

## Equation of state of metallic fluids near the critical point of phase transition

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(Received 7 July 1995)

An equation of state of expanded fluid metals near the critical point of the liquid-gas phase transition has been obtained taking into account their plasmalike nature. Both liquid and gas phases are considered to be metallic, but in contrast with normal metals they have a virtual atomic structure. A percolation model of overlapping classically accessible spheres of valence electrons has been developed. The mixed electron density of neighboring atoms on the periphery of ellipsoidal atomic cells is found sufficiently uniform providing a simple model of interaction between atoms. The first terms in asymptotical expansion of the interatomic interaction energy at large coordination numbers have been found. When the interatomic interaction has a single characteristic length, the critical parameters of metals obey scaling laws that depend on the microscopic atomic characteristics, the valence, and the ionization potential.

### I. INTRODUCTION

Metals heated and expanded up to liquid-gas critical points qualitatively change their electronic properties. These excited states of metals occur, for instance, in exploding wires and foils, in cathode spots of electrical discharges, and in laser-irradiated targets. However, basic data concerning properties of expanded metals, in particular the electrical conductivity and the equation of state, are only available for low-boiling metals, i.e., mercury, cesium, and rubidium, which allow stationary heating up to critical temperatures. Actual experimental data exist on critical parameters of potassium and sodium, but not yet for other metals.<sup>1</sup>

By their nature, expanded metals near their critical points are plasmalike matter with free valence electrons strongly coupled to ions. It is characteristic of expanded metals that the electrical conductivity decreases below its minimal metallic value, and at some threshold density the activation energy appears. All these peculiarities are connected with a gradual metal-nonmetal transition.<sup>2</sup> The background is a virtual atomic structure in a strongly coupled metallic plasma. A basic model concerning the metal-nonmetal transition is the percolation of overlapping classically accessible spheres of valence electrons.<sup>3-5</sup> Mutual screening of overlapping valence shells leads to a mixing of bound- and free-electron states characteristic of the metal-nonmetal transition. The percolation threshold is identified with the transition point defined by the appearance of the activation energy.

Metallic fluids consist of atoms which virtually all belong to percolation clusters where electrons of overlapping valence shells spread out in a larger volume. The attraction of overlapping atoms, determined by the Coulomb interaction between ions and uniformly distributed electrons, causes a phase transition identical to the condensation. It is typical of a whole number of metals near their liquid-gas critical points. Therefore, any reliable theoretical description of critical points must treat metal fluids like a strongly coupled plasma.<sup>6</sup>

Much effort in the theory of strongly coupled plasma was connected with an early prediction of the plasma phase transition in thermally ionized fluids, which has not yet been

observed experimentally.<sup>7</sup> However, concerning the liquid-vapor phase transition in the critical region of fluid metals, there exist only a few theoretical works. For the estimation of critical points, attempts have been made to use the model of a partially ionized gas again.<sup>8,9</sup> This model is quite good for the low-density plasma, but is not yet clear in the vicinity of the metal-nonmetal transition point where atomic valence shells overlap. Closer to condensed-matter physics is a model of metallic lattice gas, which was used for the estimation of the coexistence curve of some alkali metals.<sup>10</sup> Inhomogeneities due to clustering were introduced through the variable electron density dependent on the number of occupied neighboring sites. However, similar to Refs. 8 and 9, this model yields critical parameters which are still far from the experiment. In our present work, taking into account the virtual atomic structure of metallic fluids, we obtain an equation of state with reliable critical parameters for different metals. In order to describe the interaction energy of overlapping atoms in percolation clusters, we consider Wigner-Seitz cells with nearly uniform mixed electron density.

Though the equation of state itself does not allow us to determine the role played by the Coulomb interaction, the metallic character of conductivity in the critical points of cesium and rubidium correlates with a rather small critical compressibility factor as compared with dielectric fluids. It proves to be closely connected with some difference between the exponents in van der Waals' attractive energy of atomic gases, and Madelung's energy of ions and uniformly distributed electrons. Nevertheless, the van der Waals equation of state modified by the substitution for the Madelung energy cannot entirely explain the small magnitude of the compressibility factor. It will be shown that additional terms with smaller exponents must be taken into account.

