Gaseous metals

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The physics of gaseous metals in the vicinity of the critical point is analyzed. A theory is presented for mixed states of valence electrons in percolation clusters of overlapping atoms, and is used for the interpretation of experiments. It is shown that the condensation of gaseous metals near the critical point has a plasma-like nature. The electrical and electrodynamic properties, as well as plasma oscillations and optical properties are analyzed in the region of the broadened metalnonmetal transition. The cases of partial ionization at lower densities and multiple ionization at very high temperatures are discussed.

1. INTRODUCTION

It is well known that most chemical elements form condensed phases with free valence electrons, i.e. solid and liquid metals. Metals usually evaporate in the form of atomic gases, which are ionized by thermal excitation of the atoms. However, at densities comparable to those of liquids the gas phase is also metallic because of the overlap of the electron shells. Obviously, this statement is, to some extent, a matter of terminology. However, it takes on physical meaning if two different metallic phases, a liquid and a gaseous metal, can exist simultaneously in the vicinity of the critical point. This situation, the possibility of which was predicted by Zel'dovich and Landau,¹ is, according to present-day data, a common one for metalls.²

On the phase diagram the region of the critical point of metals occupies a position between that of the condensed metal and the partially ionized gas (plasma), at the junction of the interest of various fields of physics. In principle, the theory of gaseous metals should be based on the ideas of the electron theory of disordered media. The most important problem of the theory lies in the investigation of the metalnonmetal transition and its analog in extrinsic semiconductors. A distinguishing feature of metals is that the transition is broadened because of their high critical temperatures (several thousand degrees kelvin at pressures from a hundred to several thousand bars). In a broad sense the idea of a gaseous metal encompasses the entire transition region and is used as the equivalent to the English term "expanded metals".

The metal-nonmetal transition has been studied in a large number of extrinsic semiconductors. Similar studies of gaseous metals were started considerably later. Moreover, because of the great experimental difficulties, they have included only such easy-boiling metals as cesium, rubidium, and mercury. Consequently, there is a certain gap between the physics of gaseous metals and the investigations of processes in which they participate, such as the electrical explosion of wires, explosive electron emission, or the action on metals of intense energy fluxes and of high-speed impact. For the mathematical simulation of processes of this sort there exist programs for the calculation of the properties of metals over a wide region of the phase diagram. The vicinity of the critical point generally represents the greatest difficulties in broad-range calculations, which frequently are based on a model of atomic cells in compressed matter. A theoretical analysis that provides an understanding of the physical properties of gaseous metals might help us to bridge this gap.

Interest in gaseous metals is motivated by the unusual properties that distinguish these systems from systems with nearly free electrons. It has recently been shown that these properties admit of a simple theoretical interpretation. At the same time, most reviews and monographs³⁻⁵ in which expanded metals are discussed were published some ten years ago. In the present review the primary attention is given to new physical models used for the interpretation of experiments. Progress in this area is mainly associated with the concept of percolation of overlapping atoms. Since we are considering a broadened metal-nonmetal transition, we shall not discuss the theories of weak and strong localization, applicable far from this transition. These directions of investigation, which have been extensively developed in recent years, have been elucidated in the reviews of Refs. 6 and 7.

The outline of this review is clear from the section headings. We examine the electronic properties in percolation clusters and on this basis analyze the various properties of gaseous metals in the vicinity of the critical point. In the two last sections we also consider partial ionization at reduced densities and multiple ionization at very high temperatures. Some of this material has been published in Ref. 8.

2. THE METAL-NONMETAL TRANSITION

It is well known that the metallic state occurs in disordered phases because the electron-ion interaction is screened by the electron gas. If this screening were not present, the electrons would form neutral atoms with the ions, where each ion is screened by its own electron. Thus, the metalnonmetal transition is associated with a change in the nature of the screening. In the metallic phase the screening length of a homogeneous electron gas coincides with the radius of the ionic cell. In metal atoms the valence electrons (as a rule, semiclassical) screen the ion around the boundary of the classically accessible region. Clearly, in the region of the transition these distances must be of the same order of magnitude. From this consideration we obtain the criterion

$$e^2 n_1^{1/3} / I = C, (1)$$

where e is the absolute value of the electron charge, n_i is the

ion density, I is the ionization potential of a valence electron, and C is a constant of the order of unity.

Essentially, this criterion is applicable also to the metalnonmetal transition in extrinsic semiconductors. There, one must replace e^2 by e^2/ε in Eq. (1), where ε is the dielectric constant of the lattice and I is taken to be the ionization potential of an impurity in the semiconductor. According to Ref. 9, this criterion describes the correlation of the data for various extrinsic semiconductors in which the ionization potential of the dopant varies over three orders of magnitude. The average value of the constant is C = 0.52.

If the effective length $e^2/2I$ is replaced by the effective Bohr radius a_B , Eq. (1) becomes the Mott criterion¹⁰

$$n_1^{1/3}a_{\rm B}\approx 0.25.$$

In this form the criterion is useable only for hydrogen-like impurities. The well-known derivation of this criterion uses the Thomas-Fermi screening length, which is set equal to the Bohr radius.

In another interpretation, the change in the screening is related to percolation. If in a random configuration of atoms the classically accessible regions of the valence electrons overlap, then the valence shells virtually screen one another from the ions. Therefore, the overlaps of these regions can be considered as an indication of the transition between an atomic gas and a metal. The corresponding criterion is the percolation threshold of the problem of overlapping spheres

$$\frac{4\pi}{3} \left(\frac{e^2}{I}\right)^3 n_1 = 0.34.$$
 (2)

It is easy to see that this equality is identical, up to a constant factor, with criterion (1). According to criterion (2) the volume of the accessible spherical regions comprises about a third of the total volume. Here, the "pure" volume that they occupy is $1 - \exp(-0.34) = 0.29$, and the rest, 0.05, is the volume of the overlap region.¹¹ The idea of the percolation of the overlapping electron shells of the atoms has been discussed by Ziman, who analyzed a model of spheres "filled" by the wave function.¹² In the semiclassical case the role of this sphere is played by the classically accessible region, at whose boundary the wave function has a maximum.

If interactions are included which change the probability of the various configurations, the transition point is shifted in one direction or the other. Since the limited overlap possibilities of the atoms lead to an "economy" of their volume in the filling of space, the percolation threshold can be lowered by the volume of the overlap region. On the other hand, for strong interactions (in the vicinity of the melting line) a lattice is formed. In a randomly close packed structure the overlap threshold would be increased from onethird to two-thirds of the expanded volume. This limit, however, has only a remote relation to gaseous metals. For example, the metal-nonmetal transition point in mercury, where the density is 8.8 g/cm³ (Ref. 13), corresponds to a fraction 0.29 of the classically accessible region. It is worth mentioning that the volume scale is more extended than the distance scale. Therefore, in terms of the correlation formula (1), all of this region of the threshold fraction of the accessible volume does not exceed the spread in the transition points in extrinsic semiconductors studied in Ref. 9.

3. QUASIATOMIC STATES

Semiclassical electrons of the s- or p valence shells with large principal quantum numbers n in atoms of metals move in the classically accessible region of the Coulomb potential, screening the ion core. When these accessible regions overlap they expand, encompassing the adjacent ion. The overlapping atoms form percolation clusters with an interatomic distance much greater than in molecules. Complete mixing of the states does not occur; that is, the quasiatomic structure remains.

Because of exchange, the atomic core in a percolation cluster is virtually screened by the atoms of the adjacent atoms. As a result, mixed states of the valence electrons are formed, containing a mixture of the asymptotically free motion above the potential well of the screened ion. This is the reason for the formation of the continuous spectrum of excitations above the atomic level. The spectrum of the internal energy of the atom in these mixed states (or of a quasiatom) has the form¹⁴

$$E_{\rm p} = -I + \varepsilon_{\rm p}, \quad \varepsilon_{\rm p} = p^2/2m,$$
 (3)

where I is the ionization potential of the atom, ε_p is the excitation energy, p is the momentum of asymptotically free motion of the electron, and m is the electron mass. The energy of the atomic level according to the variation principle of quantum mechanics¹⁵ gives a lower bound to the internal energy of the quasiatom.

