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ON THE APPLICABILITY OF THE SPHERICAL CELLULAR MODEL FOR THE ANALYSIS OF ZERO ISOTHERMS OF HIGHLY COMPRESSED PLASMA

F.N. BOROVIK, L.I. GURSKIY, G.S. ROMANOV

Heat & Mass Transfer Institute, 15, P. Brovka str., 220072, Minsk, Belarus.
E-mail: ksi@hmti.ac.by

To construct a wide-range equation of state of plasma it is necessary to have information of zero isotherms. Zero isotherms can be determined (for example) with Korringer-Kohn-Rostoker (KKR), the argumented plane wave, the argumented spherical wave (ASW), the linear combination of Gaussian-type orbitals (LCGTO) techniques. There exists much simpler the spherical cellular model (SCM) (Gandelman, 1962) in which the Wigner-Seitz cell is replaced by the spherical cell with the equal volume of radius r_0, satisfying condition

$$\frac{4}{3}\pi r_0^3 a_0^3 = \frac{A}{\rho N_A},$$

where a_0 is the Bohr radius, A is the atomic weight of an element, N_A is the Avogadro number, ρ is the substance density. Further the atomic units are used. In the SCM the electron wave functions $\Psi(\vec{r})$ must satisfy the following boundary conditions

$$\Psi(\vec{r}_0)\, e^{-i\vec{k}\vec{r}_0} = \Psi(-\vec{r}_0)\, e^{i\vec{k}\vec{r}_0}$$

$$e^{-i\vec{k}\vec{r}_0} \frac{\partial}{\partial r}\Psi(\vec{r})_{r=r_0} = -e^{i\vec{k}\vec{r}_0} \frac{\partial}{\partial r}\Psi(-\vec{r})_{r=r_0},$$

where $\Psi(\vec{r})$ satisfies the Schrodinger equation with a spherically symmetrical potential $U(r)$. These conditions result in that the eigenvalues form bands and are functions of quasi-momentum k.. Use of spherical cells allows one to characterize bands by quantum numbers n, l_0, m corresponding to k =0. If a wave function is represented as a series

$$\Psi = \sum_{l=|m|}^{l_{max}} i^l \frac{R_{\varepsilon l}(r)}{r} A_{lm}(k) Y_{lm}(\theta, \varphi),$$

where the normalized functions $R_{\varepsilon l}$ satisfy an equation

$$R''_{\varepsilon l} + 2\left[\varepsilon - U(r) - \frac{l(l+1)}{2r^2}\right] R_{\varepsilon l} = 0,$$

the following set of equations can be obtained for odd l

$$\sum_{l'=|m|}^{l_{max}} A_{l'm}(k) a_{ll'}(k) R_{ld'}(r_0) = 0$$

and for even l

$$\sum_{l'=|m|}^{l_{max}} A_{l'm}(k) a_{ll'}(k) \frac{d}{dr}\left(\frac{R_{ld'}}{r}\right)_{r=r_0} = 0 .$$

Here

$$a_{ll'}(k) = i^{l'-l} \int Y^*_{l'm} Y_{lm} e^{ik\cos\theta} d\Omega$$

and

$$\sum_{l=|m|}^{l_{max}} A^2_{lm}(k) = 1 .$$

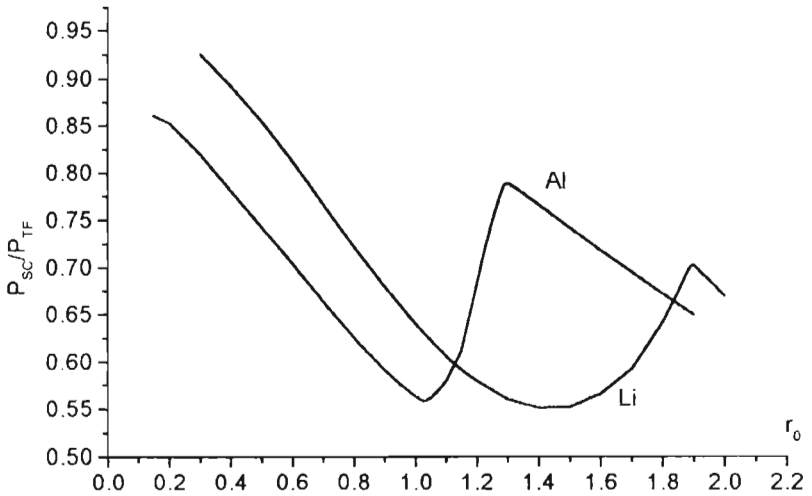
The selfconsistent potential U(r) is expressed in terms of the cell electron density computed through wave functions R_{ld}. Value l_{max} is selected from the condition of smallness $|A_{lm}|$ at $l > l_{max}$ ..

The SCM neglects dependence of the spectrum on the direction of the quasi-momentum vector. The latter is certainly an oversimplified approximation for low pressure, but it is reasonable for high values of parameters. The applicability of this model has been analyzed in (Farjam M.1988) at normal conditions. In the present work calculations for Ne, Li and Al with the purpose of comparison to results presented in (Chernov, 1988; Chernov, 1990;Boettger, 1986; Meyer - ter - Vehn, 1988) were carried out to verify the applicability of this model for analysis of zero isotherms at high compressions σ.

