

FROM THE CURRENT LITERATURE

Electric conductivity and atomic dynamics in liquid metals

V. Ya. Prokhorenko

Usp. Fiz. Nauk **115**, 521-529 (March 1974)

PACS numbers: 72.10.C, 61.25.D

Progress in the theory of electric properties, as developed by Ziman and co-workers^[1-3], was an important stimulus for the development and improvement of research on the atomic structure and electron kinetics in liquid metals. The main cause was that the theory provided, for the first time, an analytic connection between the electron mean free path and the structure factor of the liquid:

$$\frac{1}{\lambda_Z} = \frac{3\pi}{2\sqrt{2}} \frac{Zm^{1/2}}{\hbar E_F^{3/2}} \frac{1}{4k_F^4} \int_0^{2k_F} S(k) |U_k|^2 k^3 dk; \quad (1)$$

here Z is the valence, E_F and k_F are the energy and the Fermi wave vector, m is the mass of the free electron, and U_k is the form factor of the pseudopotential. The structure factor $S(k)$ describes inter-ion correlations in the melt. In contrast to a crystal, where $S(k)$ is equal to a sum of δ -functions in the reciprocal-lattice sites, in liquids it has finite values at each point of reciprocal space. The structure factor can be constructed theoretically on the basis of the a priori assumed (and, of course, simplified) model of the liquid metal, or else derived from diffraction experiments. The second method is regarded as preferable in view of the presence of data on the concrete substance. We note, however, that the experimental intensity $J(k)$ of coherent x-ray or neutron scattering, which is used in this case, yields information only on the pair correlation functions, while the single-particle motion and the higher correlations are not taken into account.

The rapid development of the theory of pseudopotentials and the enticing simplicity of expression (1) have determined the active interest in the electric properties of liquid metals^[4]. It should be noted that in most researches expression (1) is assumed a priori to be correct, and disparities between the calculated and experimental values of the kinetic coefficients is attributed to instrumental and methodological errors in the determination of $S(k)$, in the choice of the integration interval during computer solution of (1), to the method used to approximate $S(k)$ at the boundary $k = 0$, and to imperfections of the employed pseudopotential models. The bulk of the studies therefore followed three directions: precision measurements of the electric conductivity, thermoelectric power, and Hall coefficient in a wide range of temperatures and pressures; improvement of the pseudopotential models, and structure investigations.

To a considerable degree, owing to progress in the theory of the electric properties of liquid metals, the procedures in diffraction experiments have been improved in principle in recent years, both with respect to apparatus and with respect to the mathematical reduction of the results^[5,6]. The resolution of the experimental equipment and the accuracy of photography at small scattering angles have improved^[7,8] and the results of the investigations have been tabulated. The analyticity of the function $S(k)$ was investigated in the entire integration region, especially at low values of the momentum^[9,10]. The improvement of the technique

of diffraction experiments has made it possible to reveal many new features of short-range ordering in liquid metals, this being of undisputed independent interest. With respect to the electric properties, the progress in structure investigations has determined, above all, the uniqueness of the calculations of the resistance and of the thermoelectric power, since the use of the old structure data introduced a large random element in calculations of this kind.

By now there have been developed a number of pseudopotential models^[11,12] that are suitable, to one degree or another, for the calculation of electronic properties. Of course, different pseudopotential models yield significantly different calculation results. However, a comparison of a large number of experimental data on the resistance and thermoelectric power with the theoretical data show that, regardless of the pseudopotential model, the difference for most investigated polyvalent metals is of the order of 20% and more in absolute magnitude^[13]. Numerous investigations show that the obtained difference cannot be entirely attributed to instrumental errors in the determination of $J(k)$, nor to imperfections in the employed pseudopotential model.

Ziman's theory, which is based on the Born approximation, assumes the inequality $k_F\lambda \gg 1$ to hold. This inequality, however, is far from obvious for heavy polyvalent metals. In addition, the very definition of the radius of the Fermi surface of a liquid metal calls for refinement, in view of the diffuseness of this surface.

The upper limit of integration in (1) presupposes a sharp Fermi-surface boundary. The temperatures smearing of the Fermi surface remains small enough even at 2000°K. In liquid metal, however, which is a partly disordered system, an additional spread of Δk , on the order of \hbar/τ , should take place, and should be determined by the lifetime of each plane wave. It has been shown^[14] that this circumstance can be taken into account by introducing in (1) the additional factor

$$1 + A \frac{\hbar}{2\tau E_F}. \quad (2)$$

At \hbar/τ on the order of $E_F/2$, allowance for the smearing can lead to a change of λ_Z by $\pm 10\%$. According to March^[15,16], however, it is hardly reasonable to assume for arbitrary liquid metals a smearing of the Fermi surface larger than 10%. In particular, substituting $\Delta k \approx 1/\lambda$ we obtain for sodium, mercury, lead and bismuth respectively

$$\frac{\Delta k}{k} = 0.007, 0.10, 0.11, 0.15.$$

If this estimate is valid, then the contribution of (2) the mean free path is small, on the order of 2-3%. But the condition $k_F\lambda \gg 1$ does not necessarily mean that the electrons are described approximately by plane waves^[21]. Thus, for example, in silicon, germanium, and III-V compounds the value of λ is quite large, but the spectrum and wave functions of the electrons are by far not the same as for free electrons. The presented

values of the degree of smearing of the Fermi radius are therefore far from obvious.

