SOVIET PHYSICS JETP VOLUME 2, NUMBER 2 MARCH, 1956

Relaxation Fluctuations in Condensed Systems

P. S. ZYRIANOV
Ural Polytechnic Institute
(Submitted to JETP editor May 21, 1954)
J. Exper.Theoret. Phys. USSR 29, 334-338 (September, 1955)

The question of the division of fluctuations into "fine-grained" (relaxational) and "coarse-grained" (vibrational) is considered. An estimate of the role of relaxation fluctuations in the electrical conductivity of metals is given.

1. INTRODUCTION

IT is impossible to describe the thermal motion in condensed systems completely by means of sound waves or photons, inasmuch as the discrete structure of the condensate is treated extremely crudely in such a description, through the introduction of the minimum wavelength λ_{min} of the acoustical vibrations; in this procedure a physical meaning is given only to those waves of length $\lambda > \lambda_{min}$. But by means of sound waves with $\lambda > \lambda_{min}$ it is impossible to describe fluctuations in the density of the number of particles taking place in regions of spatial dimensions $L < \lambda_{min}$. An analogous situation is found in wave optics: it is impossible to obtain an image of details of an object by means of light waves of lengths exceeding the linear dimensions of those details. In this way we conclude that it is possible to describe by means of acoustical waves only density fluctuations of spatial dimensions $L > \lambda_{min}$. We shall call these fluctuations "coarse-grained". It is impossible to describe fluctuations with $L < \lambda_{min}$, or "fine-grained" fluctuations, by means of sound waves.

Such a division of the fluctuations is introduced on the basis of general ideas, and it apparently has a meaning for condensed systems at sufficiently high temperatures such that it is already impossible to neglect processes of mixing of the particles of the condensate, or self-diffusion. From experiment it is known that such processes (self-diffusion) play a considerable role in liquids, as well as in solid bodies at high temperatures.

Having divided the fluctuations into "coarse-grained" and "fine-grained", one can draw several general conclusions about both the character of the behavior of these fluctuations and the role of their interactions. A "coarse-grained" fluctuation may be represented as a superposition (packet) of sound waves, and therefore it possesses a vibrational character. It is impossible to represent a "fine-grained" fluctuation in the form of a superposition of sound waves, and it possesses a relaxational character; i.e., it is dispersed by means of diffusion, like the density fluctuations of particles in an ideal gas. The interaction of these fluctuations leads to the damping of sound waves, the energy of the sound waves being dissipated in the "fine-grained" fluctuations. The situation here strongly resembles the mechanism of dissipation of the kinetic energy of a liquid in turbulent flow[1].

Ordinarily the "fine-grained" fluctuations are neglected. However, it is certainly not obvious that they always play a negligibly small role. On the contrary, as will be shown below, in several phenomena (e.g. electrical conductivity in metals at high temperatures) the "fine-grained" fluctuations play a role equal to that of the "coarse-grained" ones.

2. "FINE-GRAINED" FLUCTUATIONS

The division of fluctuations into "coarse-" and "fine-grained" undoubtedly possesses an approximate character, but this approximation allows one to carry out a synthesis of the discrete (corpuscular) and the continuous physical properties of condensed systems.

In what follows we shall consider only the "fine-grained" fluctuations. As far as the "coarse-grained" fluctuations are concerned, they are described in the ordinary way by means of acoustical vibrations. For the special case of the electron plasma of a metal, the "coarse-grained" fluctuations are described by means of the collective density oscillations[2].

As already stated above, the relaxation fluctuations are related to the mixing processes of the particles of the condensate (self-diffusion); therefore it is convenient to use the ideas of Frenkel' concerning the "hole" mechanism of self-diffusion. According to Frenkel'[3], the number N of

[1] L. D. Landau and E. M. Lifshitz, *Mechanics of Continuous Media*, GITL (1953)

[2] P. S. Zyrianov, J. Exper. Theoret. Phys. USSR 29, 193 (1955)

[3] Ia. I. Frenkel', *Introduction to the Theory of Metals*, GITTL (1948)

holes in a unit volume may be expressed by the formula

$$N = \frac{v - v_0}{v} N_0 = \frac{\Delta V}{V} N_0,$$

where v_0 is the volume occupied by one particle in the absence of holes at pressure p_0 and temperature T_0, v is the same at temperature T and pressure p, and N_0 is the average number of particles per unit volume.