In (Boettger, 1986) a number of points on the cold isotherm of neon is calculated with the LCGTO technique and metallization is detected at r_0 =0.91a_0. Neon at densities of about 1 g/cm^3 is a Van-der-Waals crystal with a FCC lattice. Free electrons appear in the course of compression which allows one to apply the SCM.. In the present work the coincidence of eigenvalues of 2p and 3d at a zero quasi-momentum for neon occurs at r_0 =0.967. Note that the coincidence of eigenvalues means vanishing of the gap between the filled 2p zones and empty 3d zones, i.e. metallization. At smaller compression neon has filled bands with a $1s^2 2s^2 2p^6$ configuration and is a dielectric. The discrepancy with the data from (Boettger, 1986) is possibly associated with an insufficient basis for calculations with the LCGTO technique (a basis of s, p and d orbitals was used there). Calculations with the help of the SCM show that at $r_0 \cong 1$ contribution of f and g orbitals to pressure is approximately 25 percent. Thus the SCM describes exactly enough the deformation of the Ne energy spectrum at high compressions.

At the present time calculations performed with the KKR (Chernov, 1988) and ASW [Meyer - ter - Vehn, 1986] techniques for lithium for compression up to $\sigma \cong$ 1000 are available. Calculation with the SCM has shown that in conformity with KKR and ASW at $\sigma \cong 5$ ($r_0 \cong 1.9$) the zero Li isotherm experiences a sharp change in

inclination associated with formation of a cavity inside the Fermi surface. Since the 2s



zone of lithium is filled only half (lithium is a one-valence element) at $r_0 > 1.98$ the shape of the 2s zone is such that the electrons fill states in the neighbourhood of the zero quasi-momentum, i.e. are populated mainly s -orbitals. At further compression the electrons of zone 2s begin to populate states with quasi-momenta close to maximum which signifies growth of the p -orbital population. Eventually this leads to a situation in which the states in the vicinity of the zero quasi-momentum become unpopulated, i.e. a concavity is created inside the Fermi surface. In (Chernov, 1988) a small oscillation on the isotherm is also observed at $\sigma \cong 33$ ($r_0 \cong 1$), which the author attributes to squeezing with growth of compression of level 1s into a continuous spectrum. However, calculation with the SCM have shown, that level 1s is delocalized already at $\sigma \cong 12$, and at $\sigma \cong 33$ pressure due to band 1s has no peculiarities as the function of compression. The density of electrons on the cell surface has no peculiarities too. Since change in inclination of the isotherm is sometimes difficult to detect, the value $D = P_{SC} / P_{TF}$ was used, where P_{SC} is pressure, calculated as per the SCM, P_{TF} is pressure calculated as per the Thomas-Fermi (TF) model. Since the TF model isotherm does not have any peculiarity value D allows one to describe peculiarities on the quantum mechanical isotherm more evidently. The results of calculations are presented in figure. In (Chernov, 1990) value D was considered as a function of compression. In the present work D is considered as a function of the cell radius since for compression on the sections where the peculiarities are absence is practically a linear function. This explains the usefulness of argument r_0. The minimum in the curve takes place since in this range of compressions the relative contribution of the 2s band to the total pressure decreases and the relative contribution of 1s-band increases as compression increases.

Results for aluminum up to $\cong$ 2000 compression are presented in (Meyer - ter -

Vehn, 1986). Calculations of the value D for Al as per the SCM are given in the figure. It is seen (in full conformity with (Meyer - ter - Vehn, 1986)) that at $\sigma \cong 10$ ($r_0 \cong 1.3$) the cold isotherm of aluminum has a peculiarity (a sharp change in the inclination) due to the intersection of the bands 3s and 3d, which is accompanied by transition of electrons from s -states to d-states. This takes place since electrons leave the 3d0 band and occupy the 3d2 band in which s- orbitals are absence. The minimum in the curve occurs as in this range of compressions ($\sigma \cong 24$) the relative contribution of the 3d band to the total pressure decreases and the contribution of the 2p band increases as compression increases. The contribution of the 2s band is negligible in this range of compressions. In conformity with (Meyer - ter - Vehn, 1988) at $\sigma \cong 1000$- 2000 ($r_0 \cong 0.2$) zone 2s is replaced by zone 3d. This is accompanied by reduction of the population of s-states in zone 2s and by increase of the population of d- and f-states. In the curve this is represented by the appearance of a sharp change in the inclination.

Thus calculations show suitability of the SCM for analyzing zero isotherms at high compression and allow one to link various peculiarities in the behaviour of thermodynamic parameters with changes in the characteristics of the spectrum and the population of levels.. It should be noted that the SCM leads to excessively sharp changes in the inclination of zero isotherms which can be wrongly interpreted as a second-order phase transitions. Calculations have shown that deformations of the energy spectrum at large compression do not result in electron phase transitions and only generate rather sharp changes of the inclination of cold isotherms. All these peculiarities are not associated with squeezing deep shells into a continuous spectrum, but with deformation of highly positioned bands. Deep shells only modify these peculiarities.

Use of the SCM for superhigh compressions is not reasonable because the energy spectrum of the empty lattice in the SCM differs from the spectrum of free electron gas. It is found that the populations of l - orbitals also differ from the populations for the free electron gas. Calculations show that the electron density distribution for the empty lattice in the SCM is not homogeneous which results in that the ratio P_{SC} / P_f (P_f - the pressure of free electron gas) differs from unity. This ratio is 1.004 for Li, 1.128 for Al. It is largest for Mg and equals 1.133. For example by the empty lattice for Mg we mean that the spherical cell contains 12 electrons and does not the nucleus.

Hence the SCM at $\sigma \to \infty$ does not contain the free electron gas limit.

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