The conclusion that the Fermi surface is sharply outlined is corroborated by March by his own calculations of the interatomic potential $\varphi(r)$, which has in accord with these calculations a long-oscillating form, whereas the oscillations should become rapidly damped if $\Delta k/k > 0.1$.

The study of the form of the inter-ion potential in liquid metals in comparison with the potential in liquid argon is of fundamental significance for the description of the metallic bond. This problem is the subject of a large number of studies^[15-20], the results of which are quite contradictory. The reasons for which are quite understandable.

It is known that the calculation of $\varphi(r)$ is based on the solution of the approximate Born-Green, Percus-Yevick, and the superconcatenated equations, the degree of applicability of which to liquid metals has not yet been fully clarified. In addition, the inter-ion potential is determined in these calculations from the direct and paired correlations functions, the principal role in its determination at large distances being played by information on small-angle scattering, which is obtained with minimal accuracy from diffraction measurements and which is therefore the least reliable. Yakovlev^[19] has made a detailed analysis of the introduced approximations and has shown that for a correct solution of the problem of determining $\varphi(r)$ it is necessary to refine the existing data on $S(k)$ in the region of small scattering angles.

Thus, on the basis of the available information on the pair potential of inter-ion interaction it is impossible to arrive at an unambiguous conclusion that the Fermi surface of a liquid metal has a sharp outline.

Direct information on the degree of smearing of the Fermi surface can be obtained from experiments on positron annihilation in liquid metals. Such experiments were performed on solid and liquid mercury^[22]. On the basis of the diffusion spectrum of the electron momenta observed in the melt, the authors of^[22] have reached the conclusion that $\Delta k/k_F \approx 0.2$. Incidentally, according to^[15], so large a smearing could be the result of an incorrect interpretation of the experimental results.

The scattering probability was calculated in Ziman's theory in the Born approximation. Accordingly, the matrix element between the states ψ_1 and ψ_2 , constituting plane waves, was considered. Thus, the complete wave function, including all the scattered waves that modulate the amplitude and the phase of the incident wave, are replaced by a plane wave.

On the whole, there are no grounds for using such a simplification. It is shown in^[14] that the formalism used in the Born approximation can be used here, except that the true potential $V(r)$ must be replaced by an effective potential $V'(r)$:

$$V'(r) = [1 + \gamma(r)] V(r), \quad (3)$$

where $\gamma(r)$ can depend on k and, moreover, the spherical symmetry of the potential $V(r)$ does not imply a spherical symmetry of $\gamma(r)$. Therefore $V'(r)$ can be complex and can depend both on the value of k and on the scattering angle. To calculate the scattering in the Born approximation using an effective potential instead of a true potential it is necessary to know correlation functions higher than the binary one.

The higher correlation functions cannot be obtained from diffraction experiments. This makes it difficult to account for the deviations from the Born approximation. According to the estimate^[14], however, this deviation can be appreciable for polyvalent liquid metals, where the mean free path is commensurate with the interatomic distance.

We turn now to a more detailed analysis of the influence of the atomic structure in both the static and dynamic sense) on the electric properties of the liquid metals. New information on this problem follows primarily from experiments on the scattering of slow neutrons, and is also confirmed by the results of investigations of the properties of the electron kinetics.

The main idea on which Ziman's theory is based is that the scattering of the conduction electrons is determined by the same structure properties as the scattering of x rays or neutrons. It is therefore expedient to assess how complete an information is obtained on the structure from the diffraction experiment.

In the conventional theory of x-ray scattering one analyzes only coherent scattering. Incoherent scattering produces a continuous background and is not taken into account in the analysis. Thus, x-ray diffraction studies of liquids yields integrated information on the pair correlation and does not make it possible to analyze individual translational motion of atoms, nor higher correlations. The same conclusion pertains equally well to coherent scattering of slow neutrons. According to statements by the very author of the theory of almost-free electrons^[3], allowance for only the pair correlation function may be insufficient for a description of the scattering of electrons in a liquid metal.

It is important to note one more feature of the interaction of x rays with a melt, namely, they are strongly absorbed, and the absorption increases with increasing atomic number of the metal. This circumstance has that important advantage that one can neglect in practice the multiple scattering and this, naturally, facilitates the interpretation of the intensity curve. But large absorption limits the experimental procedure—the x-ray diffraction of liquid metals is based on reflection, and transmission of samples with realistically attainable thicknesses is excluded. As a result, the region investigated in practice is that of small scattering angles.