The outline of this paper is as follows: In Sec. II a phenomenological description of the attractive interaction between overlapping metal atoms is given. A microscopic atomic cell model is analyzed in Sec. III. In Sec. IV an equation of state is given which depends on three parameters found from the available experimental critical data for cesium. Approximate similarity laws for critical parameters of fluid metals are presented in Sec. V.

## II. ENERGY OF OVERLAPPING ATOMS

In the vicinity of the metal-nonmetal transition point, gaseous metals have an atomic structure with overlapping classically accessible spheres of valence electrons forming percolation clusters of different scales. The classically accessible radius is

$$R_a = e^2/I, \quad (1)$$

where  $e$  is the electron charge, and  $I$  is the ionization potential of atoms. Nearest neighbors of one atom form a coordination sphere of the radius equal 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.<sup>5</sup> Under any perturbations the ground level is the low limit of internal energy, hence an internal energy spectrum of atom counting from the ionic core energy

$$E(p_1, \dots, p_z) = \sum_1^z (-I_k + \varepsilon_{pk}), \dots, \varepsilon_{pk} = p_k^2/2m, \quad (2)$$

where  $z$  is the valence,  $I_k$  are the sequential ionization potentials of atom,  $\varepsilon_{pk}$  are the electron excitation energies,  $p_k$  are the momenta of electrons far from a screened ionic core, and  $m$  is the electron mass.

In general, the interaction energy of overlapping atoms in percolation clusters is not pair additive, since the dependence of energy per atom upon the coordination number obviously saturates with an increase in this number (the effect of critical fluctuations is then diminished). In this limit the distribution of mixed density of valence electrons near the boundary between one central atom and its neighbors is nearly uniform (see Sec. III below). Then the problem of interatomic interactions reduces to the calculation of the atomic cell energy.

The simplest atomic cell is a Wigner-Seitz sphere of the radius

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

where  $n_i$  is the ion (atom) density. The central part of the cell represents an ionic core occupying up to 10–20 % of the cell volume,<sup>11</sup> which 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

$$n_e(r) = 0, \dots, r < R_c, \dots$$

or

$$\dots = n_e/(1-a), \dots, R_c < r < R_s,$$

where  $n_e = zn_i$  is the averaged electron density.

The interaction energy per atom is given by an integral

$$u = -\frac{1}{2} \int_{R_c}^{R_s} \frac{e^2 z(r)}{r} n_e(r) 4\pi r^2 dr, \quad (5)$$

with the charge number depending on the radius

$$z(r) = z - \frac{4\pi}{3} (r^3 - R_c^3) n_e(r). \quad (6)$$

The coefficient  $\frac{1}{2}$  in Eq. (5) corresponds to the fraction of valence electrons of neighboring atoms in the total electron density, and so precludes the internal energy of atoms, which is taken into account by Eq. (2), from being counted twice. Simple calculation yields

$$u = -\gamma(a) \frac{z^2 e^2}{R_s}, \quad (7)$$

where the Madelung coefficient is

$$\gamma(a) = \frac{1}{2} [0.9 - 1.5a^{2/3}(1-0.4a)](1-a)^{-2}. \quad (8)$$

This coefficient is reasonably well defined because of a rather weak dependence upon the core volume. Indeed, for  $a$  in a range from zero to 0.2, the magnitude of  $\gamma$  varies from 0.45 to 0.34 (the coefficient  $\alpha_M$  in the equation  $u = -\alpha_M z^2 e^2 n_i^{4/3}$  varies from 0.725 to 0.55, respectively).

Obviously, the model of interatomic interactions is considerably simplified since neither the interelectron correlation nor the nonuniform distribution of the valence electron density are taken into account. However, this is more than compensated for by the advantage of excluding a more complex problem of the atomic internal energy.

