Oscillations of the elastic parameters of compressed matter

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A theory of the oscillations of the elastic parameters of compressed matter with changes in the composition or pressure (volume) is developed on the basis of a previously proposed generalization of the Thomas–Fermi method that can be used to describe shell effects. It is shown that in strongly compressed matter the oscillatory effects arise from the successive entry of energy levels into the continuous spectrum, and that they are equivalent to a series of first-order phase transitions with characteristic pressure plateaus, atomic-volume discontinuities, and so on. The oscillation energy of an uncompressed atom is estimated. Applications to the theory of white dwarf stars are discussed.

1. INTRODUCTION

One familiar manifestation of Mendeleev's periodic law is the nonmonotonic, oscillatory behavior of the atomic volume of the elements $V = A/\rho$ (where A is the atomic weight and ρ is the density) as a function of their atomic number Z. This behavior under normal conditions was mentioned, for instance, in[1,2]. The maxima (more accurately, the salient points) of the V(Z) curve correspond to the alkali metals. The atomic volumes of the group-zero elements do not lie at the minima of this curve, as might be expected from our knowledge of the extreme compactness of the corresponding atoms, but rather differ comparatively little from the atomic volumes of the neighboring alkali metals.

In recent years experimental data have been obtained about the behavior of the V(Z) curve at different pressures P[2]. According to these data, as the pressure P rises up to 10 Mbar the shape of the V(Z) curve and the positions of the extrema do not change, but the amplitude of the oscillations decreases and (at P ~ 10 Mbar) practically disappears. Directly related to the oscillations of the atomic volume as a function of Z is the oscillatory dependence of other elastic characteristics of matter on Z. Among these are the pressure itself, the elastic modulus, the Gruneisen coefficient, etc., measured at fixed volume. The oscillations of these quantities have also been observed experimentally.

The elastic parameters of matter also display nonmonotonic behavior under changes in P or V. This generally occurs in the vicinity of a phase transition, either of the structural (lattice) or electronic type. We need only cite here the transition of electrons from the s to the d band when an alkali metal is compressed[3]. As a result of this rearrangement, which behaves like a typical first-order phase transition, a plateau appears in the P(V) curve and the V(P) curve shows a discontinuous jump from the atomic volume of the s phase to that of the d phase.

It has been widely believed that these oscillations in the elastic properties of matter, which reflect the individual properties of the separate elements, occur only in the region of relatively low pressures. It has been assumed that when the pressure exceeds the characteristic scale of intraatomic pressures[1)],

$$P \gg 1, \tag{A}$$

the oscillations of the physical quantities flatten out and the properties of the different elements become universal. The results of the experiments, cited above, on the behavior of V(Z) at various P[2] would appear to support this conclusion.

In the present work, which investigates the oscillations of the elastic parameters of matter in region (A), it is shown that the oscillatory effects in this region do not in fact vanish, but in a certain sense become even stronger. The theory to be developed below will show that, as Z varies or the compression is increased, the deep levels of the atom having $l = 0$ make successive transitions from the discrete to the continuous spectrum, which lead to anomalies in the elastic parameters of the matter. In the behavior of V(Z) there appear, besides the kinks, discontinuities having minima that correspond to the noble gas configuration and maxima that correspond to the alkali metal configuration. The oscillations related to the kinks do in fact disappear rapidly with increasing P, but the discontinuities only begin to appear in region (A) and are of significant size in the region[2)]

$$P \ll Z^{20/3}. \tag{B}$$

When this inequality no longer holds all the levels enter the continuous spectrum, and only then do the oscillations vanish completely.

The absence of discontinuities in the function V(Z) at low pressures is related to the fact that the atomic volume of the zero-group elements is anomalously large, due to the weakness of the interatomic interaction (in contrast to an alkali metal, this is a Van der Waals crystal). Only in region (A), when the atoms of the zero-group element come into close contact, does a sharp difference between the atomic volumes of this element and the neighboring alkali metal, based on their original atomic structure, begin to appear as a discontinuity in the function V(Z).

The appearance of this discontinuity can also be understood by analogy with the above-mentioned transitions in alkali metals. Here, in fact, we also have to do with a first-order phase transition between two phases. In one of the phases a given level will lie in the discrete spectrum, while in the other phase it lies in the continuous spectrum. In such a transition the appearance of a discontinuity in the atomic volume is unavoidable. Even stronger anomalies are displayed by the quantities obtained by taking derivatives of the pressure with respect to the volume: the elastic modulus, the Gruneisen coefficient, and so on.

In this work we make use of a generalized form of the Thomas-Fermi (TF) model, intended for the description of shell effects, that was recently proposed by the authors[4] (see also[5]).

2. OSCILLATIONS AS SHELL EFFECTS

The effects to be discussed here are due to the nature of electron shells. Their origin is apparent from Fig. 1, which shows the behavior of the atomic potential in a compressed lattice of metallized matter:

$$\Phi(\mathbf{x}) = U(\mathbf{x}) + B(\mathbf{x}) = -\frac{Z}{r} + \int \frac{d\mathbf{x}'\, n(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|}. \tag{2.1}$$

Here $n(\mathbf{x})$ is the local electron number density, R is the radius of the spherical Wigner-Seitz cell, and μ is the chemical potential. As Z or R is varied the discrete levels of bound electrons are successively "squeezed out" into the continuous spectrum, the boundary of which is denoted by $\bar{\mu}$. When a level intersects this boundary the electron becomes delocalized and the atomic volume is sharply decreased. These effects are similar to the well known oscillations of the parameters of a metal in a magnetic field (the de Haas—van Alphen effect, etc.).

In the general case a description of the oscillatory effects requires a numerical quantum-mechanical calculation; this is also true of the experimentally attainable range of pressures[6]. The problem is significantly simpler in the quasiclassical case, when the modified TF method can be used[4]. For this it is necessary, first, for the motion of electrons on the Fermi surface μ to be quasiclassical; this condition coincides with (A) (see, e.g.,[7]). The quasiclassical condition must also be satisfied on the level $\bar{\mu}$. From Eq. (2.1) and the normalization condition $\int d\mathbf{x}\, n(\mathbf{x}) = Z$ we find that near the cell boundary

$$\Phi(\mathbf{x}) \equiv -2\pi n(R)(R-r)^2, \tag{2.2}$$

whence $\bar{\mu} = 0$. The corresponding condition of quasiclassical motion $(-\Phi)^{1/2}R \gg 1$ coincides with (B).

