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PHASE TRANSITION IN METALLIC PLASMAS

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The energy of a virtual atomic structure on the metallic side of the metal-nonmetal transition in a dense plasma has been estimated. Assuming nearly uniform valence electron density, the interatomic interaction is considered a Madelung energy which has been shown to be nearly one third of that for the OCP model. It has been verified by solving numerically the pseudowave equation for the valence electrons in ellipsoidal atomic cells which are compatible with the percolation structure of overlapping classically accessible spheres. A critical value of the Coulomb coupling parameter has been shown to agree with the experiment in the liquid-gas critical points of cesium and rubidium, which can be identified with the plasma-phase-transition critical points.

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A long-standing problem in the statistical theory of the nonideal plasma is the proper description of the apparently simple and universal Coulomb interparticle interaction. During the last two decades, broad interest was elicited by the strongly coupled plasmas, especially in connection with a plasma-phase-transition (see [1] and references therein). Noteworthy is the breakdown of the symmetry in the description of the interaction between electrons and ions. In particular, the well known one-component-plasma (OCP) model, which is appropriate for the conditions in white dwarfs, treats degenerated electrons as a uniform electron background. In this model the coupling parameter is

$$\Gamma = z^2 e^2 / R_s T, \tag{1}$$

with the Wigner–Seitz radius

$$R_s = (4\pi n_i/3)^{-1/3},$$

where n_i is the ion density, z is the valence of ions, e is the electron charge, T is the temperature. If $\Gamma \gg 1$, the potential energy of a disordered ionic lattice is

$$U = -\gamma n_i z^2 e^2 / R_s, \tag{2}$$

where γ is the Madelung coefficient. Obviously, the Madelung energy does not contain the electron exchange and correlation.

The tendency to treat ions and electrons separately also exists in the theory of fluid metals which describes strong inter-ion interaction, as well as electron exchange and correlation, but which generally assumes weak electron–ion coupling. This, however, is not acceptable near the metal-nonmetal transition point in expanded fluid metals [2], where the plasma-phase-transition is the most probable. Since the metal-nonmetal transition is ultimately connected with the appearance of an atomic structure [3-5], it is reasonable to apply a quite different theoretical scheme including strong electron-ion coupling from the beginning. In such a scheme it should be possible to treat the interaction between overlapping atoms in a virtual atomic structure. The electron exchange and correlation reduce to the symmetry conditions for quasimolecular wave functions, whereas the electron density distribution can still be uniform in a considerable part of the volume. Then, the energy of the interaction between atoms in such a virtual atomic structure has the Madelung form (2). We use a simple estimation of the renormalized Madelung coefficient, assuming uniform electron density outside the ionic cores, as well as the numerical solution of the pseudowave equation for valence electrons in atomic cells. It will be shown the renormalized coefficient is nearly one third of that of the OCP, since some part of the electron–ion interaction energy relates to the internal energy of atoms. Therefore, near the metal-nonmetal transition point the OCP model strongly overestimates the cohesive power of the Coulomb interaction, and so cannot properly localize the plasma-phase-transition points.

Using the Madelung interaction energy of overlapping atoms in a van der Waals-like equation of state describing the plasma-phase transition [5], one can express the critical coupling parameter by the Madelung coefficient

$$\Gamma_c = \frac{49}{16}\frac{z+1}{\gamma}. \tag{3}$$

Thus, small γ value conjugates with a high coupling parameter at the plasma-phase-transition points.

We consider an atomic structure in the vicinity of the metal-nonmetal transition point where overlapping classically accessible spheres of valence electrons form percolation clusters of different scales. The classically accessible radius is

$$R_a = e^2/I, \tag{4}$$

where I is the ionization potential of the atoms. Nearest neighbors of one central atom form a coordination sphere the radius of which is close to the double accessible radius $2R_a$. Percolation qualitatively changes the energy spectrum of atomic gas. Because of virtual screening, a continuous spectrum of excitations arises which corresponds to an asymptotically free motion of valence electrons. Under any perturbations the free atom ground level is the low limit of the internal energy, hence an internal energy spectrum of the atom counting from the ion core energy

$$E(p_1, \ldots p_z) = \sum_{k=1}^{z}(-I_k + \epsilon_{p_k}), \qquad \epsilon_{p_k} = p_k^2/2m, \tag{5}$$

where z is the number of valence electrons of the atom, I_k are the sequential ionization potentials of the atom, ϵ_{p_k} are the electron excitation energies, p_k are the momenta of electrons far from a screened ion core, m is the electron mass.