As noted above, a necessary condition in the cell model is that the coordination number is large, i.e.,

$$N_c \sim (2R_a/R_s)^3 \gg 1.$$

As a matter of fact, the coordination number is limited, and therefore corrections for the finite  $N_c$  can be important. Considering formula (7) as the first term of an expansion on a small parameter  $N_c^{-1/3} \sim R_s/2R_a$ , we write

$$u = -\gamma \frac{z^2 e^2}{R_s} \left[ 1 + \beta \frac{R_s}{2R_a} + \delta \left( \frac{R_s}{2R_a} \right)^2 \right]. \quad (9)$$

Requiring the interaction energy at fixed  $R_s$  to be maximal by modulus if the Wigner-Seitz radius is equal to the classically accessible sphere radius, we obtain

$$\beta > 0 \quad \text{and} \quad \delta = -\beta. \quad (10)$$

Note that the density-dependent factor  $R_s$  in the second term on the right-hand side of Eq. (9) is reduced, and therefore this term does not contribute to the equation of state (see Sec. IV below).

## III. ELLIPSOIDAL ATOMIC CELLS

A main assumption in calculating the interaction energy is that the electron density is nearly uniform outside the ionic core of atoms. To elucidate whether it is reliable or not, we consider a microscopic model of atomic cells for the percolation structure of the classically accessible spheres. The simplest form of such a cell, nearest to the sphere, is an oblate ellipsoid (Fig. 1), the polar half-axis of which is equal to the classically accessible radius, and the volume is some fraction  $f$  of the Wigner-Seitz cell volume, i.e.,

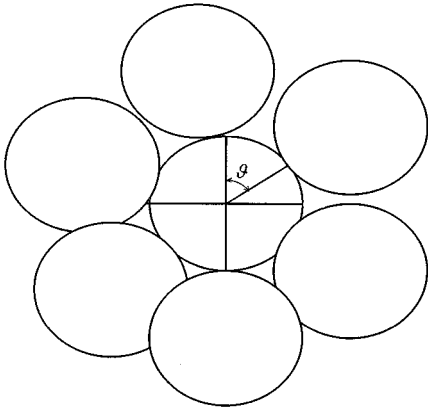


FIG. 1. The ellipsoidal atomic cells.

$$R(\vartheta) = \frac{R_a}{\sqrt{1 - (1 - \zeta/f) \sin^2 \vartheta}}, \quad (11)$$

where  $R(\vartheta)$  is the radius,  $\vartheta$  the polar angle, and  $\zeta$  the fraction of the classically accessible volume,

$$\zeta = (R_a/R_s)^3. \quad (12)$$

We consider a range  $\zeta \leq f$ , where  $f \approx \frac{2}{3}$  is the random close-packing fraction of spheres. Assuming that  $1 - \zeta/f \ll 1$ , we have

$$R(\vartheta) \approx R_a \left( 1 + \frac{1 - \zeta/f}{2} \sin^2 \vartheta \right). \quad (13)$$

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, a surface of the 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 due to the small overlap of atomic wave functions. Therefore, we use a more primitive representation of the effective potential for electrons, that is, the one-electron potential in the middle of a quasimolecule axis (for simplicity, for monovalent metal) can be written in a form

$$V(\rho, \vartheta) = -\frac{e^2}{R(\vartheta) + \rho} - \frac{e^2}{R(\vartheta) - \rho} + I, \quad (14)$$

where  $\rho = r - R(\vartheta)$  is the radial coordinate counted from the ellipsoid surface, and  $r$  is the radius. The first two terms in Eq. (14) represent the Coulomb potentials of ionic cores, and the last term the potential of a quasimolecule electron cloud within a correlation hole. This potential is normalized in such a way that in the ground-state level a valence electron can transfer just over a potential bridge between two touching classically accessible spheres. In the limit of high coordination numbers one can treat Eq. (14) as a total potential smoothed out over the polar angles for all quasimolecules with a common central atom.