When condition (A) is satisfied the oscillation effects are relatively weak, and the ordinary TF model can be used as a zeroth-order approximation. Let us write the basic expressions for the density, the pressure, and the chemical potential in this model:

$$n(\mathbf{x}) = p_F^3(\mathbf{x})/3\pi^2, \tag{2.3}$$

$$P = {}^1/_5(3\pi^2)^{2/3} n(R)^{5/3}, \tag{2.4}$$

$$\mu = {}^1/_2(3\pi^2)^{2/3} n(R)^{2/3}. \tag{2.5}$$

Here $p_F(\mathbf{x}) = [2(\mu - \Phi(\mathbf{x}))]^{1/2}$ is the momentum at the Fermi surface. These expressions refer to the zero-temperature case. In the following we shall also consider the case of a hot system, for which Eqs. (2.3)—(2.5) must be replaced respectively by the following expressions[7]:

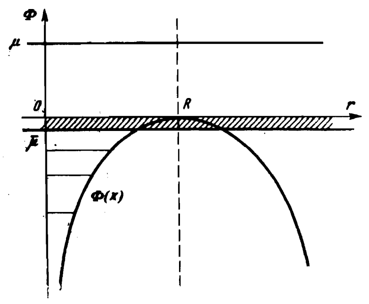

FIG. 1

$$n(\mathbf{x}) = \frac{(2T)^{3/2}}{2\pi^2} I_{1/2}(p_F^2(\mathbf{x})/2T), \tag{2.6}$$

$$P = \frac{(2T)^{5/2}}{6\pi^2} I_{3/2}(\mu/T), \tag{2.7}$$

$$n(R) = \frac{(2T)^{3/2}}{2\pi^2} I_{1/2}(\mu/T). \tag{2.8}$$

Here

$$I_n(x) = \int_0^\infty \frac{dy\, y^n}{[e^{(y-x)}+1]}$$

is the familiar Fermi-Dirac integral. Note that at high temperatures the quasiclassical condition is weakened, and the results obtained below become applicable even outside regions (A)—(B) (see[7]).

Strictly speaking, the foregoing description of level extrusion is not quite accurate. The fact is that the levels spread out into bands due to tunneling between neighboring cells. However, when the quasiclassical condition (B) is satisfied this effect appears only in the immediate vicinity of the $\bar{\mu}$ level. The ratio of the spreading width to the distance between the levels is actually specified by the well-known tunneling exponent

$$\exp\left(-2\int_{r_E}^{R} dr\,|p_E|\right), \tag{2.9}$$

where $\Phi(r_E) = E$ and $|p_E|^2 = 2(\Phi(r) - E)$. It follows from Eq. (2.2) that the exponent in Eq. (2.9) is of order $|E|/n^{1/2}(R)$, and becomes of order unity only when $|E| \sim n^{1/2}(R)$. Because of the inequalities (A) and (B), the latter quantity is small by comparison with all the characteristic energies (Z^2, Z/R, μ, and so on).

Thus, when $0 < E \leq n^{1/2}(R)$ (the shaded region in Fig. 1) we are dealing with relatively wide overlapping bands. It is convenient to take this effect into account by assuming that the actual boundary of the discrete spectrum is shifted downward:

$$\bar{\mu} = -Cn^{1/2}(R), \tag{2.10}$$

where C is a constant of order unity. This constant actually enters the following formulas only under a logarithm, and with corresponding accuracy it can be set equal to unity.

3. OSCILLATORY PART OF THE FREE ENERGY

The following calculations are based on an expression for the oscillatory part of the free energy of the system (or, at zero temperature, simply the energy). The derivatives of this quantity with respect to the volume give expressions for the oscillations in the pressure, the elastic modulus, and so on, and by converting to variable P we can obtain the oscillations in the atomic volume at fixed P.

In departing from the framework of the TF method, the relation between the local particle number density $n(\mathbf{x})$ and the Fermi momentum $p_F(\mathbf{x}) = [2(\mu - \Phi(\mathbf{x}))]^{1/2}$ is altered. On the right side of Eq. (2.6) there appears an additional term which is a functional of $p_F(\mathbf{x})$:

$$n(\mathbf{x}) = n^0(\mathbf{x}) + \delta n\{p_F\} \tag{3.1}$$

(the superscript zero refers to the TF model); this term includes quantum, oscillatory, and other effects that are not taken into account in the standard TF model. There exists a simple formula (see[7])

$$\delta F=-\int_{-\infty}^{\mu^0} d\mu \int d\mathbf{x}\, \delta n\{p_F{}^0\}, \tag{3.2}$$

that gives the total change in the free energy due to these effects.

The derivation of Eq. (3.2) is based on the general representation of the free energy in the Hartree approximation3) as the free energy of an ideal gas in an external field U and a self-consistent field B, minus half the potential energy in the field B:

$$F=\mu N+T\sum_{\nu}\ln(1-f(\mu-\varepsilon_\nu))-\frac{1}{2}\int d\mathbf{x}\, nB.$$

Here N is the total number of particles, $f(x) = [\exp(-x/T) + 1]^{-1}$ is the occupation number, and ϵ_ν is the level energy. Using the easily verifiable identity

$$T\ln(1-f(x))=-\int_{-\infty}^{x} dx\, f(x),$$

we have

$$F=\int d\mathbf{x}\left\{\mu n-\int_{-\infty}^{\mu} d\mu\, n-\frac{nB}{2}\right\}. \tag{3.3}$$

This expression specifies F as a functional of the density $n(\mathbf{x})$ and a function of the chemical potential μ. The quantity δF in Eq. (3.2) is

$$F\{n^0+\delta_t n,\quad \mu^0+\delta\mu\}-F\{n^0,\ \mu^0\},$$
$$\delta_t n=\delta n\{p_F{}^0\}+{}^1/_2\delta p_F{}^2(\partial n^0/\partial\mu),$$

where $\delta_t n$ is the total change in the density, $\delta p_F^2 = 2(\delta\mu - \delta B)$ is the change in the square of the Fermi momentum, $\delta\mu$ is the change in the chemical potential, specified by the normalization condition $\int d\mathbf{x}\,\delta_t n = 0$, and

$$\delta B=\int\frac{d\mathbf{x}'\,\delta_t n(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|}$$

is the change in the self-consistent field. By taking all these relationships into account, we easily arrive at Eq. (3.2). The important advantage of this equation is that it does not contain the variation δp_F^2, which could only be calculated by solving a complicated differential equation.

