2^{-\frac{1}{2}}r_s^{-\frac{3}{4}}R_{ij})-1], \quad (27)$$

where $\mathcal{P}$ is the probability integral, which for large x has the asymptotic expansion

$$\mathcal{P}(x)=1-\frac{\exp(-x^2)}{x\sqrt{\pi}}\left(1-\frac{1}{2x^2}+\cdots\right). \quad (28)$$

When the substitution $R_{ij}=(\pi/3)^{\frac{1}{3}}r_s n_{ij}$ is made, the right side of (27) becomes approximately

$$-Nr_s^{-5/4}[2.06(1-.32r_s^{-\frac{1}{2}})\exp(-1.55r_s^{\frac{1}{2}}) +1.16(1-.24r_s^{-\frac{1}{2}})\exp(-2.06r_s^{\frac{1}{2}})]. \quad (29)$$

EXCHANGE INTEGRAL AND ANTIFERROMAGNETISM

The spin average $\langle P_{ij}\rangle$ has its maximum value (unity) for a ferromagnetic state; thus if J_{ij} is positive, the ferromagnetic state has lowest energy. The correct expression for the exchange integral is[5]

$$J_{ij}=(ij|H(1,2)|ji)-T_{ij}^2(ij|H(1,2)|ij), \quad (30)$$

where the letters i, j indicate $\phi_0(\mathbf{r}_1-\mathbf{R}_i)$, $\phi_0(\mathbf{r}_2-\mathbf{R}_j)$ which are ground-state oscillator functions centered about lattice points i and j; T_{ij} is the overlap integral $\int\phi_0(\mathbf{r}-\mathbf{R}_i)\phi_0(\mathbf{r}-\mathbf{R}_j)d\mathbf{r}$; and $H(1,2)$ is an effective two-body Hamiltonian given by

$$H(1,2)=\frac{-\hbar^2}{2m}(\nabla_1^2+\nabla_2^2)-e^2\rho\int d\mathbf{r}\left[\frac{1}{|\mathbf{r}-\mathbf{r}_1|}+\frac{1}{|\mathbf{r}-\mathbf{r}_2|}\right] +e^2\sum_{k\neq i,j}\int d\mathbf{r}\,\phi_0^2(\mathbf{r}-\mathbf{R}_k)\left[\frac{1}{|\mathbf{r}_1-\mathbf{r}|}+\frac{1}{|\mathbf{r}_2-\mathbf{r}|}\right] +\frac{e^2}{|\mathbf{r}_1-\mathbf{r}_2|}. \quad (31)$$

It will be noticed that this exchange integral for two electrons in the many-body problem differs from the familiar hydrogen molecule exchange in that the effective Hamiltonian $H(1,2)$ in the former case is a two-body Hamiltonian in the approximate field of all the other charges.

Integrals of the type necessary to calculate J_{ij} already have been evaluated by Boys.[16] After integrating the second term on the right-hand side of (31) over a sphere to obtain const$+e^2\rho(2\pi/3)(r_1^2+r_2^2)$, one finds for the exchange

$$J_{ij}=\exp(-\tfrac{1}{2}r_s^{-\frac{3}{2}}R_{ij}^2)\Big\{2(2/\pi)^{\frac{1}{2}}r_s^{-\frac{3}{4}} -2R_{ij}^{-1}\mathcal{P}(2^{-\frac{1}{2}}r_s^{-\frac{3}{4}}R_{ij})-r_s^{-3}R_{ij}^2 +2\sum_{k\neq i,j}\int d\mathbf{r}\,\phi_0^2(\mathbf{r}-\mathbf{R}_k)\left[\frac{2\mathcal{P}(r_s^{-\frac{3}{4}}|\frac{1}{2}\mathbf{R}_i+\frac{1}{2}\mathbf{R}_j-\mathbf{r}|)}{|\frac{1}{2}\mathbf{R}_i+\frac{1}{2}\mathbf{R}_j-\mathbf{r}|} -\frac{\mathcal{P}(r_s^{-\frac{3}{4}}|\mathbf{R}_i-\mathbf{r}|)}{|\mathbf{R}_i-\mathbf{r}|}-\frac{\mathcal{P}(r_s^{-\frac{3}{4}}|\mathbf{R}_j-\mathbf{r}|)}{|\mathbf{R}_j-\mathbf{r}|}\right]\Big\}, \quad (32)$$

where $\mathcal{P}(x)$ again is the probability integral and the units are rydbergs and Bohr radii.