The electron wave function is determined by the Schrödinger equation

$$\Delta \psi + \frac{2m}{\hbar^2} [E - V(\rho, \vartheta)] \psi = 0, \quad (15)$$

where  $\hbar$  is the Planck constant, with a boundary condition on the cell surface corresponding to symmetrical states of quasimolecules,

$$\partial \psi / \partial r = 0.$$

Near the surface of a classically accessible sphere, the wave equation for the energy, equal to the height of the potential saddles at the ellipsoidal cell poles, reduces to

$$\Delta \psi + \frac{4mI}{\hbar^2} \left( \rho'^2 - \frac{1 - \zeta/f}{2} \sin^2 \vartheta \right) \psi = 0, \quad (16)$$

where  $\rho' = \rho/R_a$ . For  $s$ -wave-like states in polar and equatorial regions of the ellipsoidal cell, the angle dependence can be neglected. Then, near  $\vartheta = 0$  or  $\pi$ , we have

$$\psi(\rho') \propto 1 - \frac{2Ry}{3I} \rho'^4, \quad (17)$$

where  $Ry = me^4/2\hbar^2$ . Therefore, the electron-density distribution, determined by the squared wave-function modulus, is

$$n_e(\rho') \propto 1 - \frac{4Ry}{3I} \rho'^4. \quad (18)$$

This distribution has a plateau of a width

$$\rho' \sim (3I/4Ry)^{1/4}. \quad (19)$$

Analogously, near  $\vartheta = \pi/2$ ,

$$n_e(\rho') \propto 1 + \frac{4Ry}{I} (1 - \zeta/f) \rho'^2, \quad (20)$$

where the width of a plateau is

$$\rho' \sim [I/4Ry(1 - \zeta/f)]^{1/2}. \quad (21)$$

Estimates (19) and (21) show that the plateau can occupy a considerable part of the cell outside the ionic core. Thus, if a volume fraction of the classically accessible spheres is large enough, an approximation of the uniform electron density appears to be reliable.

Note that this fraction increases, allowing for an occupation of excited quasiatomic levels determined by Eq. (2). If the mean excitation energy is of the order of the quasiatomic Fermi energy, the volume fraction of the classically accessible spheres becomes<sup>5</sup>

$$\zeta \approx \zeta_0 (1 - \varepsilon_F/I)^{-3},$$

with

$$\frac{\varepsilon_F}{I} = \left( \frac{9\pi\zeta_0}{16g_a} \right)^{2/3} \frac{I}{Ry},$$

where  $\zeta_0$  is the accessible volume fraction without excitations,  $\varepsilon_F$  the Fermi energy, and  $g_a$  the statistical weight of the atomic ground-state level connected with the valence

electrons. Thus quasiautomic excitations lead to a more uniform electron-density distribution.

#### IV. THREE-PARAMETER EQUATION OF STATES

The attractive-interaction energy of overlapping atoms can be used to derive an equation of state describing the plasma phase transition. The total pressure consists of two different parts

$$p = p_t + p_e \quad (22)$$

where  $p_t$  and  $p_e$  are the thermal and elastic pressures, respectively. Contributions of valence electrons and ions to the thermal pressure both depend on the finite volume of atoms responsible for the limited compressibility. The model of hard spheres is appropriate for such an atomic system, assuming that their radius is proportional to the classically accessible radius of valence electrons. Using the model of hard spheres, we have

$$p_t = (z+1)n_i T F(\eta) \quad (23)$$

with  $F(\eta)$  the Carnaghan-Starling function,<sup>12</sup>

$$F(\eta) = (1 + \eta + \eta^2 - \eta^3)/(1 - \eta)^3, \quad (24)$$

$\eta$  the packing fraction,

$$\eta = (R_{hs}/R_s)^3, \quad (25)$$

and  $R_{hs}$  the radius of hard spheres,

$$R_{hs} = c R_a. \quad (26)$$

The coefficient  $c$  is smaller than unity, so that  $R_{hs} < R_a$  and classically accessible spheres of valence electrons can overlap. Note that the hard-sphere model does not introduce any additional characteristic length to the problem, if the coefficient  $c$  is fixed. The hard-sphere model, applied to quasiautoms, obviously excludes the necessity to take into account the degeneracy of electrons, which leads to the same effect of limited compressibility.