Let us apply Eq. (3.2) to the calculation of the oscillatory part of the free energy, at the same time changing the notation δA to A_{osc} for the oscillatory part of each quantity A. Introducing the "cold" one-particle Green's function $G(\mu, \mathbf{x}, \mathbf{x}')$, we can write the additional term in Eq. (3.1) in the form (see[4])

$$n_{osc}(\mathbf{x},\mu^0)=-\frac{2}{\pi}\int_{-\infty}^{\bar\mu} d\mu\, f(\mu^0-\mu)\,\mathrm{Im}\, G_{osc}(\mu,\mathbf{x},\mathbf{x}). \tag{3.4}$$

The upper bound of the integral in Eq. (3.4) is the upper limit of the discrete spectrum, $\bar\mu$; this is related to the fact that the oscillatory effects are irregularities arising from the intersection of the separate levels with the boundary $\bar\mu$ (see Sec. 2). Otherwise stated, these effects are the result of interference between incident and reflected waves from turning points, and thus are absent in the region $\mu > \bar\mu$ (see Fig. 1), where there are no turning points. In this region, accordingly, $G_{osc}(\mu, \mathbf{x}, \mathbf{x}') = 0$ (see[4]).

Considering Eq. (3.4) at T = 0 and $\mu < \bar\mu$, we can easily express the quantity

$$-\frac{2}{\pi}\int d\mathbf{x}\,\mathrm{Im}\, G_{osc}(\mu,\mathbf{x},\mathbf{x})=\frac{\partial}{\partial\mu}N_{osc}(\mu)$$

which appears when Eq. (3.4) is substituted in Eq. (3.2), in terms of the oscillatory part of the number of states at T = 0 with energies less than μ,

$$N_{osc}(\mu)=\int d\mathbf{x}\, n_{osc}(\mathbf{x},\mu). \tag{3.5}$$

From some uncomplicated calculations, using the identity mentioned above, we then obtain the final result:

$$F_{osc}=T\ln(1-f(\mu^0-\bar\mu))N_{osc}(\bar\mu)-\int_{-\infty}^{\bar\mu} d\mu\, f(\mu^0-\mu)N_{osc}(\mu). \tag{3.6}$$

From this we obtain, at zero temperature,

$$E_{osc}=-(\mu^0-\bar\mu)N_{osc}(\bar\mu)-\int_{-\infty}^{\bar\mu} d\mu\, N_{osc}(\mu). \tag{3.7}$$

4. OSCILLATORY PART OF THE NUMBER OF STATES

As is clear from Eqs. (3.6) and (3.7), the calculation of the oscillatory part of the free energy (and the other elastic parameters of matter) comes down to the determination of the oscillatory part of the number of states $N_{osc}(\mu)$ at $\mu \leq \bar\mu$ for a "cold" system. We introduce the total number of states with energies less than μ:

$$N(\mu)=2\sum_{l=0}(2l+1)\sum_{n_r=0}1. \tag{4.1}$$

The sum here is restricted by the condition $E_{n_r,l} \leq \mu$. Equation (4.1) will be calculated using the quasiclassical Bohr-Sommerfeld quantization rules

$$S_{El}=\int dr\, p_{El}(r)=\pi(n_r+{}^1/_2), \tag{4.2}$$
$$p_{El}=[2(E-\Phi(r)-(l+{}^1/_2)^2/r^2)]^{1/2},$$

where the integration is carried out over the entire classically-allowed region. Then the difference

$$N_{osc}(\mu)=N(\mu)-(3\pi^2)^{-1}\int d\mathbf{x}\, p_F{}^3(\mathbf{x}) \tag{4.3}$$

is reduced entirely to oscillatory effects and coincides with the quantity (3.5) (see Eq. (3.1)).

As in our earlier work[4], for the sums over levels we use the Poisson formula

$$\sum_{n=a}^{b}f(n)=\sum_{k=-\infty}^{\infty}\int_{a-\varepsilon'}^{b+\varepsilon} dn\, f(n)\cos 2\pi kn,\quad 0<\varepsilon,\varepsilon'<1. \tag{4.4}$$

To illustrate its use, let us consider the simplest one-dimensional case, when there is no sum over l in Eq. (4.1) and no centrifugal energy in Eq. (4.2), and in Eq. (4.3) the second term, corresponding to the TF model, is to be replaced with $(2/\pi)\int dx\, p_F(x) = 2S_\mu/\pi$.

Applying Eq. (4.4) to Eq. (4.1), it is convenient to choose ϵ so that $S_\mu = \pi(n_{max} + {}^1/_2 + \epsilon)$, where n_{max} is the largest quantum number; ϵ' is chosen to be $^1/_2$. Then the term in the series with k = 0 becomes exactly equal to $2S_\mu/\pi$ and compensates for the second term in Eq. (4.3), and the remaining terms in the k series will give the periodic function

$$N_{osc}(\mu)=-\frac{2}{\pi}[S_\mu]^*, \tag{4.5}$$

and here and below we use the notation

$$[x]^*=x,\quad -\pi/2<S_\mu<\pi/2 \tag{4.6}$$

with the periodic continuation outside this region. The resulting saw-shaped oscillations correspond to discontinuities in the variation of the number of states when the levels intersect the boundary μ.

