

i.e., we shall consider Eq. (28), dropping the unimportant factor  $\alpha(j|j')$ . The total expression for this average is

$$A_{jj'} = \frac{2}{v} \int_0^{2\pi} d\varphi \int_0^{2\pi} d\varphi' \langle [\delta(\varphi_j^> - \varphi) + \delta(\varphi_j^> - \varphi - \pi)] f_1(\varphi) \cdot \delta(\varphi - \varphi^<(j|j', \varphi')) f_2(\varphi') \delta(\varphi' - \varphi_j^<) \rangle_v.$$

Here  $\langle \delta(\varphi_j^>(j|j', \varphi) - \varphi) \rangle$  and  $\langle \delta(\varphi - \varphi^<(j|j', \varphi')) \rangle$  are, respectively, the probability distribution function and the transition probability referring to the interval  $(0, 2\pi)$ .

We have

$$A_{jj'} = \frac{2}{v} \int_0^{2\pi} d\varphi \int_0^{2\pi} d\varphi' \langle \delta(\varphi_j^> - \varphi) [f_1(\varphi) \delta(\varphi - \varphi^<(j|j', \varphi')) + f_1(\varphi + \pi) \delta(\varphi + \pi - \varphi^<(j|j', \varphi'))] f_2(\varphi') \delta(\varphi' - \varphi_j^<) \rangle_v \\ = \frac{2}{v} \int_0^{2\pi} d\varphi \int_0^{2\pi} d\varphi' \langle \delta(\varphi_j^> - \varphi) [f_1(\varphi) \delta(\varphi - \varphi^<(j|j', \varphi')) f_2(\varphi') \delta(\varphi' - \varphi_j^<) + f_1(\varphi + \pi) \delta(\varphi - \varphi^<(j|j', \varphi')) f_2(\varphi' + \pi) \delta(\varphi' + \pi - \varphi_j^<) ] \rangle_v.$$

As was explained above

$$\langle \delta(\varphi_j^>(j|j') - \varphi) \rangle = \langle \delta(\varphi_j^>(j|j') - \varphi - \pi) \rangle = \frac{1}{2} w^>(\varphi),$$

where  $w^>(\varphi)$  is the probability distribution (29) referring to the interval  $(0, \pi)$ . If the functions  $f_1$  and  $f_2$  are both even or odd with respect to the substitution  $\varphi - \varphi \pm \pi$  we get again Eq. (31).

When there are several energies we can perform the indicated transformations independently for each variable  $\varphi_{\xi_i}$ .

<sup>1</sup>Hence it follows that in the averaged single-particle Green functions there is no information about localization or delocalization.

<sup>2</sup>Writing it down in terms of the spectral density means that among all integrations the integration over  $E$  must be performed last. In accordance with §37 of Ref. 8 we must then drop the term with  $e^2 \bar{\rho} A/m$ .

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## Kinetic phenomena in semiquantum liquids

A. F. Andreev and Yu. A. Kosevich

*Institute of Physics Problems, USSR Academy of Sciences*

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The temperature dependence of the viscosity and of the thermal conductivity of liquids is obtained in the semiquantum region, i.e., below the Debye temperature but above the quantum degeneracy temperature. The viscosity is inversely proportional and the thermal conductivity is proportional to the temperature.

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From the point of view of the symmetry of particle arrangement, liquids do not differ from gases and are on the average homogeneous and isotropic systems that have no long-range order. In contrast to gases, however, they have a clearly pronounced short-wave order, a substantial manifestation of which is the presence of the vibrational particle motion characteristic of solids. Melting of a solid is accompanied by a relatively small change of the density and therefore affects relatively little the properties of short range order and of the vibrational motion. In liquids, however, there is a translational particle motion much more pronounced than in solids. This motion, however, which in fact is what destroys the long-range order, has nothing in common with the free translational motion of particles in gases. It is the result of individual acts of jumping from one equilibrium position, about the

particle had executed oscillatory motion, to a neighboring vacant equilibrium position. It is of course more accurate to speak of acts of the simultaneous rearrangement of the configuration of the equilibrium positions of a group of particles. Since any such rearrangement entails the surmounting of a potential barrier, the characteristic frequency  $1/\tau$  ( $\tau$  is the lifetime in the given equilibrium position) of the translational motion decreases very rapidly (exponentially) when the interaction increases. In a strong-interaction system, such as a liquid, this frequency is much lower than the characteristic frequency  $\Omega$  of the vibrational motion of the particle about the equilibrium positions.