For the present case of large r_s (and assuming $\mathbf{R}_k\neq\frac{1}{2}\mathbf{R}_{ij}$) the integral term in (32) may be approximated sufficiently well by

$$2\sum_{k\neq i,j}[2|\tfrac{1}{2}\mathbf{R}_i+\tfrac{1}{2}\mathbf{R}_j-\mathbf{R}_k|^{-1}-|\mathbf{R}_i-\mathbf{R}_k|^{-1} -|\mathbf{R}_j-\mathbf{R}_k|^{-1}], \quad (33)$$

which by manipulating subscripts may be written as

$$-\frac{4}{R_{ij}}+4\sum_{k\neq 0}[|\tfrac{1}{2}\mathbf{R}_{ij}-\mathbf{R}_k|^{-1}-R_k^{-1}]. \quad (34)$$

If i and j are nearest or next-nearest neighbors, the approximate value of (34) is given by $-4R_{ij}^{-1}$. Thus by replacing $\mathcal{P}$ with unity, and R_{ij} with $(\pi/3)^{\frac{1}{3}}r_s n_{ij}$, (32) becomes approximately

$$J_{ij}\approx[1.6r_s^{-\frac{3}{4}}-6n_{ij}^{-1}r_s^{-1}-n_{ij}^2r_s^{-1}] \times\exp(-0.515n_{ij}^2r_s^{\frac{1}{2}}). \quad (35)$$

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[16] S. F. Boys, Proc. Roy. Soc. (London) **A200**, 542 (1950).

The only positive contribution to this integral comes from the $|\mathbf{r}_1-\mathbf{r}_2|^{-1}$ term in the Hamiltonian.

For nearest and next-nearest neighbors, one has

$$J_{\mathrm{n.n.}}\approx(1.6r_s^{-\frac{3}{4}}-6.5r_s^{-1})\exp(-1.55r_s^{\frac{1}{2}}), \tag{36}$$

$$J_{\mathrm{n.n.n.}}\approx(1.6r_s^{-\frac{3}{4}}-7r_s^{-1})\exp(-2.06r_s^{\frac{1}{2}}). \tag{37}$$

The integral for the third-nearest neighbors is considerably smaller.

Strictly speaking, as $r_s\rightarrow\infty$, the exchange integrals become positive and ferromagnetism should result. This occurs, however, only when r_s has the large value of 270 or greater, for which case the exchange energy is so small as to have no physical interest. For cases of practical interest, one may assume the dilute electron gas is antiferromagnetic. Although the exact spin eigenfunction of an antiferromagnetic state is a matter of some complexity, for the present purpose a two-sublattice approximation will be made. The spins on one sublattice are taken to be positive; those on the other negative. Thus, nearest neighbors are antiparallel, for which $\langle P_{ij}\rangle=0$. Next nearest neighbors, which are on the same sublattice, are parallel and $\langle P_{ij}\rangle=1$.

Therefore, from (26) and (37), the exchange energy per electron is approximately

$$(6/2)(7r_s^{-1}-1.6r_s^{-\frac{3}{4}})\exp(-2.06r_s^{\frac{1}{2}}), \tag{38}$$

since there are six next-nearest neighbors. In the paramagnetic state, where there is little correlation between spins, the next-nearest-neighbor exchange energy would be approximately one-half the above, and the nearest neighbor contribution $-\frac{1}{2}\times(8/2)\times J_{nn}$, since there are eight nearest neighbors. The difference between the energies of these two states, divided by the Boltzmann constant, gives an order of magnitude for the "Néel" temperature, θ. The result is given in Eq. (4). For $r_s=9$, $\theta\approx1000$; for $r_s=16$, $\theta\approx120$; and for $r_s=25$, $\theta\approx15$ in degrees Kelvin.

Previously, various calculations have been made on a free-electron model which shows the dilute electron gas to be ferromagnetic. As already mentioned by Wigner,[1] these calculations are incorrect because of the lack of correlation. In the free-electron model, the kinetic energy is proportional to r_s^{-2}, whereas actually the electrons occupy only a fraction, $(r_s^{\frac{3}{4}}/r_s)^3=r_s^{-\frac{3}{4}}$, of the total volume and therefore have a larger kinetic energy, proportional to $r_s^{-2}(r_s^{\frac{3}{4}})^{\frac{2}{3}}$ or $r_s^{-\frac{3}{2}}$.