In passing to the real three-dimensional case we include the sum over l (see Eq. (4.1)), which tends to smooth out the oscillations. As a result, the discontinuities of the function $N_{osc}(\mu)$ are transformed into deflection points (points of discontinuous derivatives). By treating the sums over n_r in Eq. (4.1) exactly as in the one-dimensional case, we can easily put Eq. (4.1) in the form

$$N(\mu)=\frac{1}{\pi}\sum_{k,\,s=-\infty}^{\infty}\frac{(-1)^{k}}{k}\int_{-\varepsilon'}^{l_{max}+\varepsilon} dl\,(2l+1)\sin(2kS_{\mu l}+2\pi sl),$$

where l_{max} is the largest integer at which $S_{\mu l}$ retains a real value. Choosing ϵ', as before, to be $\frac{1}{2}$, and ϵ from the condition $S_{\mu,\, l_{max}+\epsilon} = 0$, and changing to the variable $\lambda = l + \frac{1}{2}$, we have

$$N(\mu)=\frac{1}{\pi}\sum_{k,\,s=-\infty}^{\infty}\frac{(-1)^{k+s}}{k}\int_{0}^{(\lambda_{max}+\varepsilon)^2} d\lambda^2 \sin(2kS_{\mu,\,\lambda-1/2}+2\pi s\lambda).$$

Let us take out the term with k = s = 0. By using the identity

$$S_{\mu,\,\lambda-1/2}\equiv-\frac{2}{3}\frac{\partial}{\partial\lambda^2}\int dr\, r^2 p^3_{\mu,\,\lambda-1/2},$$

we can easily verify that this term exactly compensates for the second term in Eq. (4.3). The remaining terms contain a rapidly-varying sine function whose argument is very large and has a large derivative with respect to λ^2. At small λ

$$S_{\mu,\,\lambda-1/2}=S_{\mu,\,-1/2}-\pi\lambda-{}^1/_2\delta_\mu\lambda^2+\ \ldots, \qquad (4.7)$$
$$\delta_\mu=\lim_{\lambda\to 0}\left(\int\frac{dr}{r^2 p_{\mu,\,\lambda-1/2}}-\frac{\pi}{\lambda}\right)$$

(see [4]).

When k ≠ s a linear term remains in the argument of the sine, and the corresponding terms in $N(\mu)$ are small. When k = s, λ = 0 becomes a saddle point, so that

$$N_{osc}(\mu)=-\frac{2}{\pi\delta u}\sum_{k=1}^{\infty}\frac{\cos(2kS_{\mu,-1/2})}{k^2}. \qquad (4.8)$$

This expression contains the action at a nonphysical value of the angular momentum. Taking into account the Coulomb character of the field in Eq. (4.2) at small r, we can easily obtain $S_{\mu,-1/2} = S_{\mu,0} + \pi/2$, where the quantity $S_{\mu,0}$, denoted below simply by S_μ, is the action for the s-wave at energy μ:

$$S_\mu=\int dr[p_F{}^2(r)-1/4r^2]^{1/2}. \qquad (4.9)$$

By substituting this in Eq. (4.8) and omitting the nonoscillatory terms we obtain the final result

$$N_{osc}(\mu)=-\frac{2}{\pi\delta_\mu}[S_\mu{}^2]^{*}. \qquad (4.10)$$

5. OSCILLATIONS OF THE FREE ENERGY AND THE ENERGY

By substituting Eq. (4.10) in Eqs. (3.6) and (3.7) we can verify, first of all, that in region (A) the second (integral) terms in the expressions for F_{osc} and E_{osc} are small compared to the first terms. Under certain conditions, this fact gives rise to a simple relation between F_{osc} and E_{osc}.

In order to prove the above statement, we begin by noting that the integral in Eq. (3.6) contains both smooth functions of μ ($f(\mu^0-\mu)$, δ_μ) and the rapidly-varying function $[S^2_\mu]^*$. The given integral is thus reduced to an integral over the neighborhood of the upper bound $\bar\mu$ (there are no turning points in this case), where the functions S_μ behaves like $S_{\bar\mu} + (\mu - \bar\mu)\tau_{\bar\mu} + \ldots$ Here

$$\tau=\frac{\partial S_\mu}{\partial\mu}=\frac{\partial S_{\mu,\,-1/2}}{\partial\mu}=\int\frac{dr}{p_F(r)} \qquad (5.1)$$

is the crossing time of the classically-allowed region. The result of the integration is an oscillating function with amplitude of order $f(\mu^0 - \bar\mu)\tau_{\bar\mu}\delta_{\bar\mu}$. The ratio of this amplitude to that of the oscillations of the first term in Eq. (3.6) is of order

$$f(\mu^0-\bar\mu)/[T\ln(1-f(\mu^0-\bar\mu))\tau_{\bar\mu}].$$

At small T this quantity is of order $1/\mu^0\tau_{\bar\mu}$, and at large $T \gg \mu^0$ it is even smaller, of order $1/T\tau_{\bar\mu}$.

The quantities $\delta_{\bar\mu}$ and $\tau_{\bar\mu}$ can easily be determined by noting, from Eq. (2.2), that the primary contributions to them are from the vicinity of the cell boundary. Setting $\bar\mu = -Cn^{1/2}(R)$ (see Eq. (2.10)), we obtain

$$\delta_{\bar\mu}=\ln\gamma/2\gamma, \quad \tau_{\bar\mu}=R^2\ln\gamma/2\gamma, \qquad (5.2)$$

where $\gamma = (4\pi n(R))^{1/2}R^2 \gg 1$; the unknown constant C, which appears only under the logarithm sign, is omitted here. The difference of $\bar\mu$ from zero is significant only for the derivation of Eq. (5.2), so we shall set $\bar\mu = 0$ in the following. It follows from Eq. (5.2) that in the given compression region, $1/\mu^0\tau_0 \sim P^{-1/10} \ll 1$; in the high-temperature region, $1/T\tau_0$ will be even smaller. Accordingly, in Eq. (3.6) and similarly in Eq. (3.7), only the first terms need to be retained.