In the simplest case, the energy representation of the density matrix of the quasiatom contains only two diagonal elements, corresponding to the probabilities of the ground state and the state of free motion. These matrix elements are related by

$$a_{\rm pp}/a_{\rm 00} = p^2/2mI, \tag{4}$$

where the subscript 0 refers to the ground state and p to the state of free motion. One can easily show, using this ratio and the normalization condition $a_{00} + a_{pp} = 1$, that the internal energy of the quasiatom corresponds to the spectrum of asymptotically free motion, formulas (3). It follows from (4) that weakly excited quasiatomic states differ little from the ground state of the atom (excluding the asymptotic part), since the mixture of free motion in them is small.

The radius of localization of the quasiatomic states is determined by the time of transition of an electron to a virtual hole in a neighboring atom. During this time the electron wave corresponding to free motion with a velocity vtravels a distance

$$l' = \sigma r', \tag{5}$$

where τ' is the transition time. Here the primes indicate that this time is different from the mean free time, and, accordingly the radius of localization is different from the interatomic distance. It must be mentioned that in a partially ionized plasma the quasiatomic states correspond to atoms excited above the ionization threshold, and the localization length usually is the same as the mean radius of the ion cell. Indeed, these are the ideas on which Menzel based his derivation of Saha's equation of ionization equilibrium in terms of the Boltzmann formula for excited atoms.¹⁶

It was mentioned above that in gaseous metals the metal-nonmetal transition is broadened. It is easy to understand that this corresponds to the continuous spectrum of quasiatomic excitations. If the width of the energy distribution of the quasiatoms is of the order of the temperature T, it follows from (2) that the relative width of the metal-nonmetal transition is

$$\Delta n_i/n_i \sim -3T/I. \tag{6}$$

As the minus sign in expression (6) shows, the transition is broadened towards lower density.

At a temperature of the order of the ionization potential, the gas will, of course, remain in the plasma state regardless of the density.

4. PLASMA CONDENSATION

As is the case for any gas, when the temperature is reduced below the critical temperature at a subcritical pressure, a gaseous metal will condense. Figure 1 shows an example of a phase diagram for copper. The region of the metallic state lies above the metal-nonmetal transition line, which should be considered as being somewhat broadened from below. The extension of this line in the two-phase region bounds that part of the latter region around the critical point, where both the liquid and the gas are in the metallic state. From the point of view of the theory of condensation the special feature of this diagram is that the Coulomb interaction between the electrons and ions is responsible for the phase transition in the vicinity of the critical point (plasma condensation).

It should be noted that the Coulomb type of critical point of the condensation of gaseous metals is not the only type. Other examples are the critical point of the condensation of excitons created during optical pumping in semiconductors,¹⁷ and the critical point of the solubility of metals in liquid ammonia.¹⁸

On the other hand, there have been many predictions of more complicated phase diagrams of a partially ionized plasma with an additional plasma phase transition not related to the usual condensation and its critical point.^{19,20} As a rule, however, the equation of state used for the analysis does not give the precision required to draw this conclusion. This appears to be the reason why additional phase transitions have not been observed experimentally.

The description of plasma condensation is based on the



FIG. 1. Phase diagram of copper (the boundary of the two-phase region is shown similar to the case of $\operatorname{cesium}^{22}$). *C* is the critical point, *OM* is the metal-nonmetal transition line, *OL* is the boundary of the region of the two metallic phases.

analysis of the Coulomb energy of a strongly coupled plasma. In the semiclassical approximation this energy is given by the Madelung formula

$$U = -\alpha_{\rm M} z^2 e^2 n_{\rm i}^{4/3},$$

where z is the charge number of the ions. The coefficient in this expression depends on the model, and is in general unknown. To obtain the equation of state it is necessary to use the virial theorem, according to which the contribution to the pressure from the Coulomb interaction is one third of the potential energy. In addition, it is necessary to take into account the repulsion effect. A qualitative description of plasma condensation is given by a modified van der Waals equation^{2,21}

$$p = \frac{nT}{1 - n_{\rm l}b_{\rm l}} - \frac{1}{3}\alpha_{\rm M}z^2 e^2 n_{\rm l}^{4/3},\tag{7}$$

where $n = n_e + n_i$ is the total density of particles contributing to the pressure, $n_e = zn_i$ is the density of valence electrons, z is the number of valence electrons of an atom, b_i is the van der Waals minimum volume, and α_M is the (renormalized) Madelung constant. This equation takes into account the quasiatomic structure of the strongly coupled plasma. The parameter b_i has the meaning of a minimum volume per atom

$$b_{\rm j} \sim (e^2/I)^3.$$
 (8)

The second term in Eq. (7), which is related to the Madelung energy, describes the attraction of the overlapping quasiatoms. Clearly, part of the Madelung energy, which in this model corresponds to the inner energy of the quasiatoms, must be excluded. This is reflected in the value of the Madelung constant. The most reliable estimates² give $\alpha_{\rm M} \approx 0.63$, whereas the known value for a single-component plasma is 1.45.

The equation of state (7) allows us to obtain approximate power-law formulas for the critical points of condensation of gaseous metals:

$$T_{\rm c} \approx 0.04 zI \ {\rm eV} \,, \tag{9}$$

$$\boldsymbol{p_c} \approx 0.4 z^2 I^4 \text{ bar},\tag{10}$$

and

$$p_{\rm c}/n_{\rm c}T_{\rm c} = 0.1,$$
 (11)

where the numerical factors are normalized to the experimental parameters of cesium.²² It must be pointed out that the critical pressures of different metals vary much more than do the critical temperatures. The correlation of the critical parameters, which follows from expressions (9) and (10) is shown in Fig. 2. It is interesting to note that according to expression (11) the strong Coulomb interaction reduces the pressure by a factor of ten as compared to the ideal pressure.

The phase diagram of the type shown in Fig. 1 corresponds to those metals for which the normal density is much higher than at the metal-nonmetal transition point. For many metals this excess in the density is actually a factor of five or more, whereas the critical density is only a factor of four or five below the normal density. A counterexample is mercury, for which the metal-nonmetal transition line lies considerably above the critical density. This situation corre-



FIG. 2. Correlation of critical parameters of gaseous metals (with cesium used as a reference point). $p_c \sim T_c^2 I^2$ (Ref. 2).

sponds to another type of phase diagram, in which there are two nonmetallic phases near the critical point, as for insulating liquids. In this case the van der Waals interaction between the atoms is responsible for the condensation, so that for a qualitative description one can use the classical van der Waals equation of state. Thus, there is no plasma phase transition in mercury, although there is a metal-nonmetal transition. Since all of this field has been well studied, this statement may be regarded as experimentally proved. This serves as an illustration to the above discussion in connection with the prediction of an additional phase transition.