The described picture is the basis of the theory developed by Frenkel<sup>1</sup> for kinetic phenomena in ordinary

classical liquids. The characteristic time  $\tau$  between the jumps, and with it, e.g., also the viscosity of the liquid, are governed in the classical case by thermal-activation over-the-barrier processes and therefore decrease exponentially with increasing temperature. In gases, as is well known, the viscosity increases, on the contrary, with increasing temperature.

The inequality  $\Omega\tau \gg 1$  is particularly important in the low-temperature quantum case, in which the time  $\tau$  is governed by the quantum tunneling of the particles and is independent of temperature. The presence in the liquid of two strongly differing characteristic frequencies of the motion leads to the appearance of two temperatures of quantum origin:  $\Theta \sim \hbar\Omega$  and  $T_d \sim \hbar/\tau$ , with  $\Theta \gg T_d$ . The first is the Debye temperature, which can be in fact easily determined for a given liquid by means of the usual equation for solids, by using the experimental data on the density and the speed of sound. The second characteristic temperature determines the quantum energy uncertainty connected with the delocalization of the particles of the liquid. It is at the same time the temperature of the quantum degeneracy (Fermi or Bose of the liquid. In fact, the quantity  $\hbar/\tau$  plays the role of the width of the energy band connected with the tunneling translational motion of the particle. The corresponding effective mass is  $m^* \sim \hbar\tau/a^2$ , where  $a$  is the distance between the atoms. The Fermi or Bose degeneracy temperature of a particle gas with density  $1/a^3$  and mass  $m^*$  is of the same order of magnitude as  $T_d$ .

There exist thus two different characteristic temperature regions ( $T \ll T_d$  and  $T_d \ll T \ll \Theta$ ) in which quantum effects play a substantial role, and accordingly there are two types of quantum liquids.<sup>2,3</sup> The first are ordinary strongly degenerate quantum liquids. The corresponding inequality  $T \ll T_d$  is in fact realized, as is well known, only for helium isotopes and their solutions. The number of liquids of the second type is larger. Besides the helium isotopes we have here also the hydrogen isotopes and their solutions. We shall call them (at I. M. Lifshitz's suggestion) semiquantum liquids. As shown by one of us,<sup>3</sup> semiquantum liquids are characterized by a universal temperature dependence of the thermodynamic quantities. The main contribution to their thermodynamics is made by a mechanism similar to that proposed by Anderson, Halperin, and Varma<sup>4</sup> and by Phillips<sup>5</sup> to explain the low-temperature properties of glasses. We emphasize also that the inequality  $T_d \ll \Theta$  plays an important role also in the fully quantum region  $T \ll T_d$  (see Refs. 6 and 3).

The present paper is devoted to the theory of kinetic phenomena in semiquantum liquids. We shall show below that the viscosity and thermal conductivity have a universal temperature dependence in the semiquantum region.

## 1. VISCOSITY

The presence of a relatively low characteristic frequency  $1/\tau$  leads to a substantial frequency dispersion of the viscosity coefficient  $\eta(\omega)$  of the liquid. The greatest interest attaches to the experimentally mea-

surable value of the viscosity  $\eta(0)$  at zero temperature. This quantity, however, is difficult to calculate directly from theory, since at frequencies  $\omega$  much lower than  $1/\tau$  the particle-delocalization processes play the decisive role. We calculate below the viscosity  $\eta(\omega)$  at high frequencies ( $\omega\tau \gg 1$ ). In this region the particle delocalization is insignificant and the liquid can be regarded as an amorphous solid (glass). It is quite important that in the semiquantum region the calculation regime the calculation result turns out to be capable of determining the static viscosity of the liquid accurate to within a certain numerical factor on the order of unity.