It follows directly from this that at pressures where the electron distribution becomes practically uniform ($P > Z^{10/3}$, see Sec. 6), and the potential depends only on the cell dimensions and thus is the same for a hot and a cold system at the same volume v, the following simple relation holds between the oscillatory correction to the free energy F_{osc} of a hot system and the correction to the energy E_{osc} of a cold system:

$$F_{osc}(v,\,T)=K(v,\,T)E_{osc}(v), \qquad (5.3)$$

where

$$K(v,\,T)=T\ln(\exp(\mu^0/T)+1)/\mu^0. \qquad (5.4)$$

Here E_{osc} is the oscillatory part of the energy of a cold substance at fixed volume. μ^0 is the chemical potential of a hot system, specified by Eq. (2.8). It follows from the properties of the function I_n (see [7]) that the coefficient (5.4), which depends only on the degeneracy parameter $\xi = T/\mu^0_{cold}$, is a monotonically decreasing function of ξ. At $\xi \ll 1$ it is equal to unity, at ξ = 1 it equals 0.24, and for $\xi \gg 1$ it drops off as $\xi^{-3/2}$. The decrease in the oscillation effects as the temperature rises is a general phenomenon related to the spreading of the distribution over the levels. It must be noted, however, that the nature of the vanishing of the oscillations as the temperature rises (in particular, the question of the existence of a critical point; see Sec. 6 below) requires further study. In the remainder of this work we shall not consider further the case T ≠ 0, but confine our discussion to cold matter.

From Eqs. (3.7), (4.10), and (5.2), the oscillatory part of the energy in a single cell (the volume of which is specified by v = V/N, where N is Avogadro's number, and which we shall also call the atomic volume below) can be written in the form

$$E_{\text{osc}}=6\left(\frac{9\pi}{4}\right)^{1/6}\frac{\mathcal{P}^{7/10}v^{2/3}}{\ln(\mathcal{P}^{3/10}v^{2/3})}[S_0^2]^{\bullet}, \tag{5.5}$$

$$S_0=\int dr\left(-2\Phi(r)-\frac{1}{4r^2}\right)^{1/2}=\int_0^R dr(-2\Phi(r))^{1/2}-\frac{\pi}{2}, \tag{5.6}$$

where we have introduced the notation

$$\mathcal{P}=5P/(3\pi^2)^{2/3}. \tag{5.7}$$

The oscillatory character of the expression (5.5) consists in the fact that it has a deflection point of the derivative at $S_0 = \pi(n - 1/2)$, where n is an integer. In agreement with the rules (4.2) this corresponds to the conditions when a level with principal quantum number $n = n_r + l + 1$ and $l = 0$ enters the continuous spectrum. It is then that irregularities appear in the elastic parameters of matter.

To conclude this section, we estimate the value of E_{osc} for an uncompressed isolated atom (corresponding to the case $R \to \infty$). It is immediately apparent that we cannot expect to obtain quantitative results, since the principal contribution to E_{osc} comes from the peripheral electrons of the atom (where condition (A) clearly breaks down). Nevertheless we can make some qualitative estimates.

In this case $\mu^0 = \bar{\mu} = 0$, and only the last term in Eq. (3.7) remains. Now, however, both δ_0 and τ_0 are infinite and the integral over μ in Eq. (3.7) can no longer be evaluated in the previous manner. To estimate this integral we start from the fact that, as in the earlier case, the principal contribution to it comes from the region of small $|\mu|$, and the effective width of this region is given by $S_\mu - S_0$. At small $|\mu|$ the spatial integral in the quantities δ_μ and $S_\mu - S_0$ depends on the far asymptotic form of the potential $\Phi(r)$, which, because of the nearly total screening of the nuclear charge, does not depend on Z. Thus the given quantities, and together with them the amplitude of the oscillations, are also independent of Z. Accordingly, the relative contribution of the oscillations to the total energy of the atom, which is proportional to $Z^{7/3}$ in the TF model, is of order[4)]

$$E_{\text{osc}}/E_0 \sim Z^{-7/3}. \tag{5.8}$$

This estimate is in qualitative agreement with the results of a calculation of the total energy E of average and heavy atoms by the improved Hartree method[9] (see Fig. 2). There are no reliable experimental data on shell effects in the total energy of heavy atoms.

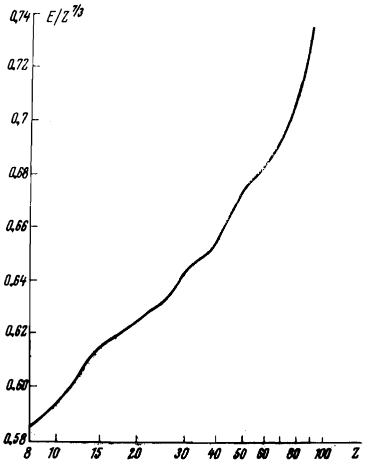

FIG. 2

We note also that the integration over μ in Eq. (3.7) leads to a further smoothing of the oscillations compared to Eq. (5.5). Then at the points $S_0 = \pi(n - 1/2)$ there will be a discontinuity in the second rather than the first derivative of E(Z). The curve of $E_{\text{osc}}(Z)$ will itself be sinusoidal. Accordingly, the extrema of this curve will be found not to coincide with the magic values of Z. The same is true of the curve in Fig. 2.

6. OSCILLATIONS OF THE PRESSURE AND ATOMIC VOLUME (SUPERHIGH COMPRESSION)

From a consideration of the region of superhigh compression, we find

$$Z^{10/3}<P<Z^{20/3},\quad Z^{-3}<v<Z^{-1}, \tag{6.1}$$

where the situation is simpler and analytic calculations are possible. In this region the density distribution is practically uniform: $n(x) \approx Z/v$ (see[7]), and, neglecting the relativistic effects that must be taken into account when $P > 10^8$, we can use the equation of state of an ideal gas:

$$\mathcal{P}=(Z/v)^{5/3}. \tag{6.2}$$

Then the potential (2.1) has the form

$$\Phi(r)=-\frac{Z}{r}\left(1-\frac{r}{R}\right)^2\left(1+\frac{r}{2R}\right).$$

Accordingly, the action (5.6) can be written in the form

$$S_0=kZ^{1/2}v^{1/6}-\frac{\pi}{2},\quad k=3\left(\frac{3}{4\pi}\right)^{1/6}\ln\frac{1+3^{1/2}}{2^{1/2}}\approx 1.56 \tag{6.3}$$

and the oscillatory part of the energy (5.5) takes the form

$$E_{\text{osc}}=36\left(\frac{9\pi}{4}\right)^{1/6}\frac{Z^{7/6}v^{-1/2}}{\ln(Z^3v)}[S_0^2]^{\bullet}. \tag{6.4}$$