In the Born approximation, the scattering of slow neutrons by a system of N atoms can be described with the aid of the function $S(k, \omega)$, which determines the probability of transferring to the neutron an energy $\hbar\omega$ from a system that acquires a momentum $\hbar k$. According to Van Hove, the differential scattering cross section is

$$\frac{d^2\sigma}{d\omega d\Omega} = Nb^2 \frac{K}{k_0} S(k, \omega), \quad (4)$$

where b is the "scattering length," a parameter that determines the intensity of scattering by the nucleus, and $K = k_0 - k$ (k_0 and k are the initial and final wave vectors).

The coherent and incoherent parts of the scattering can be separated by introducing the concept of the average scattering length $\langle b \rangle$, which takes into account, with a suitable weight factor, the statistical distribution of the isotopes and the spin effect:

$$\frac{d^2\sigma_0^{\text{coh}}}{d\omega d\Omega} = N \langle b \rangle^2 \frac{K}{k_0} S^{\text{coh}}(k, \omega), \quad (5)$$

$$\frac{d^2 \sigma^{\text{incoh}}}{d\omega d\Omega} = N \frac{(\langle b^2 \rangle - \langle b \rangle^2)}{k_0} S^{\text{incoh}}(\mathbf{k}, \omega). \quad (6)$$

Here the scattering functions $S^{\text{coh}}(\mathbf{k}, \omega)$ and $S^{\text{incoh}}(\mathbf{k}, \omega)$ are connected via a double Fourier transformation with the space-time correlation functions of (\mathbf{r}, t) -space:

$$S^{\text{coh}}(\mathbf{k}, \omega) = \frac{1}{2\pi} \iint G(\mathbf{r}, t) e^{i(\mathbf{k}\mathbf{r} - \omega t)} d\mathbf{r} dt, \quad (7)$$

$$S^{\text{incoh}}(\mathbf{k}, \omega) = \frac{1}{2\pi} \iint G_S(\mathbf{r}, t) e^{i(\mathbf{k}\mathbf{r} - \omega t)} d\mathbf{r} dt. \quad (8)$$

The function $G(\mathbf{r}, t)$ determines the space-time correlation of the density. The function $G_S(\mathbf{r}, t)$ describes the autocorrelation part of $G(\mathbf{r}, t)$, which gives the probability that an atom located at the origin at $t = 0$ will be located at the point \mathbf{r} at the instant of time t . It is obvious that the function $G(\mathbf{r}, t)$ is the sum of the autocorrelation function and the function $G_d(\mathbf{r}, t)$ that determines the probability of observing the atom at the point \mathbf{r} at the instant t if another atom was located at the initial instant in the origin.

The autocorrelation function $G_S(\mathbf{r}, t)$ takes into account the single-particle motion, whereas the pair correlations are described by a general space-time function. Thus, the atomic translational dynamics is described by coherent neutron scattering.

In the theory of x-ray scattering one uses the so-called static approximation^[23]. Its gist is that the energy transferred to the atoms is assumed to be small in comparison with the incident energy, and therefore \mathbf{k} is assumed to be constant over the entire range of values of ω in which energy transfer takes place.

As a result we have

$$\frac{d\sigma^{\text{coh}}}{d\Omega} = S(\mathbf{k}) N \langle b \rangle^2. \quad (9)$$

It is precisely this value which is taken into account in (1). Thus, when experimental information is used on coherent scattering of x rays of neutrons in integral form only Ziman's theory takes into account the atomic dynamics in the melt. In other words, only time-averaged atomic displacements that lead to a statistical distribution of the atoms are taken into account.

For a finely-dispersed solid at high temperatures, the coherent scattering of the neutrons can coincide surprisingly in its intensity spectrum with scattering in a liquid metal near the crystallization temperature^[24]. Analogously, there are known investigations on "thermal smearing" of crystal structures^[25], which yields for the radial distribution of the atoms curves that are very similar to those calculated from the plots of the intensity of coherent x-ray scattering by a melt. These two facts demonstrate convincingly the quasi-phonon character of the motion of the liquid atoms at high frequencies. It is likewise obvious that the particle motion in a liquid differs qualitatively from that in a crystal in the presence of atomic translations that give rise to high-frequency modes of motion.

It is natural to ask: is it necessary to take into account temporal correlations of the energy and density when considering conductivity in liquid crystals?