5. EXCITATION OF MIXED TERMS

The valence of the ions in a gaseous metal, as can be seen from the equation of state, has a large influence on the parameters of that equation. This influence is well defined for simple metals with s- and p- valence electrons outside the last filled inert-gas shell. From the point of view of the percolation criterion, these electrons can be regarded as equivalent, since they have either identical (in the case of the ns^2 shells), or nearly equal radii of the classically accessible region.¹⁵ In transition and noble metals, in which the inner dshell is filled, only the valence s-electrons can take part in the percolation. A property of these metals is that in the percolation clusters the valence can be changed by excitation of electrons from the d-shell. This corresponds to the excitation of the so-called mixed atomic terms. The excitation energy is compensated by the lowering of the Madelung energy, which is proportional to the square of the valence, so that an increase in valence may be energetically favorable. For example, in the case of copper (Fig. 3) in the vicinity of the critical point the principal term ²S^{1/2} of the configuration 3d¹⁰4s is lowered because of the Madelung interaction by the amount $\alpha_{\rm M} e^2 n_{\rm i}^{1/3} \approx 1$ eV, while the components of the mixed term ${}^{2}D_{3/2}$ and ${}^{2}D_{5/2}$, having the configuration $3d^{9}4s^{2}$ with two valence electrons are reduced four times as much, by 4 eV. Since the excitation energy of the mixed term is about 1.5 eV, the relative energy positions of the terms are reversed; that is, the excitation of the mixed term is energetically more favorable. A similar change in the valence of atoms has been observed to occur as a result of the transition to an excited state in the formation of a chemical bond.15



FIG. 3. Energy diagram of an atom with a mixed term.

The excitation of the mixed term changes both the position of the critical point, mainly because of the increase in the valence, and the metal-nonmetal transition point. Actually, in this case the radius of the classically accessible region is determined by the ionization potential of the mixed term, and, consequently, it increases. As a result, the density at the metal-nonmetal transition decreases by a factor of two in copper. It is obvious that this has an important effect on all the characteristics of the gaseous metal.²³

6. DENSITY OF QUASIATOMIC STATES

For a complete characterization of the quasiatomic states it is necessary to determine, besides the spectrum (3), also the density of states. It is easy to see that this density of states is higher than in a homogeneous electron gas, since the quasiatomic states belonging to different atoms can overlap. The density of states per atom is proportional to the volume of the sphere of localization, whose radius is given by formula (5). For nearly-free electrons it would not be possible to distinguish the overlapping states, so that the corresponding volume coincides with the ion cell. In the general case the volume of the sphere of localization is

$$\Omega = n_i^{-1} (\tau'/\tau)^3, \ \tau < \tau', \tag{12}$$

where τ is the mean free time of an electron between adjacent ions. The ratio of the mean free time to the transition time, which is less than unity, characterizes the degree of localization of the electrons.

In the case of well defined quasiatomic states the transition time of an electron is much longer than the mean free time, and the volume of the localization sphere is much larger than the ion cell. At large distances the potential of the ion is screened, and therefore over a large part of the localization sphere the electron moves as a nearly-free electron. Then the density of states of the quasiatom also corresponds to free motion. In this approximation the density of states is

$$\frac{\mathrm{d}g}{\mathrm{d}p} = g_{\mathrm{B}} \cdot \frac{4\pi p^2 \Omega}{(2\pi\hbar)^3},\tag{13}$$

where g_{a} is the statistical weight of the atomic level.

Therefore, by comparison with an ideal plasma, the continuous spectrum in a gaseous metal is shifted with respect to the internal energy of the atom by an amount -I, and the density of states increases in proportion to $(\tau'/\tau)^3$.

A direct consequence of the increase in the density of states is a decrease in the Fermi energy. The renormalized Fermi momentum in the case of atoms with s valence electrons is

$$p_{\rm F}' = p_{\rm F} \tau / \tau',$$

where $\hbar (3\pi^2 n_e)^{1/3}$ is the Fermi momentum of a homogeneous electron gas. It is clear that a decrease in the Fermi energy will contract the region of densities where the electrons are degenerate. In fact, in the case of well-defined quasiatomic states, where $\tau \ll \tau'$, Boltzmann statistics is almost always applicable.²⁴

The increase in the density of states is an effect that is in some sense inverse to the formation of a pseudogap in the electronic spectrum around the Fermi level in the wellknown scenario of Mott for the localization of free electrons.^{25,26} Nonetheless, this effect is responsible for a definite stage in the metal-nonmetal transition. This topic will be revisited later.

7. MINIMUM METALLIC CONDUCTIVITY

In percolation clusters the electrons undergo random walks, making transitions to virtual holes on the neighboring atoms. This motion is described by a diffusion coefficient

$$D_{\rm e} = \frac{l^2}{3\tau'} = \frac{1}{3} l v \frac{\tau}{\tau'} , \qquad (15)$$

where l is the mean interatomic distance and v is the average velocity of the electrons. As can be seen, the diffusion constant of the electrons is given by the product of the minimum gas-kinetic diffusion coefficient times the ratio of the mean free time to the transition time, which characterizes the localization of the electrons. According to the criterion of Ioffe and Regel,²⁷ localization occurs when the mean free path determined for the gas-kinetic regime, decreases to its minimum value, equal to the interatomic spacing. Using the Einstein relation between the diffusion coefficient and the mobility, one can at once write an expression for the mobility

$$\mu = \frac{er}{m} \frac{\tau}{\tau'},\tag{16}$$

where the first factor is the minimum gas-kinetic mobility. Because of the localization factor, the mobility of the electrons can be much less than the gas-kinetic value.

If the electrons are degenerate, the mean free time is inversely proportional to the renormalized Fermi momentum. Because of relation (14), the localization factor in the mobility is canceled out, so that formula (16) reduces to the gas-kinetic expression with the usual Fermi momentum. Thus, in a degenerate gas we would not have anything larger than the minimum gas-kinetic mobility, and consequently, the minimum metallic mobility in the Ioffe–Regel sense

$$\sigma_{\mathbf{m}} = e^2 n_e l/p_{\mathbf{F}}.$$
 (17)

The localization in this case occurs indirectly. Specifically, as has been mentioned, when $\tau \ll \tau'$ Boltzmann statistics becomes applicable. Thus, the minimum metallic conductivity is not the lower bound, but only characterizes a change in regimes of conduction. The more complicated question, that of the minimum of the conductivity at T = 0, was formulated by Mott²⁶ and thereafter excited a long controversy.^{6,7} At the present time the prevailing point of view, based on the scaling theory of localization, is that such a minimum does not exist. This issue, however, lies somewhat outside the scope of this review.

8. PERCOLATION MOBILITY OF ELECTRONS

(14)

The expressions for the kinetic coefficients, which include the localization factor, remain rather formal, since this factor is not determined. Specific calculations are based on the one-electron model of percolation diffusion and mobility. It is assumed that an electron, moving in the classically accessible region of the Coulomb potential of the ion, "sees" one ion and the rest are screened. The electron can change its ion when it is in the region of overlap of the classically accessible regions. Clearly, diffusion occurs when the fraction of the accessible volume exceeds the percolation threshold.

If the fraction of accessible volume is large enough the diffusion becomes gas-kinetic diffusion, that is, the transitions of the electron between the ions occurs via free motion.

Because of the continuous spectrum of excitations of the quasiatom, the fraction of accessible volume is a continuous function of the energy

$$\zeta(E_{\rm p}) = \frac{4\pi}{3} \left(\frac{e^2}{-E_{\rm p}} \right)^3 n_{\rm i},\tag{18}$$

where the energy spectrum E_p is given by formula (3). Therefore, the mobility edge corresponds to the percolation threshold of the problem of spheres. The gas-kinetic value of the mobility is reached when $\zeta(E_p)$ is of the order of the degree of dense packing, since the major part of the volume is accessible.

The corresponding excitation energy ε_{p} is

$$\Delta_{k} = I - e^{2} (4\pi n_{1}/3\zeta_{k})^{1/3}, \quad k = 1, 2,$$
⁽¹⁹⁾

where we take, for example, $\zeta_1 = 0.29$ for the mobility edge, and for the minimum gas-kinetic mobility $\zeta_2 = 0.74$. At the transition point the metal-nonmetal gap vanishes. Above this point $\Delta_1 < 0$, i.e., the (virtual) mobility edge lies below the ground state level of the atom.