The oscillatory part of the pressure is specified by the usual formula $P_{\text{osc}} = -\partial E_{\text{osc}}/\partial v$. In applying this to Eq. (6.4) we must keep in mind that the derivative of the rapidly-varying quantity $[S_0^2]^*$, equal to $2[S_0]^*\partial S_0/\partial v$, is very large (in the ratio $Z^{1/2}v^{1/6}$) compared to the derivatives of the remaining factors in Eq. (6.4). Thus

$$P_{\text{osc}}=-12\left(\frac{9\pi}{4}\right)^{1/6}k\frac{Z^{5/3}v^{-4/3}}{\ln(Z^3v)}[S_0]^{\bullet}. \tag{6.5}$$

This quantity has discontinuities at

$$v=v_n=Z^{-3}\left(\frac{\pi}{k}n\right)^6 \tag{6.6}$$

(see the dashed line in Fig. 3; the dot-dash line in this figure corresponds to the pressure $P_0(v)$ in the TF model).

It is well known, however, that such a situation is unstable; the elastic modulus is negative at the points v_n. The actual situation will be that represented by the solid line in Fig. 3. It corresponds to a first-order phase transition in which the n-th level lies in the discrete spectrum in one phase and in the continuous spectrum in the other. The corresponding curve of the oscillations of the atomic volume may be seen by rotating Fig. 3 through 90°. The values of the pressure at which the phase transition occurs can be found from Eqs. (6.2) and (6.6):

$$\mathcal{P}_n=\left[\frac{k}{\pi n}\right]^{10}Z^{20/3}, \tag{6.7}$$

and the size of the jump $\Delta v/v$ is specified by the condition of equal pressure on the phase coexistence curve and by the fact that the discontinuous change in $[S_0]^*$ is

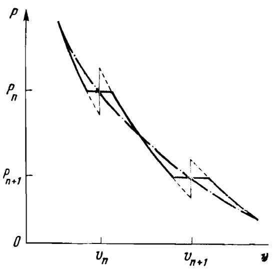

FIG. 3

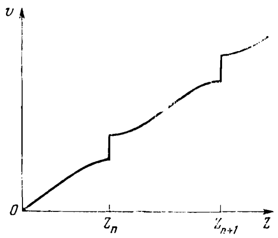

FIG. 4

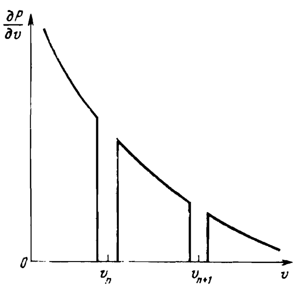

FIG. 5

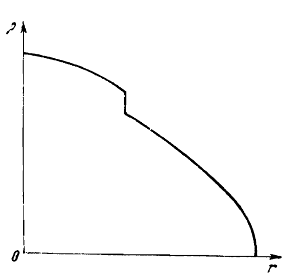

FIG. 6

equal to π:

$$\left(\frac{\Delta v}{v}\right)_n = 3{,}6\left(\frac{9\pi}{4}\right)^{1/6}\frac{\pi^3}{k(3\pi^2)^{2/3}}\frac{n^2}{Z\ln n}. \qquad (6.8)$$

The dependence of v_{osc}/v itself on P and Z can be obtained from Eqs. (6.5) and (6.2) by changing variables from v to P with the help of the formula $v_{osc}/v = P_{osc}/P\kappa$, where $\kappa = 5/3$ is the polytropy index:

$$\frac{v_{osc}}{v} = -36\left(\frac{9\pi}{4}\right)^{1/6}\frac{k}{(3\pi^2)^{2/3}}\frac{Z^{1/3}}{\mathscr{P}^{1/5}\ln(Z^{20/3}/\mathscr{P})}[S_0]^{\bullet} \qquad (6.9)$$

with

$$S_0 = kZ^{2/3}/\mathscr{P}^{1/10} - \pi/2.$$

This dependence is displayed by the jumps in the atomic volume as Z varies at fixed P (see Fig. 4). The maximum value of v to the right of a discontinuity corresponds to the value of Z at which the level with the given n and with $l = 0$ still lies in the discrete spectrum. The corresponding configuration is similar to that of an alkali metal. When Z is decreased by unity we pass to a minimum of v to the left of the discontinuity, where the given level has already entered the continuous spectrum, corresponding to a noble-gas configuration. The resulting "magic" values of Z_n are

$$Z_n = (\pi n/k)^{3/2}\mathscr{P}^{3/20}. \qquad (6.10)$$

The rise of these numbers with pressure is related to the increasing influence of the neighboring cells, which causes the character of the population of the spectrum levels to become still less hydrogen-like. In this connection we note that an increase in pressure causes an increase in the values of Z_l at which all the levels with given l are "extruded" from the discrete spectrum$^{5)}$:

$$Z_l = a(\mathscr{P}Z^{-10/3})^{3/10}(2l+1)^3,\ a = \frac{2^{5/2}}{9}\pi^{1/2}\left(\frac{2}{\sqrt{3}}+1\right) \approx 3.53. \qquad (6.11)$$

This formula was obtained from the conditions $p_{0l}^2 = 0$ and $(p_{0l}^2)' = 0$ (see[9]) and from the expression for Φ given at the beginning of this section.

Equation (6.9) shows that, although the relative value of the oscillations in the atomic volume is actually quite small in the region where this formula is applicable, it is nevertheless significant because of its large numerical coefficient. For example, even at $Z = 100$ and $P \sim Z^{10/3}$ the value of (6.8) is about 0.2.

The oscillation effects are particularly evident in quantities that are obtained by taking derivatives of the pressure with respect to the volume. In particular, the elastic modulus is generally zero in the phase coexistence region (see Fig. 5), and the Gruneisen coefficient, which represents the next derivative, becomes negative at the oscillations, and so on.