In general, the interaction energy of overlapping atoms in percolation clusters is not pair-additive, i.e. the dependence of energy per atom upon the coordination number saturates with an increase in this number. At large coordination numbers, the density of valence electrons in a mixture of quasimolecular states, formed by one central atom with each of its neighbors, is nearly uniform near the boundary between them. Then, the problem of interatomic interactions reduces to the calculation of the atomic cell energy. The simplest atomic cell is the Wigner–Seitz sphere with the ionic core occupying up to 20% of the cell volume [6], this part is

$$a = (R_c/R_s)^3,$$

where R_c is the core radius. The density of valence electrons, uniformly distributed outside the ionic core, is

$$n_e(r) = \begin{cases} 0, & r < R_c, \\ n_e/(1-a), & R_c < r < R_s, \end{cases} \tag{6}$$

where n_e is the averaged electron density. The interaction energy per atom is given by an integral

$$u = -\frac{1}{2}\int_{R_c}^{R_s} \frac{e^2 z(r)}{r} n_e(r) 4\pi r^2 dr, \tag{7}$$

with the charge number depending on the radius

$$z(r) = z - \frac{4\pi}{3}(r^3 - R_c^3)n_e(r). \tag{8}$$

The coefficient 1/2 in equation (7) corresponds to the fraction of valence electrons of neighboring atoms in the above mentioned (two-atomic) quasimolecules, and so precludes the internal energy of the atom, which is already taken into account by equation (5), from being counted twice. Simple calculation yields

$$u = -\gamma(a)\frac{z^2e^2}{R_s}, \tag{9}$$

where the Madelung coefficient is

$$\gamma(a) = \frac{1}{2}\left[0.9 - 1.5a^{2/3}(1 - 0.4a)\right](1-a)^{-2}. \tag{10}$$

This coefficient is reasonably well defined despite the uncertainty in the core volume. Indeed, for a in a range from zero to 0.2, the γ value varies from 0.45 to 0.34, that is one half, or even less, of the Madelung coefficient for the OCP model. Obviously, the model of the interatomic interaction is very simplified for the uniform valence electron distribution. However, this is more than compensated by explicitly excluding the atomic internal energy.

We estimate the cohesion of atoms, that is the minimal energy needed to evaporate one atom into a vacuum (at low temperature). Using the volume fraction of the classically accessible spheres

$$\zeta = (R_a/R_s)^3, \tag{11}$$

equation (9) can be expressed by the atomic characteristics

$$u = -\gamma z^2 I\zeta^{1/3}. \tag{12}$$

Taking into account the Fermi energy of the quasiatomic excitations (5), the cohesion energy above the metal-nonmetal transition point is

$$\epsilon_{ch}/I = \gamma z^2\zeta^{1/3} - b\zeta^{2/3},$$

where $b = (9\pi/16g_a)^{2/3}(I/Ry)$, and g_a is the statistical weight of the atomic ground level. For example, for cesium at $\zeta = 0.5$ we get $\epsilon_{ch} \sim (0.1 - 0.2)I$. This estimate can be compared with the cohesion at normal densities of heavy alkali metals, which is $\sim 0.2I$.

A main assumption in calculating the interaction energy is that the electron density is nearly uniform outside the ion core of atoms. Beyond this approximation, we consider a microscopic model of atomic cells for the percolation structure of the slightly overlapping classically accessible spheres. In a density range $\zeta < f$, where $f \approx 2/3$ is the random close packing fraction of spheres, an atomic cells can be substituted by closely packed (if directionally ordered) ellipsoids circumscribing the classically accessible spheres. The nearest to the sphere is an oblate ellipsoid, the polar half-axis of which is equal to the classically accessible radius, and the volume is the fraction f of the Wigner–Seitz cell volume,

$$R(\vartheta) = \frac{R_a}{\sqrt{1 - (1 - \zeta/f)\sin^2\vartheta}}, \tag{13}$$

where $R(\vartheta)$ is the radius, ϑ is the polar angle. In the case $\zeta = f$ the cell coincides with the classically accessible sphere. By definition, the surface of a Wigner–Seitz atomic cell consists of symmetry planes which are orthogonal to the axes of quasimolecules formed by a central atom and its neighbors. Analogously, the surface of an ellipsoidal cell can be considered a geometrical place of centers of symmetry in many such two-atomic quasimolecules.