Baym^[26] has attempted to take into account time-dependent correlations for the calculation of the perturbations introduced by the conduction electrons into the atomic system. By drawing a definite analogy between inelastic scattering of slow neutrons and of conduction

electrons, Baym assumes that in the Born approximation the electron is scattered with a change of momentum from \mathbf{k} to \mathbf{p} and a change of energy from $E_{\mathbf{k}}$ to $E_{\mathbf{p}}$. The scattering process is accompanied by oscillations of the atomic density, determined by the momentum \mathbf{k} and by the energy $\hbar\omega$. As a result, the correlation function of the density is a Van-Hove function. Assuming furthermore that the form of the pseudopotential depends only on \mathbf{k} , Baym obtains the following expression for the relaxation time:

$$\frac{1}{\tau} = \frac{\pi}{12\pi^2 Z} \int_0^{2k_F} k^3 |U_k|^2 dk \int_0^\infty \frac{S(\mathbf{k}, \omega) \hbar\omega}{2\pi (e^{\hbar\omega/k_B T} - 1) k_B T} \frac{d\omega}{2\pi}. \quad (10)$$

This formula goes over into the scattering integral (1) if we put $\hbar\omega/k_B T [\exp(\hbar\omega/k_B T) - 1] = 1$, for then the integral with respect to ω yields the structure factor $S(\mathbf{k})$. This is a reasonable approximation, inasmuch as $\hbar\omega \ll k_B T$.

We can now formulate the problem in the following manner: How is the electron scattering affected by the natural spontaneous density fluctuations of thermal character if account is taken not only of the phonon spectrum but also of thermal translations of the atoms?

The appreciable contribution of the translational motion to the atomic dynamics is confirmed by the considerable increase of the specific heat in the course of melting: c_p is of the order of 6.2 ± 0.4 cal/deg-mole for solid metals and increases to 7–10 cal/deg-mole after melting^[27]. This is corroborated also by all the information on atomic transport phenomena.

The thermal density fluctuations due to the translational motion of the atoms determine the fluctuations of the main short-range characteristics, particularly of the coordination number. Fisher and Prokhorenko^[28] have shown, on the basis of statistical theory, that the mean-square fluctuation of the coordination number in liquid metals amounts to 0.15–0.20 of the average value already at the crystallization temperature. With further heating, the fluctuations increase significantly. The concept of a coordination number that is constant in space and in time has no meaning for a liquid. Instead, it is an expedient to introduce the concept of the probability function of the coordination numbers.

The structure of liquid metals, unlike the crystal structure, has a statistical character, and this concept must be understood both in the temporal and in the spatial sense. Accordingly, one cannot speak of identity of the "instantaneous" structure with that averaged over a large time. The very concept of the structure of a liquid is best tied in with the relaxation time of the considered process.

The question of the influence of the translational dynamics of the atom on the electric properties of the melt can be reduced to a certain sense to a relation between the period of the thermal oscillation τ_D and the "settled lifetime" τ_0 . Until recently, the predominant estimate was that of Ya. I. Frenkel¹, namely $\tau_0/\tau_D \approx 500$. Experiments on incoherent scattering of slow neutrons have shown, however^[24], that τ_0 and τ_D differ by only one order of magnitude in the case of liquid metals, even at large heat rises above the melting temperature. For example, for liquid sodium the reciprocal "settled lifetime" is $\tau_0^{-1} = 1.8 \times 10^{12} \text{ sec}^{-1}$, while the Debye frequency is $\omega_D \approx 1.8 \times 10^{13} \text{ sec}^{-1}$. It is expedient to compare the energy of the corresponding

high-frequency modes with the thermal energy $k_B T$, viz., $\hbar\omega_D = 1.8 \times 10^{-21}$ J, $\hbar\omega_0 = 18 \times 10^{-21}$ J, and $k_B T = 6.9 \times 10^{-21}$ J.

The fact that all three values are commensurate favors the need for taking the diffusion modes into consideration when relaxation processes in liquids are considered. Krasnyĭ and Kovalenko^[29] postulate that the electric conductivity should be expressed in terms of a dynamic structure factor $S(\mathbf{k}, \omega)$ that contains information on all types of collective motions in the ion-subsystem, which are connected with the change of density. They obtained for the relaxation time the expression

$$\frac{1}{\tau} = \frac{1}{4\pi\hbar^2 k_F} \frac{V}{N} \int_0^\infty |U_x|^2 x dx \int_{|x-k_F|}^{x+k_F} S\left(x, \frac{\hbar k_F^2}{2m} - \frac{\hbar k^2}{2m}\right) [x^2 - (k_F - k_1)^2] dx. \quad (11)$$