SPECIFIC HEAT

In zeroth order approximation the specific heat coming from the vibrational spectra is that for a set of harmonic oscillators with the energy levels previously given. For long wavelengths the expression for the "transverse" modes becomes [from Eq. (18) in reference 11]

$$\omega_t=fr_s^{-\frac{3}{2}}\{0.177-0.306[S\pm(S^2-3P)^{\frac{1}{2}}]\}^{\frac{1}{2}}, \tag{39}$$

where

$$S=f^{-4}(f_x^2f_y^2+f_x^2f_z^2+f_y^2f_z^2) \quad\text{and}\quad P=f^{-6}(f_x^2f_y^2f_z^2).$$

After a change in units, the sound velocity, which is proportional to ω_t/f, for a transverse mode becomes $2.2\times10^8r_s^{-\frac{1}{2}}\{0.177-0.306[S\pm(S^2-3P)^{\frac{1}{2}}]\}^{\frac{1}{2}}$ in cm/sec, and the "low"-temperature specific heat per particle is

$$C_V=62kr_s^{9/2}[(kT)_{\mathrm{ry}}]^3. \tag{40}$$

The only unusual feature of the calculation is that only the transverse modes contribute to C_V, since the longitudinal mode behaves like an optical branch.[17] A numerical integration was used to obtain the average of the reciprocal cube of the velocity. The smallness of C_V is due to the large velocity, and it is obvious that (40) has interest, if any, only in the high-temperature region. The Debye temperature is given by $2.45\times10^5r_s^{-\frac{3}{2}}$ in degrees Kelvin and therefore the term "low temperature" includes all ordinary temperatures for reasonable densities.

APPENDIX I

In the Taylor expansion of

$$1/|\mathbf{r}_i-\mathbf{r}_j|=1/|\mathbf{R}_i-\mathbf{R}_j+\mathbf{u}_i-\mathbf{u}_j|$$

in (8), the first term obviously is canceled; the next term

$$\sum\sum_{i\neq j}(\mathbf{u}_i-\mathbf{u}_j)\cdot\boldsymbol{\nabla}_{ij}1/|\mathbf{R}_i-\mathbf{R}_j|,$$

which would be zero by symmetry except for the fact it diverges, must be canceled by a corresponding term from the integrals in (8).

The part of (8) given by

$$\sum_j\left[\int\frac{d\mathbf{r}}{|\mathbf{r}-\mathbf{R}_j|}-\int\frac{d\mathbf{r}}{|\mathbf{r}-\mathbf{r}_j|}\right]$$

is a sum over the difference in potential at $\mathbf{R}_j$ and that at $\mathbf{r}_j$ due to a uniform charge density. For a large spherical region about $\mathbf{R}_j$, this difference is $(2\pi/3)\sum_j u_j^2$. The part of the integral outside this spherical region can be shown to cancel the above linear term in **u**.

APPENDIX II

The unperturbed wave functions, Ψ_α, consist of products of one-dimensional oscillator functions, $\psi_n(q_k)$, where n is the quantum number to which the oscillator is excited. The matrix elements of q_k are $(q_k)_{n,n+1}=[(n+1)/2\omega(k)]^{\frac{1}{2}}$ and $(q_k)_{n,n-1}=[n/2\omega(k)]^{\frac{1}{2}}$, with all others zero.

Consider the second-order perturbation from the ground state, Ψ_0, caused by the quantity

$$F=\sum\sum_{i\neq j}[(\mathbf{u}_i-\mathbf{u}_j)\cdot\boldsymbol{\nabla}_{ij}]^3\frac{1}{|\mathbf{n}_i-\mathbf{n}_j|}. \tag{A1}$$

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[17] The "longitudinal" mode is given by $\omega_1=r_s^{-\frac{3}{2}}[3-0.354f^2+0.612Sf^2+O(f^4)]^{\frac{1}{2}}$.

Upon substituting for $\mathbf{u}$ from Eq. (18) in the text and replacing the subscript i with $j+m$, one obtains

$$F=(2N)^{-\frac{3}{2}}\sum_{m\neq 0}\sum_{j}\Big[\sum_{\mathbf{f}}\sum_{s}\exp(i\mathbf{f}\cdot\mathbf{n}_j)\times[\exp(i\mathbf{f}\cdot\mathbf{n}_m)-1]Q_{\mathbf{f}s}\mathbf{v}(\mathbf{f}s)\cdot\boldsymbol{\nabla}_{m'}\Big]^3\frac{1}{n_{m'}}. \quad \text{(A2)}$$

After the indicated differentiation the subscript m' is to be set equal to m.