An estimate of the critical exponent of the mobility in the scaling theory of localization indicates a linear behavior of the mobility around the threshold⁶

$$\mu(E_{\rm p}) \propto (E_{\rm p} - E_{\rm c})^{\nu}, \quad \nu \approx 1, \tag{20}$$

where E_c is the mobility threshold. In this case one can interpret the mobility μ_p as a linear function over the entire interval from Δ_1 to Δ_2 (Fig. 4). Thus, instead of a direct calcula-



FIG. 4. Percolation mobility. Δ_1 is the percolation threshold, Δ_2 is the minimum gas-kinetic mobility μ_m .

tion of the percolation mobility, normalization to the gas-kinetic limit is used, which radically simplifies the problem.

The percolation mobility averaged over the Boltzmann distribution with the density of states (13), $\langle \mu_p \rangle$, automatically takes the form (16) with a definite localization factor.²⁸ Above the metal-nonmetal transition point the localization factor has the form

$$\frac{\tau}{\tau'} \approx \frac{(3T/2) - \Delta_1}{\Delta_2 - \Delta_1},$$

$$\Delta_1 \le 0, \ \Delta_2 \gg T.$$
(21)

Below the transition point this factor is

$$\frac{\tau}{\tau'} \approx \frac{2}{\sqrt{\pi}} \frac{(\Delta_1 T)^{1/2}}{\Delta_2 - \Delta_1} e^{-\Delta_1/T},$$

$$\Delta_2 > \Delta_1 \gg T.$$
(22)

The exponential dependence of the localization factor on the temperature below the metal-nonmetal transition is due to the vanishing of the activation energy (excitation to the mobility edge) at the transition. Thus, formula (22) describes the broadening of this transition. In the region of applicability of one-electron theory the activation energy must be much less than the ionization potential of the atom. Otherwise, the excited electron sees not an ion, but an atom, and so its percolation in the fields of the ions is not possible. This condition limits the applicability of the formula in a certain vicinity of the transition. The extension of this line of reasoning leads to the separating out of a subsystem of excited quasiatoms and an analysis of partial ionization.²⁹

For degenerate electrons a layer of width $\sim T$ around the Fermi level contributes to the conductance. Therefore, when the Fermi level is above the mobility edge the localization factor depends only on the position of this level. However the criterion for degeneracy, $\varepsilon_F^2 = p'_F/2m \gg T$, is usually satisfied when the usual Fermi level is $\varepsilon_F > \Delta_2$, since it already lies above the level of the gas-kinetic mobility. Here the localization factor tends to unity. Therefore, in addition to the reduction of the localization factor discussed above, the factor itself in the case of degeneracy is close to unity.²⁴

9. ELECTRICAL PROPERTIES IN THE REGION OF THE METAL-NONMETAL TRANSITION

The broadening of the metal-nonmetal transition has been observed experimentally as a continuous but more or less sharp change in the electrical properties, in particular in the conductivity, as functions of the density. According to the theory of percolation mobility of electrons, the change in the conductivity is explained by the localization factor. When this factor is taken into account the Drude formula is modified

$$\sigma = e n_e \langle \mu_p \rangle = \frac{e^2 n_e^{\tau}}{m} \frac{\tau}{\tau'}.$$
 (23)

In the region of its applicability the formula is in agreement with experiment for various metals with an accuracy to a factor of 2 or 3. (Figs. 5a,b). The metal-nonmetal transition point is determined by an extrapolation of the density dependence of the activation energy (Fig. 6). The theory of



FIG. 5. Conductivity in the vicinity of the metal-nonmetal transition (shown by the arrows). a) Cesium, T = 2115 K; 1) experiment³⁰; 2) theory¹⁴. b) Mercury, T = 1800 K; 1) experiment¹³, 2) theory¹⁴. c) Copper, T = 7600 K, theory.²³

percolation mobility also gives qualitative agreement with the experimental curves.

Since the only specific parameter that determines the mobility gap in formula (19) is the ionization potential of the free atom, the formulas for the localization factor, (21) and (22), make it possible in practice to estimate the conductivity of any metal. In the special case of the excitation of the mixed term discussed above, the ionization potential of this term must be inserted into formula (19). For example, this is the way in which the conductivity of copper was calculated²³ (Fig. 5c). We should draw attention to the magnitude of the regions of the metallic state in various metals. While for mercury the unactivated metallic conduction is



FIG. 6. Temperature coefficient of the conductivity of mercury (dashes are the extrapolation of the activation energy). 1) Experiment¹³; 2) theory¹⁴.

retained as the material expands to a factor of 1.5 below the normal density, in the case of cesium it is retained to a reduction in density by a factor of 5, and for copper, a factor of 15.

The Hall coefficient is given by the expression²⁸

$$R = -\frac{1}{en_e} \frac{\langle \mu_p^2 \rangle}{\langle \mu_p \rangle^2}.$$
 (24)

The distinction between the mean square of the percolation mobility and the square of the mean in this expression is important only when there is a threshold, that is, below the metal-nonmetal transition. The result of the averaging in this case is

$$R = -\frac{\sqrt{\pi}}{en_e} \left(\frac{T}{\Delta_1}\right)^{1/2} e^{\Delta_1/T}, \quad \Delta_1 \gg T.$$
 (25)

Thus, the Hall coefficient below the transition point behaves as the reciprocal of the conductivity (Fig. 7).

The thermoelectric coefficient (or the thermal emf, in units of V/K) is qualitatively described by the formula²⁸

$$\alpha \approx -\frac{k_{\rm B}}{eT} \frac{\langle \mu_{\rm p} \epsilon_{\rm p} \rangle}{\langle \mu_{\rm p} \rangle},\tag{26}$$

where $k_{\rm B}$ is the Boltzmann constant. In this expression the weighted-average excitation energy, with a weighting factor proportional, to $\mu_{\rm p}$, differs considerably from 3T/2 if there is a mobility threshold, i.e., below the metal-nonmetal transition. Here, the thermal emf is

$$a \approx -\frac{k_{\rm B}}{e} \frac{\Delta_1}{T}, \quad \Delta_1 \gg T.$$
 (27)

Below the transition point, therefore, the thermal emf is negative and varies as the logarithm of the conductance (Fig. 8). It is difficult to interpret the positive peak of the thermal emf measured in the direct vicinity of the critical point of mercury.³³ However, it is possible that the reason for this anomaly is related to the divergence in the thermal conductivity at the critical point, which makes it difficult to measure the thermal emf itself.³⁴

10. OPTICAL CONDUCTIVITY

The metal-nonmetal transition is accompanied by a change in the spectral distribution of the optical conductivity from the Drude-Lorentz distribution, which has a de-



FIG. 7. Hall coefficient (mercury, T = 1800 K). 1) Experiment³¹; 2) theory²⁸.



FIG. 8. Thermoelectric coefficient (mercury, T = 1800 K). 1) Experiment³²; 2) theory²⁸.

scending frequency dependence, to one typical of an insulator, with a window of transparency at low frequencies. These spectra were obtained as a result of the analysis of an experiment on the reflection of light from the interface between expanded mercury and sapphire.³⁵ The evolution of the spectrum can be explained by the theory of percolation mobility.

In the classical case $\hbar\omega \ll T$ formula (23) for the dc conductivity is generalized by modifying the Drude-Lorentz formula

$$\sigma(\omega) = \frac{e^2 n_e^{\tau}}{m} \frac{\tau}{\tau'} \frac{1}{1 - i\omega\tau},$$
(28)

where ω is the frequency of the external field. In a further generalization to the quantum mechanical case it is assumed that the interaction of an electron with the external field during the diffusion reduces to the absorption (emission) of photons. From this point of view the major effect in the percolation mobility consists of a lowering of the threshold by an amount $\hbar\omega$ as a result of the virtual absorption of photons. This effect gives a spectral maximum in Re $\sigma(\omega)$ above the metal-nonmetal transition, unlike the monotonically decreasing dependence of the Drude-Lorentz formula (Fig. 9). Below the transition point the lowering of the threshold leads to an exponential form of the spectrum at low frequencies³⁶

Re
$$\sigma(\omega) \approx \sigma_0 e^{\hbar \omega/T}$$
,



FIG. 9. Optical conductivity (mercury, T = 1800 K; Ref. 36).

where σ_0 is the dc conductivity. Thus, the decay of the dc conductivity below the metal-nonmetal transition results in the formation of a window of relative transparency at low frequencies.