This expression goes over into Ziman's expression of $S(\mathbf{k}, \omega)$ as a δ function in ω at arbitrary \mathbf{k} , i.e., $S(\mathbf{k}, \omega) = S(\mathbf{k})\delta(\omega)$. Then the second integral is not equal to zero only at $0 \leq x \leq 2k_F$. The upper limit of the first integral can therefore be restricted to the value $2k_F$, and the limits of the second can be moved to $\pm\infty$. Finally, by making the change of variable $\hbar(k_F^2 - k_1^2)/2m \approx -\omega$, in the second integral, we arrive at the integral (1), assuming that $\int_{-\infty}^\infty S(\mathbf{k}, \omega) d\omega = S(\mathbf{k})$ in

accord with the static approximation for scattering. This is precisely the approximation used by Rice^[30,31], but Krasnyĭ and Kovalenko consider it to be too rough. They base themselves on the results of neutron-diffraction experiments^[32] according to which there exist, besides the maximum responsible for elastic scattering, also to side maxima corresponding to the presence collective modes of motion of the ion subsystem, of the acoustic-wave type, from which the electrons are scattered. So complicated a scattering picture is observed already in the hydrodynamic limiting case $\omega \rightarrow 0$, $k \rightarrow 0$. Unfortunately, the properties of the function $S(\mathbf{k}, \omega)$ remain uninvestigated, apart from this limiting case.

The inadequacy of the direct experimental information on the dynamic structure of liquids is the cause of the extensive use of model methods. Any particular model of a liquid contains more complete information than pair correlation. It is possible to extract from the model, for example, also a ternary distribution function^[6], and this offers undisputed advantages in the analysis of the properties of a melt. In addition, the analytic dependence of the model structure factor on the temperature makes it possible to avoid the errors that inevitably accompany many-temperature x-ray or neutron diffraction^[13].

A model description of the structure of a liquid metal can be proposed from two points of view: by postulating a definite short-range order, usually by "smearing" of the crystal lattice, or conversely by considering a disordered statistical disposition of the atoms. Notice should be taken of the fundamental difference between these approaches, since the former usually presupposes the existence of long-lived ordered regions, whereas the latter admits of irregularity of the structure only in the hf fluctuations of the ion density. In the former case the conditions for electron scattering differ in principle from those proposed in Ziman's theory, whereas in the latter all that is needed is additional introduction of a frequency dependence of the structure factor.

The advantage of the quasicrystalline or "cluster" approximation is justified by the singularities of the first maximum of the x-ray scattering intensity curve. These singularities appear in certain liquid metals, usually characterized by loose packing, and consist, depending on the object, in the following: asymmetry of the maximum, the presence of side maxima, and separation of the maximum in the fine structure. Since these details cannot be reproduced for fully disordered structures, partial conservation of the short-range order-structure is assumed,^[25,33] or even of several structures^[34,35], which sometimes coexist with regions where the atoms are randomly arranged^[36]. However, an essential destruction is always assumed, since the change of the first maxima on the radial-distribution curve during melting cannot be attributed only to a change in the phonon spectrum^[37].

Thus, even quasicrystalline models admit, to one degree or another, of an intense thermal motion of the atoms. It appears that the indicated models, which are based on experiment, can yield concrete information on the character of this motion near the crystallization temperature. At the present state of the art, however, they are only qualitative and are still far from an analytic description of the atomic dynamics.

New information concerning the character of the motion of the atoms in a liquid can be obtained in principle by the method of molecular dynamics^[18,38]. This method makes it possible, by performing a mathematical "experiment" on a large number of atoms with large computers, to calculate the Van-Hove space-time functions. This exclusive capability of the molecular-dynamics method makes it promising for an analytic description of atomic motion in a liquid.

Even the use of this method to calculate the motion of atoms of an idealized hard-sphere liquid with a Lennard-Jones potential has yielded quite interesting results. Figure 1 shows the trajectory of a particle in the (x, y) plane (σ is the diameter of the model sphere), and also its velocity as a function of the time. As seen from the figure, the motion of the particle describes a drift trajectory that differs greatly from Ya. I. Frenkel's simplified model—a series of oscillations as against a jump. The particle velocity varies in magnitude and direction continuously and quite smoothly. This picture can be described only by assuming participation of the chosen molecule in the collective motion of the temporal condensations of the molecules, and fluctuations of the density about a given molecule during the time of its drift along the trajectory.

Calculation of the function $G_d(\mathbf{r}, t)$ shows that the time during which the atoms change place is very short, so that the very concept of "quasicrystalline" structure is meaningless for a time $> 10^{-12}$ sec. It is concluded on this basis that the concept of the lattice structure can-

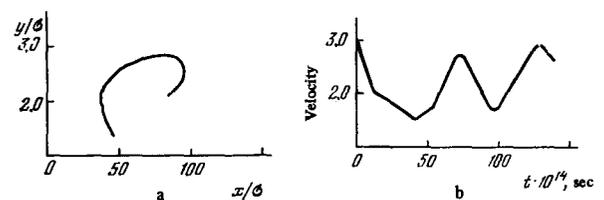


FIG. 1. Particle trajectory in the (x, y) plane (a) and time dependence of the velocity (in relative units) (b), calculated by the molecular-dynamics method.

not exist at all in the theory of liquids. To the contrary, statistical models of a liquid are quite promising. In particular, if the potential is correctly chosen, the method of molecular dynamics can yield an analytic description of the autocorrelation function of the velocity, and consequently of the function $G_S(r, t)$ which is needed to calculate the incoherent part of the scattering in accord with (6)–(8). For an idealized liquid, the frequency spectrum of the autocorrelation has already been obtained and differs noticeably from the frequency spectrum of crystals, for example in the presence of a frequency $\omega = 0$ that describe the uniformly-accelerated motion of a conglomerate of atoms as a unit.