When the bracket in (A2) is expanded and written as a six-fold summation, i.e., $\sum_{\mathbf{ff'f''}ss's''}$; a factor $\sum_j\exp[i(\mathbf{f}+\mathbf{f'}+\mathbf{f''})\cdot\mathbf{n}_j$ appears on the right-hand side of (A2). This factor equals N if $\mathbf{f''}=-\mathbf{f}-\mathbf{f'}+\mathbf{K}$, where $\mathbf{K}$ is a reciprocal-lattice vector, and zero otherwise. For a given value of $\mathbf{f}+\mathbf{f'}$ there is one, but only one, set of values for $\mathbf{f''}$ and $\mathbf{K}$ which makes the delta function nonvanishing, since $\mathbf{f''}$ must be in the basic zone. With the definition $Q_{\mathbf{f}+\mathbf{k}}=Q_{\mathbf{f}}$ and $\mathbf{v}(\mathbf{f}+\mathbf{K})=\mathbf{v}(\mathbf{f})$, one has

$$\begin{aligned}F=2^{-\frac{3}{2}}N^{-\frac{1}{2}}\sum_{m\neq 0}\sum_{\mathbf{ff'}ss's''}&[\exp(i\mathbf{f}\cdot\mathbf{n}_m)-1]\\&\times[\exp(i\mathbf{f'}\cdot\mathbf{n}_m)-1]\{\exp[-i(\mathbf{f}+\mathbf{f'})\cdot\mathbf{n}_m]-1\}\\&\times Q_{\mathbf{f}s}Q_{\mathbf{f'}s'}Q_{-(\mathbf{f}+\mathbf{f'})s''}[\mathbf{v}(\mathbf{f},s)\cdot\boldsymbol{\nabla}_m][\mathbf{v}(\mathbf{f'},s')\cdot\boldsymbol{\nabla}_m]\\&\times[\mathbf{v}(-\mathbf{f}-\mathbf{f'},s'')\cdot\boldsymbol{\nabla}_m]\frac{1}{n_m}\\=i(2N)^{-\frac{1}{2}}\textstyle\sum_{\mathbf{ff'}ss's''}&B(\mathbf{f},\mathbf{f'},s,s',s'')\\&\times Q_{\mathbf{f}s}Q_{\mathbf{f'}s'}Q_{-(\mathbf{f}+\mathbf{f'})s''},\end{aligned} \quad \text{(A3)}$$

where

$$\begin{aligned}B=\sum_{m\neq 0}&[\sin\mathbf{f}\cdot\mathbf{n}_m+\sin\mathbf{f'}\cdot\mathbf{n}_m-\sin(\mathbf{f}+\mathbf{f'})\cdot\mathbf{n}_m]\\&\times[\mathbf{v}(\mathbf{f},s)\cdot\boldsymbol{\nabla}_m][\mathbf{v}(\mathbf{f'}s')\cdot\boldsymbol{\nabla}_m]\\&\times[\mathbf{v}(-\mathbf{f}-\mathbf{f'}s'')\cdot\boldsymbol{\nabla}_m]\frac{1}{n_m},\end{aligned} \quad \text{(A4)}$$

a symmetric function in $\mathbf{f}$ and $\mathbf{f'}$.

The second-order perturbation of the energy is determined by $\sum_{\alpha\neq 0}|F_{0\alpha}|^2/(E_0-E_\alpha)$. The matrix element $F_{0\alpha}$ is zero for more than three excitations, i.e., if Ψ_α differs from Ψ_0 by more than three one-particle functions $F_{0\alpha}=0$ because (A3) is cubic in the Q coordinates. Since, respectively, N and N^2 times as many triple excitations as double and single excitations can be constructed, only the former need be considered. Consequently, for the nonvanishing values,

$$|[Q_{\mathbf{f}s}Q_{\mathbf{f'}s'}Q_{-(\mathbf{f}+\mathbf{f'})s''}]_{0\alpha}|=2^{-\frac{3}{2}}[\omega(\mathbf{f}s)\omega(\mathbf{f'}s')\omega(\mathbf{f}+\mathbf{f'},s'')]^{-\frac{1}{2}}. \quad \text{(A5)}$$