At constant $p = p_0$ this formula can be written in another way, introducing the coefficient of thermal expansion $\alpha(T)$:

$$N/N_0 = (\Delta V / V)_{p=p_0} = 3 \int_{T_0}^{T} \alpha(T)\, dT. \qquad (1)$$

For our purposes it is preferable to treat the number of "holes" N as the number of particles of the condensate taking part in the relaxation fluctuations. Inasmuch as N/N_0 is not large, in calculating the fluctuations of the density of the number of particles N it is possible to neglect their interaction and use the apparatus of the theory of fluctuations in an ideal gas. Then

$$\overline{(\Delta N)^2} = \overline{(\overline{N} - N)^2} = \frac{\Delta V}{V} N_0. \qquad (2)$$

If one neglects thermal expansion, $\overline{(\Delta N)^2} = 0$.

3. INFLUENCE OF THE "FINE-GRAINED" FLUCTUATIONS ON THE ELECTRICAL RESISTIVITY OF METALS AT HIGH TEMPERATURES

The electrical resistivity of metals , which depends on the temperature, is caused by the interaction of the conduction electrons with the internal electric field of the fluctuations, which is created, in the final analysis, by the thermal motion of the ions.

In the theory of the electrical conductivity of metals one has heretofore considered only the interaction of the conduction electrons with the electric field of the sound waves(scattering of electrons by phonons) or, in other words, the interaction of the electrons with the electric field of the "coarse-grained" fluctuations. As regards the interactions of the electrons with the "fine-grained" fluctuations, these have been neglected without any justification whatever. It is possible to try to take account of the scattering of the conduction electrons on the electric field of the "fine-grained" fluctuations in the framework of the isotropic-plasma model of a metal[2].

To solve this problem we first of all compute the potential of the electric field of the "fine-grained" fluctuations. According to the result of reference 2, within the domain of the plasma model of a metal the potential of the electric field of an ion, screened by the collectively coherent electrons, has the form

$$\varphi(r) = (e_2 / r) \exp\{-q_D r\}, \qquad (3)$$

where e_2 is the charge of the ion, and q_D is the Debye wave number, equal[2] to ω_{02}/u_0(ω_{02}= the Langmuir frequency of oscillation of the ions, u_0= velocity of sound in the metal). This form of the potential also follows from simple physical ideas. In the electron plasma a charge moving with a velocity considerably smaller than the mean velocity of the chaotic electron motion, is screened by electrons over a distance of the Debye radius of polarization. In metals, the velocity of motion of the ions is considerably smaller than the mean velocity of the chaotic motion of the electrons, which are distributed according to Fermi statistics. Therefore,the Debye cloud of polarization of the ion will be practically indistinguishable from a sphere. Formula (3) also reflects this fact. The same form for the potential of the ion is used in the work of Nordheim[4], but the quantity analogous to q_D was considered as an unknown constant.

The potential Φ created by the density fluctuations of the electric charge $e_2(\delta\rho)$ is equal to

$$\Phi = e_2 \int \frac{\delta\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \exp\{-q_D |\mathbf{r} - \mathbf{r}'|\}\, d\mathbf{r}'. \qquad (4)$$

This formula can be rewritten in another form by introducing the Fourier components of the quantity $\delta\rho$ and of the potential $\varphi(r)$:

$$\Phi = \sum_q \frac{4\pi e_2}{q_D^2 + q^2} (\delta\rho)_q e^{i\mathbf{q}\mathbf{r}}. \qquad (5)$$

It is obvious that $\overline{(\delta\rho)_q^2} = \overline{(\Delta N)^2} = (\Delta V/V) N_0$, inasmuch as

$$\overline{|\int (\delta\rho)_q e^{i\mathbf{q}\mathbf{r}} d\mathbf{q}|^2} = (\Delta V / V) N_0 = \overline{(\delta\rho)^2}.$$

The scattering of the conduction electrons by the electric field of the "fine-grained" fluctuations can be evaluated by introducing the mean free path l_M. According to Seitz[5], l_M can be expressed in

[4] L. Nordheim, Ann. Phys. 9, 607 (1931)

[5] F. Seitz, *The Modern Theory of Solids*, McGraw-Hill, New York (1940), p. 526

terms of $B(\mathbf{k}, \mathbf{k}')$, the square of the matrix element of the interaction energy of the electron with the field Φ, by the formula

$$l_M^{-1} = 16\pi^3 \left(\frac{dk}{dE}\right)^2_{E=E_0} V k_0^2 \int B(\mathbf{k}, \mathbf{k}')(1-\cos\vartheta)\sin\vartheta \, d\vartheta, \quad (6)$$

where V is the volume of the metal, $E_0 = \hbar^2 k_0^2/2m$ is the upper limit of the Fermi distribution. The quantity $B(\mathbf{k}, \mathbf{k}')$ depends on $|\mathbf{k}|$ and on the angle θ between $\mathbf{k}$ and $\mathbf{k}'$, the wave vectors of the electron in the initial and final states (elastic scattering), and it is equal to

$$B(\mathbf{k}, \mathbf{k}') = |\int \Psi_k^*(r)\, e\Phi(r)\, \Psi_{k'}(r)\, d\mathbf{r}|^2.$$