Persistent efforts were made in recent years to find a theoretical description of the autocorrelation function of the velocity. In^[39], in particular, a numerical calculation was made of $G_S(r, t)$ on the basis of a model in which the atom is bound by harmonic forces to a certain cell, and the cell itself moves through the liquid and expressions deformations. The main parameters of this theory are the dynamic coordination number (the number of atoms influencing the motion of the considered atom) and the frequency of the harmonic oscillations. They are so chosen that the obtained autocorrelation function of the velocity differs least from the exact one obtained by the molecular-dynamics method. In^[40] is given a comparison with a computer "experiment" of an autocorrelation function obtained by numerically integrating an equation with a memory function. The latter is expressed in terms of an inter-article potential calculated in the Percus-Yevich approximation, and is approximately Gaussian up to $\tau \sim 5 \times 10^{-13}$ sec, followed by a long tail. A comparison of the autocorrelation function of the velocity with the results of the computer experiment yields good agreement at small τ .

Ashcroft^[41] has analyzed in his review the development of the theory of electric resistance of liquid metals and has shown that the main difficulties in the way of further progress in this field are due to insufficient knowledge of the density correlation functions. This pertains not only to the single-particle motion, but also to higher correlations. Definite progress was made also in this direction. For example, in^[42] there is proposed a theory that connects the isothermal derivative of the structure factor with respect to pressure with the three-particle correlation function q_3 . To investigate q_3 , use was made of experimental results on neutron scattering at different pressures. An analysis was made of the applicability of the statistical theories of Bogolyubov-Born-Green and Percus-Yevich for the interpretation of the obtained ternary distribution function.

The integral equations of the statistical theory are widely used to simulate the structure of liquids. As applied to liquid metals, the solution of the Percus-Yevich equation for the hard-sphere model is used in recent years. In spite of the obvious simplicity of the hard-sphere model, its use is justified by the following circumstances: When the distance between the ions decreases to definite values, the potential energy increases strongly, and this recalls the effect that occurs when hard spheres collide. This presupposes the applicability of a simplified inter-ion potential, which may turn out to be too crude for the description of short-range forces, but accounts sufficiently accurately for the long-range correlations. Accordingly, the model describes in a sufficiently likely manner the structure

factor at small values of the momentum—approximately in the region of the first maximum of $S(k)$. It is precisely this region which is the most interesting for the description of the scattering of electron waves in a liquid metal.

The solution of the Percus-Yevich equation for the direct correlation function yields an expression for a structure factor^[43] that is determined only by the density of the packing of the hard sphere (η). This non-ambiguity is a great advantage of this method. Unlike earlier studies, where the value of η was chosen arbitrarily to reconcile the model and experimental structure factors, in the latest studies the packing density was determined from independent experiments. One starts here from the thermodynamic relation

$$S(0) = k_B T \frac{N}{V} \beta_T = \frac{(1-\eta)^4}{(1+2\eta)^3}, \quad (12)$$

where N/V is the atomic density. Thus, the packing density of the spheres is determined by the value of the isothermal compressibility β_T .

The isothermal compressibility can be calculated from experimental information on the equation of state of the metal at high temperature and pressure. This method is unique in a definite way, since other methods, for example based on the ultrasound propagation velocity, yield only the adiabatic compressibility. The experimental P–V–T diagram of mercury was used to simulate the structure and electric properties of mercury at high temperature and pressure^[44,45], when different methods of investigating the structure are technically not realizable.

Figure 2 shows the structure factors of liquid mercury, calculated in the range $0 < k < 2k_F$ on the 2000 atm isobar of the experimental P–V–T diagram^[46] for the densities 11, 15, 10.26 and 9.71 g/cm. The corresponding packing density of the hard spheres was 0.28, 0.17, and 0.07. For comparison, the same figure shows the experimental structure factor obtained by x-ray diffraction at room temperature and atmospheric pressure^[47]. The structure-factor curves on Fig. 2 are plotted against $k/2k_F$, since the radius of the Fermi sphere k_F at decreased density turned out to depend on the Mott factor g , which is determined by the

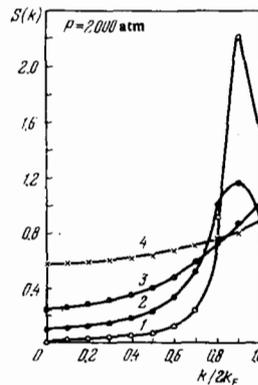


FIG. 2

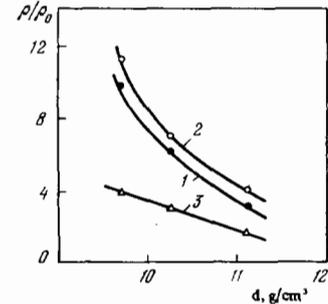


FIG. 3

FIG. 2. Structure factors of liquid mercury: 1—experimental for 13.6 g/cm³ density; 2, 3, 4—calculated for densities 11.15, 10.26, and 9.71 g/cm³.