If $Q_{\mathbf{f}s}$ has a nonvanishing matrix element, then the corresponding element of $Q_{-\mathbf{f}s}$ (which is equal to $Q_{\mathbf{f}s}{}^*$) likewise does not vanish. Because of this fact and because of the six ways of permuting three Q's,

$$\begin{aligned}\sum_{\mathbf{f}_1\mathbf{f}_1's_1s_1's_1''}&[Q_{\mathbf{f}s}Q_{\mathbf{f'}s'}Q_{-(\mathbf{f}+\mathbf{f'})s''}]_{0\alpha}B^*(\mathbf{f}_1\mathbf{f}_1's_1s_1's_1'')\\&\times[Q_{\mathbf{f}_1s_1}Q_{\mathbf{f}_1's_1'}Q_{-(\mathbf{f}_1+\mathbf{f}_1')s_1''}]_{0\alpha}{}^*\\=6B^*(\mathbf{ff'}ss's'')&|(Q_{\mathbf{f}s}Q_{\mathbf{f'}s'}Q_{-(\mathbf{f}+\mathbf{f'})s''})_{0\alpha}|^2\\&-6B(\mathbf{ff'}ss's'')\{[Q_{\mathbf{f}s}Q_{\mathbf{f'}s'}Q_{-(\mathbf{f}+\mathbf{f'})s''}]_{0\alpha}\}^2.\end{aligned} \quad \text{(A6)}$$

The second term on the right of (A6), which is the square of the matrix element, goes to zero when summed over α since the nonvanishing elements are either purely real or purely imaginary and the squares will cancel in pairs. The first term, the square of the absolute value of the matrix element, is nonvanishing for eight triply excited states, α, because of the fact $Q_{\mathbf{f}s}$ contains both $q_{\mathbf{f}s}$ and $q_{-\mathbf{f}s}$. With these considerations and the use of (A5),

$$\begin{aligned}\sum_{\alpha\neq 0}\frac{|F_{0\alpha}|^2}{E_0-E_\alpha}=-\frac{3}{2N}\sum_{\mathbf{ff'}ss's''}&|B(\mathbf{ff'}ss's'')|^2\\&\times[\omega(\mathbf{f}s)\omega(\mathbf{f'}s')\omega(\mathbf{f}+\mathbf{f'}\,s'')]^{-1}\\&\times[\omega(\mathbf{f}s)+\omega(\mathbf{f'}s')+\omega(\mathbf{f}+\mathbf{f'}\,s'')]^{-1},\end{aligned} \quad \text{(A7)}$$

where the substitution

$$E_0-E_\alpha=-2[\omega(\mathbf{f}s)+\omega(\mathbf{f'}s')+\omega(\mathbf{f}+\mathbf{f'}\,s'')] \quad \text{(A8)}$$

has been made.

From Eq. (10) in the text it is seen that Eq. (A7) above must be multiplied by $(3/\pi)^{8/3}r_s{}^{-8}/36$ in order to give the contribution to the energy (in second-order perturbation) of the third-order terms in the expansion of the potential energy. The value of the right-hand side of (A7) has been estimated in two ways: firstly, by using the independent oscillator model where the ω's all equal $r_s{}^{-\frac{3}{2}}$; and secondly, by a numerical integration of the isotropic term in an expansion of the function $F(\mathbf{f},\mathbf{f'})$ in terms of cubic symmetry. This isotropic term is just the value of the function in the [100] direction. The result of the first method is $-17.5r_s{}^6N$ and that of the second is essentially the same. This estimate of (A7) gives a contribution to the energy of $-0.4r_s{}^{-2}N$ ry.