Condition (6.1) is realized in white dwarf stars, whose substance consists of a degenerate electron gas and a crystal lattice of ions[7]. For $Z \sim 10-20$ these conditions correspond to a range of densities from 10^3 to 10^6 g/cm^3. These numbers are typical for white dwarfs. The fact noted above, that the elastic modulus of matter drops to zero at pressures near to P_n, leads to a discontinuity in the matter density distribution $\rho(r)$ of the white dwarf at the corresponding point (see Fig. 6). Such discontinuities have been discussed earlier in relation to phase transitions of hydrogen from the molecular to the metallic phase in the substance of giant planets[10].

7. THE HIGH-COMPRESSION REGION

Let us now turn to the region of lower pressures

$$1 < P < Z^{10/3}, \qquad (7.1)$$

which, by convention, we shall call the high-compression region. The density distribution in this region is already nonuniform because of the significant interaction effects of electrons with nuclei and with each other. For this reason the answer must be expressed in terms of the solutions of the TF equation for a compressed atom, which are available only in numerical form. We shall confine our discussion here to the results that can be obtained without numerical calculations.

Basing our argument on the self-similarity of the TF equation, we can write the equation of state and the expression for the action as

$$P = Z^{10/3}f(Zv), \quad S_0 = Z^{1/3}\varphi(Zv) - \pi/2,$$

where f and φ are some functions. We shall use the polytropic form of the equation of state:

$$P \backsim Z^{10/3}(Zv)^{-\varkappa}, \qquad (7.2)$$

where the index κ is greater than 5/3. There are arguments indicating that as $Z \to \infty$ this index tends to the value 10/3 (see[11,12])$^{6)}$.

As to the action, the argument of the function φ in the given region is small. Thus we can write S_0 in the form

$$S_0 = Z^{1/3}a_1[1 - b(PZ^{-10/3})^{\sigma} + \ldots] - \pi/2, \qquad (7.3)$$

where a_1 and b are numerical factors of order unity, and $\sigma = (3\kappa - 5)/15\kappa$. a_1 can be expressed in terms of the TF function $\chi(x)$ (see, e.g.,[13]) and equals[14]

$$a_1 = \left(\frac{3\pi}{4}\right)^{1/3}\int_0^\infty dx\left(\frac{\chi(x)}{x}\right)^{1/2} \cong 1.33\cdot 3.20 = 4.25. \qquad (7.4)$$

The index σ in Eq. (7.3) can be obtained from the argument that at relatively low compression the external pressure deforms only the neighborhood of the cell boundary. Thus

$$S_0 \approx \int_0^R dr(-2\Phi^0)^{1/2} - \frac{\pi}{2},$$

where Φ^0 is the potential of the uncompressed atom. Then

$$\partial S_0/\partial R \sim n(R)^{1/3} \sim P^{1/5} \tag{7.5}$$

and with the help of Eq. (7.2) it is not hard to obtain Eq. (7.3).

Starting with the expression (5.5) and continuing as in Sec. 6, we can arrive at a similar qualitative picture for the oscillations of the pressure and the atomic volume (see Figs. 3–5). Taking Eq. (7.5) into account, the oscillatory part of the atomic volume takes the form

$$v_{\text{osc}}/v \sim -[P^{1/10}\ln(Z^{20/3}/P)]^{-1}[S_0]^*. \tag{7.6}$$

As may be seen from a comparison of Eqs. (7.6) and (6.9), the amplitude of the oscillations also decreases with rising pressure in region (7.1), although the decrease is slower than in region (6.1). At the boundary between these regions the expressions obtained here and in the preceding section match very well.

The values of the pressure at which discontinuities in v occur are specified by Eq. (7.3):

$$P_n \sim Z^{10/3}(1-(Z_n^0/Z)^{1/3})^{1/\sigma}, \tag{7.7}$$

where $Z_n^0 \equiv (\pi n/a_1)^3$, and n runs over all integers for which $Z_n^0 < Z$. The magic values of Z_n, specified by the same formula, are

$$Z_n = Z_n^0[1+3b(PZ^{-10/3})^\sigma]. \tag{7.8}$$

Note that, although the pressure-dependent term in Eq. (7.8) is small compared to unity, its contribution to Z_n is still significant in the absolute sense. Finally, because of the above-noted closeness of the potential Φ to the TF potential, the values Z_l at which all levels with a given l move into the continuous spectrum are specified by the usual relation[13]

$$Z_l \cong 0.155(2l+1)^3. \tag{7.9}$$

8. EXTRAPOLATION TO THE LOW-PRESSURE REGION

Although the results obtained above are not immediately applicable to the low-compression region ($P \leq 1$), by extrapolating them to this region we can gain a qualitative understanding of a number of experimentally observed laws of behavior.

We begin with the problem of the magic numbers Z_n at which the atomic volume has a maximum. At small P Eq. (7.8) gives

$$Z_n = 0.41n^3. \tag{8.1}$$

This formula gives the set of numbers 3, 11, 26, 51, 88 for n = 2 to 6, where, as we have already noted, these values correspond to the appearance of the levels with the given values of the principal quantum number n and with $l = 0$ in the discrete spectrum. In the range of P that has been investigated experimentally the magic values of Z_n are those corresponding to the alkali metals (i.e., they also represent the appearance of the levels (n, 0) in the discrete spectrum) and are equal to 3, 11, 19, 37, 55, ...

The difference between these sets of numbers can be attributed to the unsuitability of the quasiclassical description near the E = 0 level at low pressures. In fact, however, a positive conclusion can be drawn from Eq. (8.1). It is well known that in weakly compressed matter there are anomalies in the filling of the levels with high angular momenta, and that as the pressure rises these anomalies must disappear. The filling of the levels should accordingly have a tendency to become more hydrogen-like; for instance, at pressures $P \sim 1$ nickel should be transformed into a "noble gas" with completely filled shells, and the role of an alkali metal passes to copper[15]. Hydrogen-like level filling produces a set of "alkali metals" with Z_n = 3, 11, 29, 61, 111, ... A comparison of these numbers with the set specified by Eq. (8.1) shows that the latter formula correctly reflects the indicated tendency.