The elastic pressure is determined by the derivative of the interaction energy with respect to the volume

$$p_e = -N_i (\partial u / \partial V)_{N_i}, \quad (27)$$

where  $N_i = n_i V$  is the number of ions, and  $V$  is the volume of the system. Substituting (9) into Eq. (27) and differentiating, we obtain

$$p_e = -\frac{1}{3} \gamma \frac{z^2 e^2 n_i}{R_s} \left( 1 + \beta \frac{R_s^2}{4R_a^2} \right), \quad (28)$$

where Eq. (10) is also used.

Substituting (23) and (28) into Eq. (22), we represent the equation of state of metallic fluids in a form

$$p = (z+1)n_i [TF(\eta) - A\eta^{1/3} - B\eta^{-1/3}], \quad (29)$$

with coefficients

$$A = \gamma z^2 I / 3c(z+1) \quad (30)$$

and

$$B = \gamma \beta c z^2 I / 12(z+1). \quad (31)$$

In fact, this equation of state contains three parameters  $\gamma$ ,  $\beta$ , and  $c$ , which are not exactly known. However, these parameters can be determined through the critical density, temperature, and pressure found experimentally at least for one of the metals having metallic gas phases near the critical point (in particular, for cesium).

The critical point is determined by the following conditions:

$$(\partial p / \partial n_i)_T \propto T(\eta F)' - \frac{4}{3} A \eta^{1/3} - \frac{2}{3} B \eta^{-1/3} = 0 \quad (32)$$

and

$$(\partial^2 p / \partial n_i^2)_T \propto T(\eta F)'' - \frac{4}{9} A \eta^{-2/3} + \frac{2}{9} B \eta^{-4/3} = 0, \quad (33)$$

where primes denote derivatives with respect to  $\eta$ :

$$(\eta F)' = (1 + 4\eta + 4\eta^2 - 4\eta^3 + \eta^4)/(1 - \eta)^4$$

and

$$(\eta F)'' = (8 + 20\eta - 4\eta^2)/(1 - \eta)^5.$$

Solving Eqs. (32) and (33) with respect to fractional powers  $A\eta^{1/3}$  and  $B\eta^{-1/3}$ , we obtain

$$A\eta_c^{1/3} = \frac{3}{8} T_c [(\eta F)'_c + 3\eta_c (\eta F)''_c] \quad (34)$$

and

$$B\eta_c^{-1/3} = \frac{3}{4} T_c [(\eta F)'_c - 3\eta_c (\eta F)''_c], \quad (35)$$

where the subscript  $c$  corresponds to the critical point. Substituting (34) and (35) into equation of state (29), we express the critical compressibility factor by the function  $F$  and their derivatives,

$$\kappa_c = \frac{p_c}{(z+1)n_i c T_c} = F_c - \frac{9}{8} (\eta F)'_c + \frac{9}{8} \eta_c (\eta F)''_c. \quad (36)$$

Thus the compressibility factor is connected with the packing fraction of hard spheres.

Let us determine the critical packing fraction through the experimental value of the compressibility factor found in the plasma critical point of cesium,<sup>13</sup>

$$\kappa_c = 0.1.$$

Substituting this value on the left-hand side of Eq. (36), we have

$$9\eta^5 - 125\eta^4 + 140\eta^3 + 860\eta^2 + 205\eta - 9 = 0.$$

For small  $\eta$ , this equation reduces to a quadratic one with a solution:

$$\eta_c = 0.03785. \quad (37)$$

Thus at the critical point the hard spheres system is rather rarefied. For this case the Carnaghan-Starling function  $F(\eta)$  reduces to  $(1-4\eta)^{-1}$ , which corresponds to the van der Waals model of the excluded fourfold volume of hard spheres.

The volume fraction of classically accessible spheres found on the experimental density in the critical point of cesium<sup>13</sup> is

$$\zeta_c = 0.365.$$

Hence the ratio of sphere radii, defined by Eq. (26), is

$$c = (\eta_c / \zeta_c)^{1/3} \approx 0.47, \quad (38)$$

i.e., the radius of hard spheres, responsible for the limited compressibility, is approximately half the classically accessible radius of valence electrons.