At low densities, the applicability of the local-density approximation, the main computational method for nonuniform electronic systems, is questionable because the overlap of the atomic wave functions is small. Therefore, we use a more primitive representation of the effective potential for electrons, namely, one-electron potential on the quasimolecule axis has a form

$$V(\rho, \vartheta) = \phi[R(\vartheta) + \rho] + \phi[R(\vartheta) - \rho], \tag{14}$$

where ϕ – functions are pseudopotentials of the ionic cores including the contributions of the quasimolecule electron cloud, $\rho = r - R(\vartheta)$, r is the radial coordinate. Using the Heine–Abarenkov pseudopotential with the parameters A and r_c chosen to fit the ground atomic level [7], we write

$$\phi(r) = \begin{cases} -A, & r < r_c, \\ -(ze^2/r) + \frac{1}{2}\xi I, & r > r_c. \end{cases} \tag{15}$$

An additional term outside the core region in equation (15) represents the potential of a quasimolecule electron cloud within a correlation hole, where ξ is a factor which depends on the electron density distribution. At the limit of high coordination numbers, one can treat equation (14) as a total potential smoothed out over the polar angles for all quasimolecules with a common central atom.

The ξ-factor is selfconsistently determined by a classical percolation condition such that in the ground level a nearly bound valence electron can transfer to the neighboring cells just over the potential saddles at the poles, i. e.

$$E = (-2 + \xi + \delta)I, \tag{16}$$

with the δ – term taking into account the centrifugal potential. Obviously, this percolation principle can justifiably be introduced for the quasiclassical states of valence electrons. This is the case for heavy alkali metals, which have large main quantum numbers and classically accessible radii much greater than the Bohr radius.

The electron wave function is determined by the Schrödinger equation,

$$\Delta\psi + \frac{2m}{\hbar^2}[E - V(\rho,\vartheta)]\psi = 0, \tag{17}$$

where $\hbar$ is the Planck constant, with the boundary conditions of zero radial derivatives on the cell surface corresponding to symmetrical states of the quasimolecules, as well as at the origin

$$\partial\psi/\partial r = 0, \qquad r = 0, R(\vartheta). \tag{18}$$

The Schrödinger equation with the percolation condition allowing for the centrifugal potential yields the second derivative zero at the cell poles

$$\partial^2\psi/\partial r^2 = 0, \qquad r = R(\vartheta); \vartheta = 0, \pi. \tag{19}$$

Obviously, equation (19) defines a separatrix for the different behavior of wave functions. This is an additional condition for the determination of the ξ-factor.

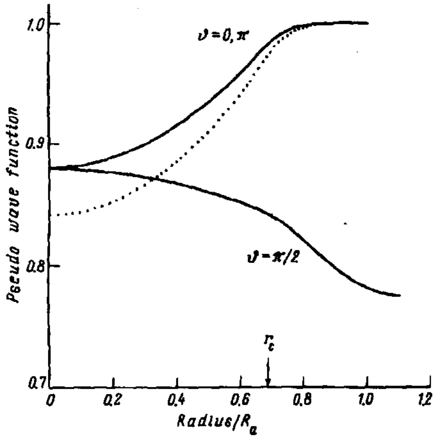

Fig.1. Radial dependencies of the ground state pseudo-wave function at the volume fractions of the classically accessible apheres $\zeta/f = 0.8$ (solid line) and $\zeta/f = 1$ (dotted line)