In a similar way it is found, for the first-order perturbation part, that

$$\left\langle\sum\sum_{i\neq j}[(\mathbf{u}_i-\mathbf{u}_j)\cdot\boldsymbol{\nabla}_{ij}]^4\frac{1}{n_{ij}}\right\rangle=\frac{3}{N}\sum_{m\neq 0}\left[\sum_{\mathbf{f}}\sum_{s}\frac{D_m(\mathbf{f},s)}{\omega(\mathbf{f},s)}\right]^2\frac{1}{n_m} \quad \text{(A9)}$$

where

$$D_m(\mathbf{f},s)=(1-\cos\mathbf{f}\cdot\mathbf{n'}_m)[\mathbf{v}(\mathbf{f},s)\cdot\boldsymbol{\nabla}_m]^2,$$

and $\mathbf{n'}=\mathbf{n}$ after the differentiation. A numerical integration over the points in $\mathbf{f}$ space given in Table I gives the value $10.6Nr_s{}^3$ for the right-hand side of (9). This value multiplied by $(3/\pi)^{5/3}r_s^{-5}/4!$ gives a contribution of $0.4r_s^{-2}N$ to the energy, which just cancels the second-order perturbation result. Within the accuracy of these estimates the constant b in Eq. (3) of the text is zero; its exact value is evidently smaller than unity.

APPENDIX III

The exchange part of the matrix element

$$1/N!\int (A\Phi_n)(H-E)A\Phi_m d\tau$$

will contain terms of the type $\int \Phi_n(H-E)P_\nu\Phi_m d\tau$. A permutation which interchanges the i and jth electrons will change $\mathbf{u}_j=\mathbf{r}_j-\mathbf{R}_j$ into $\mathbf{u}_i+\mathbf{R}_{ij}$. Therefore the integrand will contain factors such as

$$\exp\{-\tfrac{1}{2}r_s^{-\frac{3}{2}}(u_i^2+u_j^2)\}\exp\{-\tfrac{1}{2}r_s^{-\frac{3}{2}}[(\mathbf{u}_i+\mathbf{R}_{ij})^2+(\mathbf{u}_j+\mathbf{R}_{ji})^2]\},$$

or

$$\exp\{-r_s^{-\frac{3}{2}}[(\mathbf{u}_i+\tfrac{1}{2}\mathbf{R}_{ij})^2+(\mathbf{u}_j+\tfrac{1}{2}\mathbf{R}_{ji})^2]\}\exp\{-\tfrac{1}{2}r_s^{-\frac{3}{2}}\mathbf{R}_{ij}^2\}.$$

The last exponential, equivalent to

$$\exp\{-\tfrac{1}{2}(\pi/3)^{\frac{2}{3}}r_s^{\frac{1}{2}}n_{ij}^2\},$$

comes out of the integral and terms of this type always appear in the exchange.

Next examine $\int \Phi_n(H-H_{\text{series}})\Phi_m d\tau$, which is done by comparing the difference between integrals of the type

$$\frac{\int \phi_{n1}(\mathbf{r}_1-\mathbf{R}_1)\phi_{n2}(\mathbf{r}_2-\mathbf{R}_2)\phi_{m1}(\mathbf{r}_1-\mathbf{R}_1)\phi_{m2}(\mathbf{r}_2-\mathbf{R}_2)}{|\mathbf{r}_1-\mathbf{r}_2|},$$

when evaluated exactly and when evaluated term by term for a Taylor expansion of $|\mathbf{r}_1-\mathbf{r}_2|^{-1}$.

By using generating functions for the Hermite polynominals, the integral can be expressed as a differential operator operating on $\mathbf{p}_1$ and $\mathbf{p}_2$ in the expression

$$\frac{\int \exp\{-r_s^{-\frac{3}{2}}[(\mathbf{r}_1-\mathbf{R}_1-\mathbf{p}_1)^2+(\mathbf{r}_2-\mathbf{R}_2-\mathbf{p}_2)^2]\}d\tau}{|\mathbf{r}_1-\mathbf{r}_2|} \quad \text{as} \quad \mathbf{p}_1, \mathbf{p}_2\rightarrow 0.$$

The exact value of the above integral is

$$\pi^3 r_s^{9/2}\frac{\mathcal{P}[2^{-\frac{1}{2}}r_s^{-\frac{3}{4}}|\mathbf{R}_{12}+\mathbf{p}_{12}|]}{|\mathbf{R}_{12}+\mathbf{p}_{12}|}.$$

If

$$|\mathbf{r}_1-\mathbf{r}_2|^{-1}=|\mathbf{u}_1-\mathbf{u}_2+\mathbf{R}_{12}|^{-1}$$

is expanded and the integration done term by term, the result obtained is the series expansion for $\pi^3 r_s^{9/2}\times|\mathbf{R}_{12}+\mathbf{p}_{12}|^{-1}$. Thus the difference is proportional to $\mathcal{P}(x)-1$ which vanishes exponentially as $x\rightarrow\infty$.