Namely, it will be shown below that at frequencies  $\omega$  satisfying the conditions  $1/\tau \ll \omega \ll T/\hbar$  the viscosity does not depend on frequency. We denote this value of the viscosity by  $\eta_\infty$ . In the general case, when  $\hbar\omega \ll T$  but generally speaking  $\omega\tau \lesssim 1$ , the frequency dependence of the viscosity takes the form

$$\eta(\omega) = \eta_\infty \varphi(\omega\tau), \quad (1)$$

where  $\varphi$  is a certain dimensionless function of the order of unity. We make here the natural assumption that there are no other characteristic frequencies much smaller than  $1/\tau$  in the liquid. The static value of the viscosity is

$$\eta_0 = \eta(0) = \eta_\infty \varphi(0),$$

i.e., it differs from  $\eta_\infty$  by a factor on the order of unity.

To determine the viscosity, we calculate the energy dissipation in the presence of a uniform shear deformation  $e = \partial u_x / \partial y$  in the system ( $u_x$  is a component of the displacement vector of the medium,  $x$  and  $y$  are Cartesian coordinates), which varies with time at a frequency  $\omega$ . Since the condition  $T \ll \Theta$  is satisfied in the semiquantum liquid, the thermal phonons are hardly excited and their contributions to all phenomena can be neglected. On the other hand, the conditions  $T \gg \hbar/\tau$  and  $\omega \gg 1/\tau$  allow us to regard the liquid particles as localized near equilibrium positions that are randomly disposed in space. The main contribution to the viscosity, just as to the thermodynamics, is made here by excitations corresponding to particle transitions to nearby vacant equilibrium positions, with small increase in energy.

We consider now some particle that has two close equilibrium the first being the ground state and the second an excited state with excitation energy  $\varepsilon$ . The change  $\delta H_{12}$  of the off-diagonal matrix element of the Hamiltonian, due to the presence of the deformation, is equal to  $V e$ , where the coefficient  $V$  is of the order of the overlap integral of the wave functions of the considered states. The energy dissipated per unit time on account of the transitions of the particle between the states is<sup>7</sup>

$$\dot{\varepsilon} = \frac{\pi\omega}{2} \text{th} \frac{\hbar\omega}{2T} |V|^2 |e|^2 \delta(\varepsilon - \hbar\omega). \quad (2)$$

Let  $\nu \varepsilon$  be the probability that a certain given liquid particle has a neighboring vacant equilibrium position with an excitation energy  $\varepsilon$  in the interval between  $\varepsilon$

and  $\varepsilon + d\varepsilon$ . At  $\varepsilon \ll \Theta$  the quantity  $\nu$  is an energy-independent constant that determines (see Ref. 3) the coefficient in the linear law of the heat capacity of semiquantum liquids. With the aid of (2) we obtain the energy dissipated per unit volume:

$$\dot{E} = \frac{\pi\omega}{2} \text{th} \frac{\hbar\omega}{2T} \langle |V|^2 \rangle |e|^2 n\nu; \quad (3)$$

here  $n$  is the number of liquid particles per unit volume, and the averaging is over the pairs of close levels of the various particles. On the other hand, in accord with the general definition of the viscosity coefficient, the same energy dissipation is equal to  $\frac{1}{2}\eta\omega^2|e|^2$ . From this we get

$$\eta(\omega) = \frac{\pi}{\omega} \text{th} \frac{\hbar\omega}{2T} \langle |V|^2 \rangle n\nu. \quad (4)$$

Going to the limit  $\hbar\omega \ll T$  and taking (1) into account, we get ultimately

$$\eta_0 \sim \eta_\infty = \frac{\pi\hbar}{2T} n\nu \langle |V|^2 \rangle. \quad (5)$$

Thus, in place of the exponential law of classical liquids, the decrease of the viscosity with increasing temperature is much slower in semiquantum liquids.