After substituting the  $\eta_c$  value from (37) into Eqs. (34) and (35), the coefficients  $A$  and  $B$  are expressed by the critical temperatures

$$A = 2.854T_c \quad (39)$$

and

$$B = 0.03643T_c. \quad (40)$$

The ratio of the critical temperature to the ionization potential found for monovalent cesium from the experimental data<sup>13</sup> is

$$T_c / I = 0.0425.$$

From definitions of  $A$  and  $B$ , Eqs. (30) and (31), after substitution of this value  $T_c / I$ , and  $c$  from Eq. (38), we obtain the other two parameters

$$\gamma = 0.34 \quad (41)$$

and

$$\beta = 0.23. \quad (42)$$

Obviously, the given value of the Madelung coefficient  $\gamma$  agrees reasonably with theoretical estimates based on the atomic cell model [cf. a range of  $\gamma(a)$  given after Eq. (8)]. In addition, a rather small  $\beta$  value makes the expansion of the interaction energy in the derivation of the three-parameter equation of state sensible, if the expansion parameter  $R_s/2R_a$  is not very small. Since the universal parameters  $\gamma$ ,  $\beta$ , and  $c$  are known, the equation of state can predict the critical parameters of other metals (see Sec. V below).

Dividing equation (29) by the identity

$$p_c = \kappa_c(z+1)n_{ic}T_c,$$

we obtain a dimensionless equation of state

$$\pi = 10\nu[\tau F(\eta) - 2.854\eta^{1/3} - 0.03643\eta^{-1/3}]$$

with the relative pressure  $\pi = p/p_c$ , density  $\nu = n_i/n_{ic}$ , temperature  $\tau = T/T_c$ , and the packing fraction  $\eta = \eta_c \nu$ . A phase diagram, constructed for this equation of state using the Maxwell rule, is shown in Fig. 2 in comparison with experimental data for cesium and rubidium. Only a flat part of the coexistence curve with the critical point is reproduced. However, even in a larger range experimental data are well fitted by the scaling laws of the fluctuation theory of the critical point

$$\nu_l - \nu_v \propto |1 - \tau|^\beta$$

and

$$(\nu_l + \nu_v)/2 - 1 \propto |1 - \tau|^{1-\alpha},$$

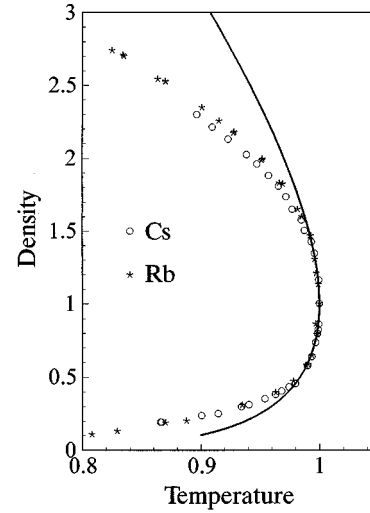


FIG. 2. Phase diagram in the vicinity of the critical point of metallic fluids. The theoretical curve is obtained using conditions of equal pressures and chemical potentials for liquid and gaseous phases. Experimental points for cesium and rubidium are from Ref. 13.

with exponents  $\beta \approx 0.35$  and  $\alpha \approx 0.87$ , which are close to the theoretical values.<sup>13,14</sup> Apparently, a regular behavior for metallic fluids can be to some extent similar to the scaling. Surprisingly, scaling laws fit better far from the critical point than the regular equation does. But as a matter of fact, outside of the flat part of the coexistence curve, densities of both phases go out of the range where this equation of state is expected to be applicable. Contrary to the classical van der Waals equation, it nevertheless shows a large asymmetry of boiling and condensation curves, in qualitative agreement with the experiment. In addition, the main feature of the equation of state under consideration is the ability to predict critical parameters of metals.