In the presence of the window of transparency it is more convenient to analyze the absorption coefficient, related to the conductivity by

$$K = (4\pi/cn) \operatorname{Re} \sigma,$$

where c is the velocity of light and n is the refractive index. In addition to the optical absorption we have considered, due to the diffusion of electrons, atoms in clusters can cause absorption, undergoing transitions to excited levels (which also are broadened into a band). A formal indication of interband absorption is the fact that because the localization factor is included, the modified Drude-Lorentz formula does not satisfy the optical sum rule

$$\int_{0}^{\infty} \operatorname{Re} \sigma(\omega) \mathrm{d}\omega = \frac{\pi n_{e} e^{2}}{2m}.$$

Interband absorption is not necessarily associated with percolation, since the effect of clusters reduces to a shift and a broadening of the levels.

11. FLUCTUATION-INDUCED ABSORPTION OF LIGHT IN MERCURY

The absorption spectrum with a window of transparency has been directly observed in mercury at densities a factor of two below that at the metal-nonmetal transition (Fig. 10).^{37,38} The absorption edge at such densities is formed as a result of the shift and broadening of the resonance line of the atoms in the fluctuation-induced clusters.³⁹

Two main broadening mechanisms are considered.⁴⁰ The first is related to the fact that the levels are broadened into a band (Fig. 11). The interband transition with a frequency ω_0 is collision-broadened into a Lorentzian shape with a halfwidth $\gamma = 2/\tau$. However the low frequency branch, corresponding to transitions from the high-lying levels of the main band, are cut off exponentially by the Boltzmann factor, so that the shape of the band is



FIG. 10. Absorption spectra of mercury (T = 1754 K; Ref. 38).

FIG. 11. Energy bands of quasiatoms.

$$a(\omega, \omega_0) = \frac{\gamma/\pi}{(\omega - \omega_0)^2 + (\gamma/2)^2} \frac{\Gamma(3/2, y)}{\Gamma(3/2)},$$
 (29)

where

$$\Gamma(3/2, y) = \int_{y}^{\infty} x^{1/2} e^{-x} \mathrm{d}x$$

is the incomplete gamma function in the parameter $y = \hbar(\omega_0 - \omega)/T$. The edge of this band has an exponential shape

$$a(\omega, \omega_0) \propto e^{\overline{h}\omega/T}$$

The second mechanism involves a shift in the bottom of the resonance band. In mercury (also in nickel and cadmium) the radius of the classically accessible region of an electron excited to the resonance level increases by a factor of three. This region encompasses surrounding atoms, whose polarization also causes a shift. The narrowing of the gap between the bands is given by the formula

$$\Delta_{\mathbf{g}} = \varepsilon_{\mathbf{r}} - sq, \tag{30}$$

where ε_r is the energy of the resonance excitation in the atom, q is the average polarization energy of the atoms, and s is the fluctuating number of atoms in a polarization sphere of radius $e^2/(I - \varepsilon_r)$. If interatom correlation is neglected, the probability of fluctuations is given by the Poisson distribution

$$P_{s} = (\overline{N}^{s}/s!)e^{-\overline{N}}, \qquad (31)$$

where $\overline{N} = n_a \Omega$ is the average number of atoms in the polarization sphere and Ω is the volume of this sphere. For large s the Poisson distribution has the form

$$P_s \propto (e\overline{N}/s)^s$$
,

so that the probability of large shifts falls off exponentially.

The absorption edge is formed by the summation of the partial bands with centers $\omega_0 = \Delta_s / \hbar$, with weighting factors proportional to the Poisson distribution of the fluctuations. The results of the calculations for the band edge (with the summation replaced by an integral by the method of Laplace) is⁴⁰

$$a(\omega) \propto \exp\left[-\frac{\varepsilon_{\rm r} - \hbar\omega}{T} + \bar{N}(e^{q/T} - 1)\right]. \tag{32}$$

By formula (32) one can explain the experimentally ob-

served exponential shape of the absorption edge and the exponential dependence on the density.

At higher energies a plateau in the absorption, sometimes attributed to free electrons⁴¹ or electrons captured by clusters,⁴² appears near the absorption edge. The data of Ref. 42 indicate, however, that this plateau is related to critical phenomena. It is shown that a change in the shape of the absorption edge near the critical point can be explained by a non-Poisson (a two-humped) distribution in the fluctuation probability. The plateau is related to the second maximum of the distribution of the fluctuations, corresponding to droplets of the liquid phase, this second maximum increasing as the critical point is approached from the gas phase.⁴³

12. POLARIZABILITY OF ATOMS AND BONDS

In addition to the diffusion of electrons investigated above, the electrodynamic properties of gaseous metals depend on the polarization of the atoms in the percolation clusters. The dielectric permittivity is expressed in terms of the atomic polarizability, which is divided into two parts: the polarizability of the atoms themselves and the polarizability of the atomic bonds (quasimolecules). The polarizability of metal atoms with *s*-type valence electrons lends itself to a simple semiclassical description, which is equally applicable to atoms in percolation clusters. The principle is that the polarization in an external field is due to the shift of the classically accessible sphere together with the localization of electron charge around it. The shift is found from the equation for the radius of the classically accessible region

$$(-e^2/r) - e\,\,\vartheta r\,\cos\,\vartheta = -I,\tag{33}$$

where \mathscr{C} is the external electric field and r and ϑ are the polar coordinates. The result for the polarizability of an atom is⁴⁴

$$\alpha_{a} = ze\delta x/\delta = z(e^{2}/I)^{3}, \tag{34}$$

where $\delta x = \delta r/\cos \vartheta$ is the absolute value of the shift of the accessible sphere in the direction opposite to the electric field. Formula (34) is in agreement with the data obtained by experimental methods (Fig. 12) for metals with *s*-type valence electrons, which indicates the applicability of the semiclassical approach. An additional contribution comes from the polarization of overlapping atoms with the transfer of electric charge between them, or else the polarization of bonds or quasimolecules. The transport of charge indicates a virtual excitation of the ion term of the quasimolecule

$$U(R)\approx I-\frac{e^2}{R}\approx \frac{1}{2}I,$$

where R is the interatomic spacing. The degree of polarization varies from zero in a free quasimolecule to unity for complete polarization. For a small degree of ionization δ the excitation energy of a quasimolecule is equal to $I\delta^2/2$, and the energy in an electric field is

$$\frac{1}{2}I\delta^2 - \delta e \vartheta \cdot 2\frac{e^2}{I}\cos\vartheta,$$

where ϑ is the angle between the axis of the quasimolecule and the direction of the field. Minimization of this expression determines the dependence of the degree of polarization on the electric field, that is, the polarizability of the bonds¹⁴



FIG. 12. Polarizability of ns and ns² valence shells in metal atoms.⁷⁴

$$\alpha_{\rm b} = 4 \left(\frac{e^2}{I}\right)^3 \langle \cos^2 \vartheta \rangle = \frac{4}{3} \left(\frac{e^2}{I}\right)^3. \tag{35}$$

The total atomic polarizability, including both contributions discussed is

$$\boldsymbol{\alpha} = \boldsymbol{\alpha}_{\mathbf{a}} + C\boldsymbol{\alpha}_{\mathbf{b}},\tag{36}$$

where C is the average number of bonds or quasimolecules per atom, given by the integral

$$C = 2\pi n_{\rm a} \int_{0}^{2e^2/I} g(R)R^2 dR, \qquad (37)$$

and g(R) is the radial distribution function of the atoms. In this way the polarizability in percolation clusters is a function of the density and temperature.