FIG. 3. Relative change of the resistance of mercury as a function of the density: 1—experiment, 2—calculation with Heine-Animalu pseudopotential, 3—calculation with Evans pseudopotential.

ratio of the real density of the electron states to the free-electron density in the vicinity of the Fermi level. The values of the Mott factor were taken from^[49].

Figure 3 shows the relative change of the resistance of mercury as a function of its density. Besides the experimental data, the figure shows, the results of a calculation by the Ziman formula (but with variable integration limit in accordance with the decrease of the Mott factor), using the pseudopotentials of Heine-Animalu and of Evans. The latter, which gives good results for the calculation of ρ of mercury at normal density, is not suitable at decreased densities. At the same time, the Heine-Animalu pseudopotential accounts quite satisfactorily for the variation of the resistance with density.

The results of the calculations show that the use of the model structure factor and allowance for the change in the density of the electronic states makes it possible to extend the applicability of the Ziman theory to melts of much higher density (by ~30% above normal). This is a somewhat unexpected result. However, the apparent disparity can be easily resolved by the following considerations: The structure factor at zero momentum $S(0)$ is determined from a thermodynamic relation and therefore contains information on the variation of the ion interaction in the melt with changing density. Thus, the calculated values of the packing density reflect not only geometric effects due to the thermal expansion of the melt, but also contain information on the concomitant change of the ion-ion interaction. The latter circumstance is reflected by a decrease of the effective diameter of the model spheres. This effect becomes stronger when the electron-ion interaction begins to change as a result of localization of part of the conduction electrons, a fact manifest by the deviation of the factor g from unity. Guiding ourselves by Mott's known premises^[49], it can be stated that introduction of the factor g in the expression for k_F in addition to the model structure factor makes it possible to make adequate use of the theory of the electric properties of normal liquid metals for the calculation of the resistance of metals at reduced density.

Summarizing, we note that new serious progress was made in recent years in the theory of liquids. This progress is due primarily to the new experimental results of investigations of the dynamic atomic structure of liquid metals by the methods of slow neutron diffraction, interaction of ultrasound and electromagnetic radiation with the melt, and the development of model methods for the study of the structure of liquids.

¹J. M. Ziman, *Phil. Mag.* 6, 1013 (1961).

²C. C. Bradley, T. E. Faber, E. J. Wilson, and J. M. Ziman, *ibid.* 7, 865 (1962).

³J. M. Ziman, *Proc. Roy. Soc.* 318, 401 (1970).

⁴V. A. Alekseev, A. A. Andreev, and V. Ya. Prokhorenko, *Usp. Fiz. Nauk* 106, 393 (1972) [*Sov. Phys.-Uspekhi* 15, 139 (1972)].

⁵A. F. Skryshevskii, *Strukturnyi analiz zhidkostei (Structural Analysis of Liquids)* Vysshaya Shkola, 1971.

⁶D. K. Belashenko and E. Z. Spektor, *Itogi nauki i tekhniki, ser. "Teoriya metallurgicheskikh protsessov" (Progress in Science and Engineering, "Metallurgical Process Theory" series)*, Vol. 3, VINITI (1973), p. 5.

⁷A. V. Romakova, *Metallofizika (Resp. mezhved. sb.) (Metal Physics, Inter-agency Collection)*, No. 36, Kiev, Naukova dumka (1971), p. 3.

⁸H. F. Böhner and S. Steeb, *Zs. Metallkunde* 62, 27 (1971).

⁹L. S. Reut and I. Z. Fisher, *Ukr. Fiz. Zh.* 18, 1265 (1973).

¹⁰I. Z. Fisher, *Zh. Eksp. Teor. Fiz.* 59, 1336 (1970) [*Sov. Phys.-JETP* 32, 729 (1971)].

¹¹W. A. Harrison, *Solid State Theory*, McGraw, 1970.

¹²V. Heine et al. *Pseudopotential Theory (Russ. transl.)*, Mir, 1973.

¹³V. Ya. Prokhorenko, L. A. Efremenko, and I. M. Bilyi, *Visnyk L'vivsk'k-Univ., ser. fiz.* No. 7(15), 65 (1973).

¹⁴J. M. Ziman, *Physics of Metals. 1, Electrons*, Cambridge, 1969.

¹⁵N. G. March, *Zhidkie metally (Liquid Metals)*, Metallurgiya (1973).