## V. CRITICAL PARAMETERS OF METALLIC FLUIDS

Critical densities, temperatures, and pressures of metals with the plasmalike critical state can be expressed by the ionization potential and the valence of atoms. First, by the definition of the packing fraction, we have

$$\begin{aligned} n_{ic} &= \frac{3\eta_c}{4\pi} \left( c \frac{e^2}{I} \right)^{-3} = \frac{3\zeta_c}{4\pi} \left( \frac{e^2}{I} \right)^{-3} \\ &\approx 2.92 \times 10^{19} (I/eV)^3, \quad \text{cm}^{-3}, \end{aligned} \quad (43)$$

where in the last equality we substitute the numerical values of parameters. Thus the critical density is proportional to the ionization potential cubed. This conclusion results directly from the simplest assumption, made from the beginning, that the radius of hard spheres is proportional to the classically accessible radius, and does not depend on the valence. It is an interesting fact that matter with the ionization potential  $I = 1$  eV would have a critical density as high as the normal gas density. Actually the plasma critical point can only exist if the critical density, determined from Eq. (43), is from 5–10 times smaller than the normal density of this metallic liquid, i.e.,

TABLE I. Critical temperatures  $T_c$ , pressures  $p_c$ , and ion densities  $n_{ic}$  of metals estimated by scaling on the ionization potentials  $I$  and valences  $z$  through the experimental critical data of cesium. In the last but one column, the critical expansion  $n_{in}/n_{ic}$ , with  $n_{in}$  the ion density at normal conditions, is given. Experimental data are given in additional lines with the references in the last column.

Metal	$z$	$I$ (eV)	$T_c$ (K)	$p_c$ (bar)	$n_{ic}$ ( $10^{21}$ cm $^{-3}$ )	$n_{in}/n_{ic}$	Reference
Li	1	5.392	2660	342	4.6	10	
Be	2	9.322	9195	12 250	24	5.2	
B	3	8.298	12 300	17 300	17	7.8	
Na	1	5.139	2535	282	3.95	6.4	
			2485	248	7.8	3.2	15
Al	3	5.986	8860	4680	6.3	9.6	
K	1	4.341	2140	144	2.4	5.5	
			2178	150	2.6	5.1	1
Rb	1	4.177	2060	123	2.1	5.1	
			2017	124.5	2.05	5.3	13
Cs	1	3.894	1924	92.5	1.7	5	13
Cu	2	7.726	7620	5770	13	6.3	

$$n_{ic} \ll n_{in},$$

where  $n_{in}$  is the normal liquid density.

Reading Eq. (39) from right to left, and substituting the coefficient  $A$ , Eq. (30), for the critical temperature we have

$$T_c = 0.35 \gamma z^2 I / 3c(z+1) \approx 0.085 z^2 I / (z+1), \quad (44)$$

where in the last equality  $\gamma$  and  $c$  are substituted from Eqs. (41) and (38).

With the definite value of the compressibility factor, the critical pressure is directly expressed by the density and the temperature:

$$p_c = 0.1(z+1)n_{ic}T_c \approx 0.405z^2(I/eV)^4, \quad \text{bar}, \quad (45)$$

where in the last equality Eqs. (43) and (44) are used. Thus the critical pressure is proportional to the valence squared, and the ionization potential to the fourth power.

The dependencies (43)–(45) upon  $z$  and  $I$  are all simple powers except (44), where the quadratic  $z$  dependence for  $z \ll 1$  crosses over into the linear law for  $z \gg 1$ . Moreover, within the range of uncertainty this function can be also reduced to the linear law continued from  $Z \gg 1$  down to  $z = 1$ . With the correct description of monovalent metals, we obtain reduced formula with the renormalized coefficient

$$T_c \approx 0.0425zI. \quad (46)$$

Then the critical temperature is proportional to the valence and the ionization potential.

If the valence is not well defined, excluding it from Eqs. (45) and (46), we will obtain a relationship between the critical pressure, the temperature, and the ionization potential:

$$p_c = 225(I/eV)^2(T_c/eV)^2, \quad \text{bar}. \quad (47)$$

Note that the power dependencies for plasma critical points follow from a consideration of the similarity and dimensions. These simple similarity laws are connected with the assumption that interaction can be described by a single

characteristic length, the classically accessible radius  $R_a$ . The description of deviations from these similarity laws requires a detailed analysis which is out of scope of this paper.