Introducing the complete correlation function

$$h(R)=g(R)-1,$$

one can rewrite the integral in Eq. (37) as

$$C = \frac{16\pi}{3} \left(\frac{e^2}{I}\right)^3 n_{\mathbf{a}} + \frac{1}{2} n_{\mathbf{a}} \int_{\Omega} h(R) d\Omega, \qquad (38)$$

where the integration is carried out over a sphere of radius twice the classically accessible radius. This integral is related to the fluctuation characteristics by the known relation⁴⁵

$$n_{a}\int_{\Omega}h(R)\mathrm{d}\Omega=\frac{\langle\Delta N^{2}\rangle}{\langle\bar{N}\rangle}-1,$$

where N is the fluctuating number of atoms in the volume Ω . It can be shown⁴⁶ that

$$\frac{\langle \Delta N^2 \rangle}{\bar{N}} \le \max N, \tag{39}$$

where max N is the largest possible number of atoms in the volume Ω . Since the classically accessible regions can overlap, there are no less than two atoms in a sphere with the doubled radius, that is, max $N \ge 2$.

In an ideal gas or in a macroscopic volume the mean square of the fluctuations is related to the compressibility by

$$\frac{\langle \Delta N^2 \rangle}{\overline{N}} = T \left(\frac{\partial n_{\mathbf{a}}}{\partial p} \right)_T$$

Using the difference $T(\partial n_a/\partial p)_T - 1$ as an expansion parameter, we can use this expression to construct a Padé approximation that satisfies condition (39). In the case max N = 2, for example, this approximation is

$$\frac{\langle \Delta N^2 \rangle}{\overline{N}} = 2 - \frac{1}{T} \left(\frac{\partial p}{\partial n_a} \right)_T. \tag{40}$$

It is therefore sufficient to know the equation of state to estimate the number of bonds per atom on which the atomic polarizability depends. In the vicinity of the critical point one can use the asymptotic expansion of the equation of state. In particular, near the critical isotherm⁴⁵

$$\frac{1}{T} \left(\frac{\partial p}{\partial n_{\mathbf{a}}} \right)_{T} = D |\Delta n_{\mathbf{a}}|^{\delta - 1} + F \Delta T |\Delta n_{\mathbf{a}}|^{\delta - (1/\beta) - 1}$$

for $|\Delta T| \ll |\Delta n_a|^{1/\beta}$, here $\Delta n_a = n_a - n_c$, $\Delta T = T - T_c$, $\delta = 4.8$ and $\beta = 0.34$ are the critical exponents, and D and F are positive amplitudes. It follows from this development that the lower the temperature the larger is the number of bonds per atom, and, consequently, the higher is the atomic polarizability. The increase in the atomic polarizability is responsible, for example, for the dielectric anomaly in mercury.⁴⁶ This phenomenon will be discussed in the following section.

13. DIELECTRIC PERMITTIVITY

The electrodynamic properties of gaseous metals depend on two different contributions, due to the polarization of electrons in nearly localized states and drift in the electric field. The real part of the permittivity, including these contributions, has the form

Re
$$\varepsilon = 1 + 4\pi \chi \left(1 - \frac{\tau}{\tau'}\right) - \frac{4\pi}{\omega} \operatorname{Im} \sigma,$$
 (41)

where χ is the dielectric susceptibility due to the atomic polarizability. According to Eq. (28), Im σ varies as τ/t' , and therefore formula (41) can be considered as the first term in the expansion of Re ε in powers of the localization factor. The dielectric term gives the main contribution in the case of strong localization (when $\tau/\tau' \rightarrow 0$) but vanishes in the case of weak localization (when $\tau/\tau' \rightarrow 1$). In the latter case formulas (28) and (41) go over to the usual Drude-Lorentz expressions, which describe free electrons. The dielectric permittivity in this case changes sign from positive to negative.

The dielectric susceptibility is expressed in terms of the atomic polarizability by the Clasius-Mossotti formula

$$\chi = \frac{n_{a}\alpha}{1-\kappa}, \quad \kappa = \frac{4\pi}{3}n_{a}\alpha. \tag{42}$$

$$d_l = \sum a_{ik}(R_{lk})d_k, \tag{43}$$

where d_i are the components of the dipoles, and a_{ik} (R_{ik}) are coefficients that depend on the interatomic spacings. In the usual formulation the determinant of the system is nonzero

$$|a_{ik}(R_{ik}) - \delta_{ik}| \neq 0.$$

Therefore, the only solution to equations (43) is the null solution, i.e., $d_i = 0$.

Thus, for a disordered medium the Clasius-Mossotti formula (42) must be regularized, for instance, with the use of the expansion

$$(1 - x)^{-1} = 1 + x + x^2 + \dots, x \le 1.$$

As usual, in the case of an asymptotic expansion the determination of the number of terms to be retained involves some compromise (the number of terms cannot be large; suppression of new terms must not strongly change the sum).

The dielectric permittivity can be measured using the reflection of light at the interface between a gaseous metal and a transparent medium, since the reflection coefficient depends on the difference between the refractive indices. Such measurements, carried out for mercury, led to the discovery of the dielectric anomaly—a strong deviation from the Clausius–Mossotti equation, which works well in the case of dielectric liquids.⁴⁸ Later, a connection was discovered between this anomaly and the critical point.³⁸ Specifically, for this reason attempts to explain the dielectric anomaly by an increase in the polarizability of the atoms resulting from the shift of the levels was not entirely successful.⁴⁹ Actually, the connection with critical phenomena comes from the influence of fluctuations on the number of quasimolecules.

The behavior of the dielectric permittivity can be accounted for by taking into account simultaneously the polarization of the quasimolecules and the diffusion of electrons (Fig. 13).⁴⁶ The former of these factors causes the permittivity to be larger than that given by the Clausius-Mossotti formula with a constant atomic polarizability, an effect that becomes stronger as the temperature is reduced. The latter factor explains the descending branch of the permittivity with the change of sign to negative above the metal-nonmetal transition.

14. PLASMA OSCILLATIONS

The dispersion of the permittivity at frequencies lower than the resonance energies of excitation of the atom is mainly related to the conductivity. Substituting the imaginary part of the conductivity into expression (41) one can rewrite the latter as

$$\operatorname{Re} \varepsilon = \varepsilon_{a} - \frac{\omega_{p}^{2} \tau^{2}}{1 + \omega^{2} \tau^{2}} \frac{\tau}{\tau'}, \qquad (44)$$



FIG. 13. Dielectric permittivity of mercury at $T = T_c$: experimental points, Refs. 48, 50; theoretical curve, Ref. 46.

where ε_a stands for the "atomic" part of the permittivity,

$$\varepsilon_{\mathbf{a}} = 1 + 4\pi \chi \left(1 - \frac{\tau}{\tau'} \right), \tag{45}$$

and $\omega_{\rm p}$ is the plasma frequency of the free electrons

$$\omega_{\rm p} = (4\pi e^2 n_e/m)^{1/2}$$

The frequency at which the real part of the permittivity goes to zero corresponds to the long-wavelength plasma oscillations. Under conditions of weak damping, $\omega \tau \ge 1$, the zero of the permittivity (44) occurs at the frequency¹⁴

$$\omega_{\mathbf{p}}' = \frac{\omega_{\mathbf{p}}}{\varepsilon_{\mathbf{a}}^{1/2}} \left(\frac{\mathbf{r}}{\mathbf{r}'}\right)^{1/2}.$$
(46)

In this way the plasma frequency is renormalized because of the atomic part of the permittivity and the localization factor. The physical meaning of the renormalization is that the action of the external electric field on an electron is effectively weakened.