Let us now consider the shape of the curve describing the Z dependence of the atomic volumes. At first glance we seem to have encountered a qualitative contradiction here, since the theory developed above predicts discontinuities in the curve v(Z), while experiments show discontinuities in the derivative $\partial v/\partial Z$. In fact, however, this contradiction is only apparent.

The fact is that discontinuities in the derivative also exist in the regions of high and superhigh compression, but they are of a smaller order of magnitude than the discontinuities in the function v(Z) itself. Returning to the derivation of the expression for P_{osc} (see Sec. 6), we note that in taking the derivative of expression (5.5) with respect to the volume, we retained the principal term in the given region, the derivative of the rapidly-varying quantity $[S_0^2]^*$, and omitted the smaller term arising from the differentiation of the remaining factors in Eq. (5.5). The latter term, which is proportional to $[S_0^2]^*$, is the one that specifies the discontinuities of the derivative. In the region of superhigh compression we obtain for it the following expression:

$$\left(\frac{v_{\text{osc}}}{v}\right)_2 = \frac{60}{\sqrt{\pi}}\left(\frac{3}{4\pi}\right)^{2/3}\left[\mathscr{P}^{1/10}Z^{1/3}\ln\left(\frac{Z^{20/3}}{P}\right)\right]^{-1}[S_0^2]^*. \tag{8.2}$$

The ratio of $(v_{\text{osc}}/v)_2$ to v_{osc}/v is of order

$$v^{-1/3}P^{-1/5} \sim (PZ^{-10/3})^{-\sigma}Z^{-1/3}. \tag{8.3}$$

In regions (6.1) and (7.1) this ratio is very small, so that our neglect of the term $(v_{\text{osc}}/v)_2$ in the preceding discussion was justified. But as the pressure drops, the ratio (8.3) grows larger; at $\kappa = 10/3$ it becomes of order unity just on the border of the region (7.1), i.e., at $P \sim 1$. At even lower pressures it is natural to expect that the discontinuities of the derivative will predominate over the discontinuities of the function v(Z) itself.

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[1] Here and below we use atomic units ($e = \hbar = m = 1$). In ordinary units, condition (A) corresponds to $P \gg 300$ Mbar.

[2] Conditions (A) and (B) are compatible when $Z \gg 1$, which we shall assume to be true below.

[3] Under the conditions in which a quasiclassical analysis is correct, the exchange effects are relatively small and can be considered separately.

[4] This obvious conclusion does not agree with the estimate of E_{osc} for an uncompressed atom obtained earlier [8] (in this connection, see [4]).

[5] Note that the inverse of Eq. (6.11) gives the value of $l_{\max}$, which was mentioned in Sec. 4.

[6] This value can easily be obtained by noting that as $Z \to \infty$, any distance r from the nucleus corresponds to a value of the dimensionless parameter $rZ^{1/3} \to \infty$. Then the TF function $\chi(x) \sim x^{-3}$ and the density $n^0(x) \sim x^{-6}$. From the concept of the local deformation of the electron cloud under compression (see below), we have $n(R) \approx n^0(R)$ and $P \sim n(R)^{5/3} \sim R^{-10} \sim v^{-10/3}$.

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[1] N. Bohr, Izbrannye nauchnye trudy (Selected Scientific Works), **1**, Nauka, 1970, p. 431.

[2] L. V. Al'tshuler, Usp. Fiz. Nauk **85**, 197 (1965) [Soviet Phys.-Uspekhi **8**, 52 (1965)]; L. V. Al'tshuler and A. A. Bakanova, Usp. Fiz. Nauk **96**, 193 (1968) [Soviet Phys.-Uspekhi **11**, 678 (1969)].

[3] E. S. Alekseev and R. G. Arkhipov, Fiz. Tverd. Tela **4**, 1077 (1962) [Sov. Phys.-Solid State **4**, 795 (1962)].

[4] D. A. Kirzhnitz and G. V. Shpatakovskaya, Zh. Eksp. Teor. Fiz. **62**, 2082 (1972) [Sov. Phys.-JETP **35**, 1088 (1972)].

[5] I. C. Light and I. W. Yuan, J. Chem. Phys. **58**, 660 (1973).

[6] A. I. Voropinov, G. M. Gandel'man, and V. G. Podval'nyĭ, Usp. Fiz. Nauk **100**, 193 (1970) [Sov. Phys.-Uspekhi **13**, 56 (1970)].

[7] D. A. Kirzhnits, Usp. Fiz. Nauk **104**, 489 (1971) [Sov. Phys.-Uspekhi **14**, 512 (1972)]; D. A. Kirzhnits, Polevye metody teorii mnogikh chastits (Field Theoretical Methods in Many-Body Systems), Atomizdat, 1963 (Pergamon Press, 1967).

[8] O. V. Troshin, Izv. VUZov Fizika **4**, 90 (1968); L. Ya. Kobelev and O. V. Troshin, Phys. Stat. Sol. **28**, K81 (1968).

[9] A. Rosén and I. Lindgren, Phys. Rev. **176**, 114 (1968).

[10] A. A. Abrikosov, Voprosy Kosmogonii **3**, 12 (1954).

[11] Ya. B. Zel'dovich and I. D. Novikov, Relativistskaya astrofizika (Relativistic Astrophysics), Nauka, 1967 (U. of Chicago Press, 1971).

[12] N. N. Kalitkin and L. V. Kuz'mina, Preprint of the Inst. Appl. Math., Acad. Sci. USSR, No. 55, 1969.

[13] L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika (Quantum Mechanics—Non-Relativistic Theory), Fizmatgiz, 1963 (Pergamon Press, 1965).

[14] Enrico Fermi, Sobranie trudov (Collected Works), **1**, Nauka, 1971, p. 286.

[15] G. M. Gandel'man, V. M. Ermachenko, and Ya. B. Zel'dovich, Zh. Eksp. Teor. Fiz. **44**, 386 (1963) [Sov. Phys.-JETP **17**, 263 (1963)].

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189