Let us consider several examples (see Table I, where the estimates are given in comparison with still-limited data for measurements in critical points). The plasmalike critical point is the most characteristic of the light metals, monovalent lithium and three-valent aluminum having a critical expansion of about 10. While critical ion densities of these metals are comparable, the critical temperature of aluminum is three times that of lithium, and the pressure is higher by an order of magnitude because of the threefold ionization.

For heavy alkali metals the critical expansion varies from five to six. On the whole, parameters of the plasma critical points of alkalis agree with the experimental data.<sup>1,13,15</sup> An exception is the critical density of sodium, the experimental value of which<sup>15</sup> appears to be too high, though predicted critical temperature and pressure are close to the experimental values (if this density were used to find parameters of the equation of state, they would be  $c=0.35$ ,  $\gamma=0.23$ , and  $\beta=1$ ; this is not consistent with our atomic cell model, since the smaller the ionic core, the larger  $\gamma$  must be).

All examples in the table, except copper, apply to simple nontransition metals with well-defined valence; that is, the number of electrons out of the filled inert-gas shell. Conversely, at the critical points of transition and noble metals the valence can be higher than in their atomic ground states, because of the transfer of electrons from the inner  $d$ -shell to the outer shell induced by interatomic interactions. In particular, while a free copper atom has the electron configuration  $3d^{10}4s$  with a single valence  $s$  electron, at the critical point it changes into a  $3d^9 4s^2$  with a valence 2.<sup>16</sup>

In conclusion, note that parameters of plasmalike critical points of metals often agree quite well with some semiempirical estimates which do not yet concern the physical nature of matter. For beryllium, aluminum, and copper, the deviations of critical temperatures from these estimated by Fortov, Dremin, and Leontiev<sup>17</sup> are only about 10% (but for boron the deviation exceeds 30%).

## VI. CONCLUSION

A plasmalike state of metals in the vicinity of their liquid-gas critical points presents the problem of condensation in an interesting way. Atomic gases condense into liquids because of the van der Waals attractive forces between atoms. In contrast to that, condensation of gaseous metals results from the exchange interaction in some atomic structure, characteristic of a gradual metal-nonmetal transition. Overlapping classically accessible spheres of valence electrons in the region of transition form percolation clusters which are, from another point of view, a structure of strongly coupled plasma.

When the volume fraction of classically accessible spheres is high, the mixed electron density is nearly uniform, and atomic cells are an appropriate model. Some terms in the asymptotic expansion of attractive interatomic interaction at large coordination numbers, together with the model of hard spheres for repulsion, yield an equation of state of metallic fluids, which is applicable in the vicinity of the critical point. Three parameters of this equation are determined through the critical parameters of cesium. Estimated critical parameters of other alkalis agree with the experimental data and, hence, reliable predictions of critical data of other metals. In most cases such data are hardly available by any direct experiment. In contrast with some semiempirical estimations which use the characteristics of condensed matter, like normal density and evaporation heat, critical parameters of metallic fluids are expressed by approximate scaling dependencies upon

the atomic characteristics, the valence, and the ionization potential. A lack of experimental data does not yet allow us to determine possible deviations from this atomic scaling.

In our analysis, most characteristic among other metals with the plasmalike critical points are lithium and aluminum, which remain in the metallic state after expansion by more than ten times. Obviously, lithium (with predicted critical parameters not much higher than those of sodium) must be the most interesting subject of subsequent investigations in the field of metallic fluids. A special problem of interest is a wide circle of transition metals in which, by virtue of interatomic interactions, low-lying excited atomic energy levels can be preferably occupied.

## ACKNOWLEDGMENTS

This work was made possible in part by Grant No. MEK 000 from the International Science Foundation, and was partly supported by Grant No. 94-02-04170 from the Russian Foundation of Basic Researches. Part of this work was made at the Institute of Low Temperature Plasma Physics, Greifswald (Germany), with financial support from Deutscher Akademischer Austauschdienst and Deutsche Forschungsgemeinschaft. I am very grateful Dr. Helmut Hess for his hospitality, and Dr. Hartmut Schneidenbach for providing a program for calculating the phase diagram and for his hospitality.

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