To understand the meaning of the renormalization of the plasma frequency let us consider a derivation using the equation of the drift of an electron in an electric field

$$\frac{\mathrm{d}\mathbf{v}}{\mathrm{d}t} = -\frac{e\vec{\delta}}{m}\frac{\mathbf{r}}{\mathbf{r}'} - \frac{\mathbf{v}}{\mathbf{r}}.$$
(47)

It is easy to see that the steady-state drift velocity determined by this equation corresponds to the mobility Eq. (16). Combining Eq. (47) with the equation of continuity

$$\partial \rho_e / \partial t - e n_e \nabla \mathbf{v} = 0$$

and Poisson's equation

$$\nabla \mathcal{B} = 4\pi \rho_{\rm e}/\varepsilon_{\rm g},$$

where $\rho_{\rm e} = -e\delta n_{\rm e}$ is the charge density, we obtain

$$\frac{\partial^2 \rho_e}{\partial t^2} + \omega_p'^2 \rho_e + \frac{1}{\tau} \frac{\partial \rho_o}{\partial t} = 0.$$
(48)

Equation (48) describes oscillations in the charge density with renormalized plasma frequency ω'_p and a damping rate $1/2\tau$. The concept of a resonant frequency ω'_p is meaningful if it is much larger than the damping rate, that is, if $\omega'_p \tau \gg 1$.

In a similar way, the Debye screening length of a weak external field by electrons, $r_e = \kappa_e^{-1}$ is renormalized, where

$$R_e = (4\pi e^2 n_e/T)^{1/2}$$
.

The screening is described by the Poisson-Boltzmann equation

$$\nabla^2 \varphi = -4\pi \rho_e/c_a$$

where φ is the electric potential. The charge density is expressed by the Boltzmann distribution with an effective potential that takes localization into account:

$$\rho_{\rm e} \propto \exp\left(\frac{e\varphi}{T}\frac{\tau}{\tau'}\right)$$

In the linear approximation the Poisson-Boltzmann equation takes the form

$$\nabla^2 \varphi = \kappa_{\rho}^{\prime 2} \varphi, \tag{49}$$

in which enters the inverse Debye length

$$\varkappa_{e}' = \frac{\varkappa_{e}}{\varepsilon_{a}^{1/2}} \left(\frac{\tau}{\tau'}\right)^{1/2}.$$
(50)

Thus, the relation between the plasma frequency (46) and the electron screening length of a weak external field (50) is not changed compared to that of free electrons. The Debye length has a meaning if it is considerably greater than the average interatomic spacing, i.e., if $\varkappa_c^{-} l \ll 1$.

Finally, it should be noted that the localization factor in formula (46) for the plasma frequency depends itself on that frequency because of the lowering of the percolation threshold due to the virtual absorption of plasmons. Thus, this formula is indeed an equation for ω_p° .

The change in the plasma frequency in the region of the metal-nonmetal transition has received little experimental study.⁵⁰

15. CLUSTER PLASMA

At low densities, as has been mentioned above, it is necessary to separate into distinct subsystems the atoms and the quasiatoms that overlap each other (electrons and ions). A new question that arises here is related to the considerable arbitrariness in this separation, i.e., the indeterminacy of the ionization boundary. It is most convenient to choose this boundary at the percolation level. By definition

$$\frac{4\pi}{3} \left(\frac{e^2}{I_e}\right)^3 n_1 \approx \frac{1}{3},\tag{51}$$

where I_e is the ionization potential of the quasiatoms and n_i is the density of quasiatoms (ions). At the same time I_e is equal to the maximum binding energy of the atoms. By convention, a strong interaction means that $I_e \ge T$. The potential energy of the subsystem of quasiatoms is

$$U = -n_{\rm l}I_{\rm e} - \alpha_{\rm M}e^2 n_{\rm l}^{4/3}, \tag{52}$$

where the first term corresponds to the internal energy of a quasiatom and the second term to the interaction between them (with a renormalized Madelung constant $\alpha_M = 0.63$).

With allowance for definition (51), the two terms in Eq. (52) depend in an identical way on the density. However, the roles of these terms are completely different. The latter statement is related to the principle by which the complete thermodynamic functions, including the contribution of the atomic subsystem, do not contain an explicit dependence on the ionization boundary.⁵¹ Physically, this principle is quite clear, as is emphasized by the arbitrariness of the ionization boundary. A direct consequence of the absence of any explicit dependence on the ionization boundary is that any partial derivative with respect to I_e in a thermodynamic transformation must be set to zero.

With allowance for this principle, the first (percolation) term in Eq. (52) gives the contribution to the lowering of the ionization potential, but not the pressure. Thus, we have

$$\Delta I = -I_{\rm e} - (4/3)\alpha_{\rm M} e^2 n_{\rm i}^{1/3}, \tag{53}$$

$$\Delta p = -(1/3)\alpha_{\rm M} e^2 n_1^{4/3}.$$
 (54)

Because of this asymmetry in Eqs. (53) and (54) the lowering of the ionization potential is more important than thermodynamic effects of the interaction.

If the atoms of a metal form negative ions, there is yet another characteristic density besides that of the point of the metal-nonmetal transition. This is the percolation threshold for above-barrier propagation of an outer electron of a negative ion. The percolation condition for the threshold has the form

$$\frac{4\pi}{3} \left(\frac{\alpha_a e^2}{\varepsilon_1} \right)^{3/4} n_a \approx \frac{1}{3}, \tag{55}$$

where ε_i is the electron affinity of the atom. For a density above the threshold the outer electrons of the negative ions propagate as nearly-free electrons. The electron affinity serves to lower additionally the ionization potential.⁵²

The next effect, although not the next in importance, that influences the degree of ionization is the conversion of atomic ions into cluster ions. Let us denote the fraction of atomic ions remaining after conversion as

$$n_1/n_1 = e^{-S},$$
 (56)

where n_1 is the density of atomic ions and n_i is the total density of positive ions. We assume that there are no negative ions. Then the electron density is

$$\mathbf{n}_e = n_1 e^S. \tag{57}$$

Eliminating n_1 in the Saha equation, we can rewrite it in the form⁵³

$$\frac{n_e^2}{n_a} = \frac{2g_1}{g_a} \frac{1}{\lambda_e^3} \exp\left(-\frac{I + \Delta I}{T} + S\right),\tag{58}$$

where $\lambda_e = (2\pi\hbar^2/mT)^{1/2}$. It follows that the degree of ionization increases with the degree of conversion.

In the simplest model the atoms in cluster ions move in the mean potential, in analogy with the potential acting on an atom in a two-atom ion. Otherwise, the cluster ions can be considered as fluctuations with a self-consistent potential acting on the atoms. These fluctuations are described by the Poisson distribution with a renormalized average number of atoms. The ratio of the probability that there are s atoms in some volume Ω around an atomic ion to the probability of an empty volume is

$$\frac{n_{s+1}}{n_1} = \frac{\langle s \rangle^s}{s!},\tag{59}$$

where in the absence of interaction $\langle s \rangle = n_a \Omega$. When the mean potential $\Phi(R)$ of the cluster ion is taken into account it is necessary to replace the volume Ω by the integral $\int \exp(-\Phi/T) d\Omega$, which contains the Boltzmann factor. In addition, an atom enters a cluster with a definite spin, and so n_a must be replaced by n_a/g_a . The integral is calculated by expanding the potential $\Phi(R)$ in the vicinity of the minimum. In spectroscopic notation we obtain the average number of bound atoms

$$\langle s \rangle = \frac{n_s \lambda^3}{g_a} \frac{T^2}{B\omega_r} e^{q_0/T}, \tag{60}$$

where $\lambda = (4\pi\hbar^2/m_a T)^{1/2}$, m_a is the mass of an atom, B is a rotational constant, ω_r is a quantum of the radial oscillations, and q_0 is the depth of the well. The fraction of atomic ions according to the Poisson distribution is $\exp(-\langle s \rangle)$, i.e., the parameter S in Eq. (56), which determines the degree of conversion, is equal to the average number of bound atoms. This analysis is still somewhat formal, since this number depends on the poorly determined quantities $B\omega_r$ and q_0 in formula (60). On the other hand, the parameters can be determined by using experimental information.