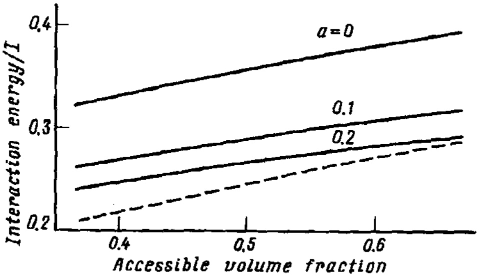

Fig.2. Interatomic interaction energy in dependence on the volume fraction of the classically accessible spheres. The solid lines are the Madelung energy for different volume fractions a of the ionic core, and the dashed line is the disturbed atom model

The interaction energy of one atom with all others is determined by the difference between the cell and the free atom ground-state levels. Summing over all the atoms, each atom interaction contributes twice, therefore the interaction energy per atom is

$$u = \frac{1}{2}(E + I) = -\frac{1}{2}(1 - \xi - \delta)I. \tag{20}$$

In our cell model excitations of quasiatoms, which effectively increase the accessible volume, were not explicitly included. In a wide ζ range, at the Fermi energy level the volume fraction of the classically accessible spheres exceeds the close packing fraction, and so quasiatomic excitations smooth out the interaction energy dependence on ζ. Therefore, our model can be adapted to take account of excitations by averaging the interaction energy in a range between ζ and f.

The Schrödinger equation (17) with the pseudopotential (14), with the boundary conditions (18) and (19), and with an additional condition that the logarithmic derivatives at the core radius are continuous, has been numerically solved (Fig. 1). The pseudopotential parameters $A = 1.45I$ and $r_c = 0.68R_a$ were chosen, which are representative for the ground states of heavy alkali metals [7]. A high-order finite-difference method [8] was used for the discrete grid in the polar coordinates (typically 30 points for the radial as well as for the angular coordinates). In the spherically symmetric case ($\zeta = f$, $\delta = 0$), we have found that the ξ-factor is equal to 0.43. Then, equation (20) gives the energy per atom $0.285I$, i.e. nearly the low limit of our direct estimates of the Madelung energy (12). In general, the interaction energy for the definite volume fraction of the classically accessible spheres has been averaged in the range between this value and the close packing fraction assuming the rectilinear probability distribution (Fig. 2). Evidently, the disturbed atom model qualitatively agrees with the simple model which assumes uniform electron density. It confirms that the interaction energy of overlapping atoms is considerably smaller than the OCP potential energy.

Substituting the estimated value $\gamma \approx 0.34$ in equation (3), for monovalent metals we get the critical coupling parameter $\Gamma_c \approx 18$. This value is very close to that of the experimental critical points of Cs and Rb [9] considered metallic. Thus, there exists strong evidence that the liquid-gas critical points of alkali metals can be identified with the plasma-phase-transition ones. From the other hand, any plasma-phase-transition predicted with the OCP model is questionable for strong electron–ion coupling.

In conclusion, we have represented the interatomic interaction energy of overlapping atoms in a virtual atomic structure connected with the gradual metal–nonmetal transition in a form of the Madelung energy, but the coefficient is shown to be nearly one third of that for the OCP model. This fact is of crucial importance for localizing the plasma-phase-transition points.

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1. W.Kraeft, D.Kremp, W.Ebeling, and G.R.Röpke, *Quantum Statistics of Charged-Particle Systems*, New York, Plenum, 1986.
2. N.F.Mott, *Metal-Insulator Transition*, London: Taylor and Francis, 1991.
3. B.I.Shklovskii and A.L.Efros, *Electronic Properties of Doped Semiconductors*, Springer-Verlag, N.Y., 1989.
4. J.M.Ziman, *Models of Disorder: The Physics of Homogeneously Disordered Systems*, Cambridge University Press, Cambridge, 1979.
5. A.A.Likalter, Usp. Fiz. Nauk, **162**(7), 119 (1992) [Sov. Phys. Usp. **35**(7), 591, 1992].
6. A.O.E.Animalu, *Intermediate Quantum Theory of Crystalline Solids*, Prentice-Hall, Englewood Cliffs, New Jersey, 1977.
7. N.F.Ashcroft and J. Lekner, Phys. Rev. **145**, 83 (1966).
8. J.R.Chelikowsky, N.Troullier, and Y.Saad, Phys. Rev. Lett. **72**, 1240 (1994).
9. S.Jüngst, B.Knuth, and F.Hensel, Phys. Rev. Lett. **55**, 2160 (1985).