¹⁶M. D. Johnson, P. Hutchinson, and N. H. March, *Proc. Roy. Soc. A282*, 283 (1964).

¹⁷P. Ascarelli, *Phys. Rev.* 143, 36 (1966).

¹⁸A. Paskin and A. Rahman, *Phys. Rev. Lett.* A16, 300 (1966).

¹⁹A. T. Yakovlev, *Zh. Strukturn. khim.* 12, 774 (1971).

²⁰Y. Waseda and K. Suzuki, *Phys. Stat. Sol.* b57, 351 (1973).

²¹N. Mott and E. Davis, *Electronic Processes in Non-crystalline Substances (Russ. transl)*, Mir, 1974.

²²D. R. Gustafson, A. R. Mackintosh, and D. J. Zaffrano, *Phys. Rev.* 130, 1455 (1963).

²³*Fizika prostykh zhidkostei. Eksperimental'nye issledovaniya (Physics of Simple Liquids, Experimental Research) (translations)*, Mir (1973).

²⁴*Fizika prostykh zhidkostei. Statisticheskaya teoriya (Physics of Simple Liquids. Statistical Theory) (translations)*, Mir (1971).

²⁵B. M. Grinberg and E. Z. Spektor, *Izv. AN SSSR (Metally)*, No. 4, 131 (1971).

²⁶G. Baum, *Phys. Rev.* 135, A1691 (1964).

²⁷D. R. Wilson, *Structure of Liquid Metals and Alloys (Russ. transl.)*, Metallurgiya, 1972.

²⁸I. Z. Fisher and V. K. Prokhorenko, in: *Kriticheskie yavleniya i fluktuatsii v rastvorakh (Critical Phenomena and Fluctuations in Solutions)*, AN SSSR (1960).

²⁹Yu. P. Krasnyi and N. P. Kovalenko, *Zh. Eksp. Teor. Fiz.* 62, 828 (1972) [*Sov. Phys.-JETP* 35, 438 (1972)].

³⁰M. J. Rice, *Phys. Rev. B2*, 4800 (1970).

³¹M. J. Rice, *Phys. Lett.* A37, 401 (1971).

³²V. V. Golikov and Zh. A. Kozlov, *Ukr. Fiz. Zh.* 15, 1773 (1970).

³³R. Hosemann, *Chem. Ing. Techn.* 42, 1252 (1970).

³⁴E. Z. Spektor, *Doklad. Akad. Nauk SSSR* 190, 1322 (1970) [*Sov. Phys.-Doklady* 15, 160 (1970)].

³⁵A. V. Roamnova and B. A. Mel'nik, *Ukr. Fiz. Zh.* 17, 79 (1972).

³⁶I. A. Novokhatskiĭ and V. I. Arkharov, *Fiz. Met. Metalloved.* 31, 1263 (1971).

³⁷H. Ruppertsberg, *Zs. Naturforsch.* 25a, 749 (1970).

³⁸A. M. Evseev, in: *Sovremennye problemy fizicheskoi khimii (Modern Problems of Physical Chemistry)*, Vol. 6, Moscow State Univ. (1972), p. 34.

³⁹Hqkyen Minh Hoang and L. Bonamy, *C. R. Ac. Sci. B272*, 8965 (1971).

⁴⁰S. K. Mitra, *Phys. Lett.* A38, 471 (1972).

⁴¹N. W. Ashcroft, *Techn. Rept. ISSP, B*, No. 15, 197 (1973).

⁴²P. A. Egelstaff, D. J. Page, and C. R. T. Heard, *J. Phys. C4*, 1453 (1971).

- ⁴³V. Ya. Prokhorenko, B. M. Gapchin, and G. V. Konstantinova, *Izv. AN SSSR (Metally)*, No. 1, 82 (1973).
- ⁴⁴V. A. Alekseev, V. Ya. Prokhorenko, and Yu. F. Ryzhkov, *Sbornik kratkikh sodержanii dokladov, predstavlenykh na I Vsesoyuznuyu konferentsiyu po fazovym perekhodam metall-dielektrik (Collection of Brief Summaries of Papers Delivered at First All-Union Conf. on Metal-Dielectric Phase Transitions)*, Moscow State Univ. (1972), p. 56.
- ⁴⁵V. Ya. Prokhorenko and L. A. Efremenko, *Izv. AN*

- SSSR (Metally)*, No. 5, 127 (1974).
- ⁴⁶I. K. Kikoin and A. P. Senchenkov, *Fiz. Met. Metalloved.* 24, 843 (1967).
- ⁴⁷Y. Waseda and K. Suzuki, *Phys. Stat. Sol.* 40, 183 (1970).
- ⁴⁸U. Even and J. Jortner, *Phys. Rev. Lett.* 28, 31 (1972).
- ⁴⁹N. F. Mott, *Phil. Mag.* 26, 505 (1972).

Translated by J. G. Adashko