In the alternative means of calculating the degree of ionization of a cluster plasma we consider the ionization of fluctuation-generated droplets of liquid metal. This method is based on the fact that the ionization potentials of the clusters (measured by photoionization of a highly expanded jet of vapor in a mass spectrometer) are correlated with the work function of an electron in the metal with a correction for the curvature of the surface (Fig. 14). Assuming that the partition functions of the charged and neutral clusters are equal, we have

$$\frac{n_e n_s^+}{n_s} = \frac{2}{\lambda_e^3} e^{-I_s/T},$$
 (61)

where I_s is the ionization potential of an *s*-atom cluster. According to the theory of condensation, the concentration of fluctuation-generated droplets in a saturated vapor is taken to be an exponential function of the surface energy

$$\frac{n_s}{n_a} = \exp\left(-\frac{4\pi\sigma_i \rho_i^2}{T} s^{2/3}\right),\tag{62}$$

where σ_i is the surface tension and a_i is the radius of an atomic cell in the liquid. The argument of the exponential in formula (62) in fact corresponds to the first term in the asymptotic expansion in the reciprocal of the droplet radius. Estimates based on formulas (61) and (62) are attractive in that in them one can use the experimental ionization poten-



FIG. 14. Correlation of the ionization potentials of clusters, $I(R) = I_{\infty} + (3/8)e^2/R$ Ref. 54.

tials of the clusters. It should be emphasized, however, that the cancellation of the partition functions in (61) is by no means an obvious approximation, since the electronic terms of the cluster ions can be quite different from those of the neutral ones.

The conversion of the ions is assumed to be responsible for the fact that the electrical conductivity of partially ionized saturated cesium or mercury vapor is an order of magnitude higher than that calculated by the usual Saha equation.^{55,56} An analysis of the experimental data based on the various versions of the cluster model with a mean field is given in Refs. 53 and 56, and an analysis based on the droplet model can be found in Refs. 57–59. Another model of the condensation of a van der Waals gas around an ion has been published in Ref. 60. These papers have also been discussed in the books of Refs. 5 and 61.

16. MULTIPLE IONIZATION

When condensed matter is heated to very high temperatures and (or) is compressed by a large factor a multiply ionized plasma is generally formed. This subject goes beyond the framework of the physics of metals and refers equally to other kinds of matter that form a high-density plasma with properties that depend strongly on the interparticle interaction (a strongly coupled plasma). Experimentally, such a plasma is produced in strong shock waves excited in a solid, for example, in an intense laser pulse. Aluminum can serve as an example. In its normal state the valence $3s^2p$ shell is ionized, since the ionic charge is three. When heated to a temperature of 100 eV at constant density the ion charge increases to six. A simple estimate of the average ion charge is given by the formula of Raĭzer⁶²

$$z = \frac{2}{n_1 l_e^3} \exp\left(-\frac{\overline{I}_z}{T}\right), \qquad (63)$$

where $\overline{I}_z = (I_z + I_{z+1})/2$ is the average ionization potential of the ions with charges z - 1 and z (this formula is easy to derive by considering two stages of ionization under the assumption of a symmetric distribution of the ions around the predominant charge z).

Except for the variable degree of ionization, this plasma is very much like liquid metals. In principle, the methods of describing it are also similar. For example, the conductivity is described by the Ziman formula and depends on the structure factor. A feature of the plasma, however, is the large range of values of the thermodynamic parameters. Therefore, the possibilities of the parametrized pseudopotential method, used in the theory of metals, are limited, as is the possibility of using the experimentally determined structure factors. The interaction of the electrons and ions in a multiply ionized plasma is characterized by the parameter

$$\Gamma = z^2 e^2 / aT, \tag{64}$$

where a is the radius of the ion cell. At the melting point of metals, that is, at a temperature of about 0.1 eV, this parameter is $\Gamma \approx 170$. At temperatures of several tens of eV, even with allowance for the increase in the ion charge, this parameter decreases to the order of unity. Therefore, at the density of a condensed metal a hot plasma is approximately the same as a gaseous plasma in terms of the relative magnitude of the Coulomb interaction. Consequently, it is possible to describe the ionization the same way as in a gas.⁶³

The greatest difficulty comes in the analysis of the electronic spectrum of compressed matter, which involves a determination of the degree of "cold" ionization. Carrying out this analysis in full detail leads to a model of the electronic structure of the atomic cells.

It is usually assumed that the potential is statically screened outside the atomic cell (Fig. 15). The static screening results in a shift in the edge of the continuous spectrum and a shift in the discrete levels in the cell potential. In principle, the potential inside the cell is determined by the self-



FIG. 15. Cell potential (Ref. 64).

consistent Hartree-Fock method with the condition $V(r) = -e^2/r$ at the boundary of the cell. In practice, the methods used are the Hartree-Slater local method which takes into account exchange or the Thomas-Fermi statistical method,⁶⁴ which are simpler for carrying out the calculations. The construction of the self-consistent potential, which depends on the density and the temperature (and, in general, on the electron state) constitutes an independent topic by itself.^{65,66}

If the cell potential is known, one can find the discrete levels and the density of states of the continuous spectrum. The distribution of the electrons in the atomic cell over these levels is given by the Fermi-Dirac function. Knowing the chemical potential, which depends on the number of electrons in a cell, one can find the number of electrons in the discrete and continuous parts of the spectrum, i.e., the average ion charge. Some of the electrons can be found in resonance states that are formed when the p- and d levels, with nonzero orbital angular momentum, go into the continuous spectrum. The resonance electrons remain partially localized, and therefore the number of conduction electrons is sometimes found from the density of states of free motion, which does not contain the resonance peaks.

The collection of cell potential wells is equivalent to a muffin tin potential, in which the free electrons are scattered by the central potential of the atomic cells. The conductivity of this system is calculated by the formula of Ziman, which is written in terms of the differential cross section for scattering by the cell potential (the *t*-matrix method).

The method of atomic cells is used for the calculation of the electronic properties of strongly ionized matter over a large region of the phase diagram.⁶⁴ It must be emphasized, however, that this method does not really work in the vicinity of the metal-nonmetal transition with partial ionization, where the properties of the material are governed by the valence electrons. In this case it is necessary to return to the quasiatom model. Both these models have a structure, that is characteristic of a strongly coupled plasma, made up of neutral atomic elements.

One of the principal applications of the method of atomic cells, and historically the first one, is the construction of the equation of state of hot compressed matter. The problem of the equation of state has been treated in the review of Ref. 67 to which the reader is referred.

17. CONCLUSIONS

In this review an attempt has been made to analyze from a unified point of view a broad range of topics in the behavior of metals at temperatures of the order of the critical temperature and above. The phenomena in the vicinity of the critical point of metals are in some way or other connected with the broadened metal-nonmetal transition. Save for certain exceptions, such as the behavior of the thermal emf near the critical point of mercury, the experimental material is explained, at least qualitatively, by the physical model, formulated in this paper, of a plasma with a strong electron-ion interaction. It must be noted that this model is a practical one, which in many cases makes it possible to carry out direct calculations.

The foundations of this model have received less attention. It must be recognized that regular methods of calculating the properties of a strongly coupled quantum plasma do not exist. Except for the case of multiple ionization, the prospects for numerical simulation also remain unclear. This situation shows that the physics of gaseous metals can in no way be considered complete. However, the level of understanding of the properties of gaseous metals that has been attained is sufficient for an adequate analysis of the physical processes in which they are involved. This success gives us confidence that the ideas presented here concerning the physics of gaseous metals will be useful for various applications.

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