Substituting into this the wave functions of the free electron $\Psi_k(r)$, normalized with respect to the volume V, we find

$$B(\mathbf{k}, \mathbf{k}') = (4\pi e_2 e)^2 N V^{-1} [q_D^2 + (\mathbf{k}-\mathbf{k}')^2]^{-2}. \quad (7)$$

Substituting this expression into Eq. (6) we obtain

$$l_M^{-1} = [4\pi m^2 e_2^2 e^2 \, (\hbar^4 k_0^4)]\, \Gamma(q_D, k_0)\, N. \quad (8)$$

Here

$$\Gamma(q_D, k_0) = q_D^2 (q_D^2 + 4k_0^2)^{-1} + \ln[1 + (4k_0^2/q_D^2)] - 1.$$

The electrical resistivity ρ_M caused by the scattering of the conduction electrons by the "fine-grained" fluctuations, is calculated by the well-known formula

$$\rho_M^{-1} = \frac{e^2 n_0}{m v(k_0)} l_M, \quad (9)$$

in which n_0 is the density of conduction electrons and $v(k_0)$ is the electron velocity at the Fermi surface. Substitution of (8) into (9) gives a formula for ρ_M:

$$\rho_M = \frac{\pi\sqrt{2m}\, e_2^2}{E_0^{3/2} n_0} \Gamma(q_D, k_0)\, N. \quad (10)$$

Noting (1) and the equality $N_0 = n_0/z$ (z is the number of conduction electrons per ion), we transform (10) into the form

$$\rho_M = \frac{\pi\sqrt{2m}\, e_2^2}{E_0^{3/2}} z \left(\frac{\Delta V}{V}\right) \Gamma(q_D, k_0). \quad (11)$$

The ordinary electrical resistivity ρ is composed of ρ_M and ρ_K, due to the scattering of the conduction electrons by the "fine-grained" and by the "coarse-grained" fluctuations respectively. The electrical resistivity ρ_K was computed in reference 2. Evaluation of ρ_M and ρ_K carried out for $T \gg \Theta_D$ (in the region in which our calculations are justified) shows that ρ_M and ρ_K are quantities of the same order of magnitude.

Let us consider the qualitative conclusions which can be drawn from equation (11).

(a) The temperature dependence of ρ_M is determined by the integral

$$\left(\frac{\Delta V}{V}\right)_{p=p_0} = 3\int_{T_0}^{T} \alpha(T)\, dT.$$

According to the Grüneisen rule[6], the ratio of the specific heat c_v to the coefficient of thermal expansion $\alpha(T)$ does not depend on the temperature. For $T \gg \Theta_D$ (Θ_D is the Debye temperature) the specific heat c_v does not depend on T; consequently α also does not depend on T, so that $\rho_M \sim T$.

(b) ρ_M is proportional to the relative change of volume and does not depend on the causes of that change – external pressure or thermal expansion. This conclusion is apparently supported by the experimental data in the case of mercury[7].

(c) Equation (11) reflects the experimental fact of the discontinuous change of electrical resistivity of metals upon melting and the proportionality of the size of the discontinuity to the volume change at the melting point. For the metals Bi, Ga, and Sb, $\Delta V/V$ is negative at the melting point; consequently the electrical resistivity at the melting point must decrease. The thermodynamical theory of Mott[8] leads to an increase of the electrical resistivity of these metals, which is found to contradict experiment.

The order of magnitude of the discontinuity in the electrical resistivity also agrees with experiment. According to the experimental data the jump in the electrical resistivity is of the order of magnitude of the electrical resistivity in the solid phase. From reference 2 it follows that ρ_K does not change significantly in melting (by

---

[6] E. Grüneisen, Ann. Phys. **26**, 211, 393 (1908).

[7] S. Shubin, J. Exper. Theoret. Phys. USSR **3**, 461 (1933)

[8] N. F. Mott, Proc. Roy. Soc. **146**, 465 (1934)

only a few percent) in comparison with ρ_M. Consequently the discontinuity is essentially caused by the change in ρ_M in melting. It is known[3] that the volume change in melting is, for instance, equal to the increase in volume upon heating the metal from absolute zero to the melting point. Thus the change in ρ_M on melting is of the order of $\Delta\rho_M \sim \rho_M \sim \rho$.

I take this opportunity to thank Prof. V. L. Ginzburg for valuable advice.

Translated by C. W. Helstrom
200