Figure 1 shows experimental data<sup>8,9</sup> on the dependence of the viscosity of hydrogen and helium on the ratio  $\Theta/T$  at constant density. The Debye temperature was calculated from the formula  $\Theta = \hbar c(6\pi^2 n)^{1/3}$  using the low-temperature experimental speed of sound  $c$ . The results are  $\Theta = 107, 46.6,$  and  $31.9$  K respectively for hydrogen of density  $0.0869$  g/cm<sup>3</sup> and helium with densities  $0.200$  and  $0.176$  g/cm<sup>3</sup>. The agreement with the inverse proportionality of the viscosity and temperature is fair, with the exception of the helium with the lower density, where the regions in which low-temperature deviations from the  $1/T$  law are observed are due to quantum degeneracy, and the high-temperature deviations are quite close to one another.

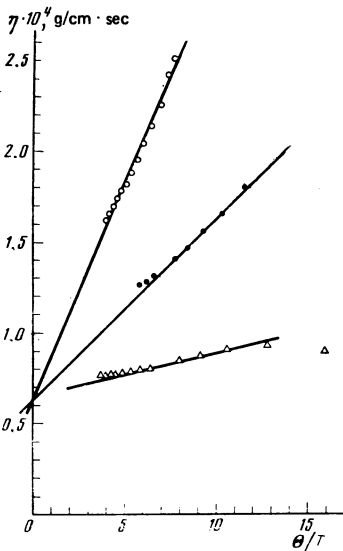


FIG. 1. Temperature dependence of the viscosity of liquid hydrogen and helium at constant density:  $\circ$ —hydrogen, density  $0.0869$  g/cm<sup>3</sup>,  $\bullet$ —He<sup>4</sup>, density  $0.200$  g/cm<sup>3</sup>,  $\Delta$ —He<sup>4</sup>, density  $0.176$  g/cm<sup>3</sup>.

We note also that the  $1/T$  law for the viscosity of liquids in the semiquantum region are in accord with the well known<sup>4</sup> linear frequency dependence of the absorption of high-frequency sound in glasses. At high-frequencies  $\hbar\omega \gg T$  the quantity  $1/T$  in the expression for the viscosity is replaced, as seen from (4) by  $1/\omega$ . The sound absorption is proportional to  $\eta\omega^2$ , i.e., it is directly proportional to the frequency.

## 2. THERMAL CONDUCTIVITY

The situation with the thermal-conductivity coefficient  $\kappa(\omega)$  regarded as a function of the frequency  $\omega$  turns out to be analogous to the case of the viscosity. Calculations in the region  $1/\tau \ll \omega \ll T/\hbar$  lead to a frequency-independent value  $\kappa_\infty$  which is connected with the static thermal-conductivity coefficient  $\kappa_0$  by an equation similar to (1). In contrast to the viscosity, however, in this case an important role is played by migration of the excitations in space, i.e., the transitions of the particles from excited states to others that are also excited. The main contribution to the thermal conductivity is therefore made by particles that have not two but three neighboring equilibrium positions with close energies. Let  $\rho(\varepsilon_1, \varepsilon_2)d\varepsilon_1 d\varepsilon_2$  be the probability that a given liquid particle has beside the ground-state position also two close excited positions with excitation energies  $\varepsilon_1$  and  $\varepsilon_2$ . At small  $\varepsilon_1$  and  $\varepsilon_2$  we can regard  $\rho$  as a constant of the order of  $\nu^2$ .

To calculate the thermal conductivity coefficient we consider the formal problem of energy dissipation when the particle is acted upon by a perturbation with a Hamiltonian in the form  $-fq$ , where  $q$  is the operator of the energy flux between the excited states with energies  $\varepsilon_1$  and  $\varepsilon_2$ , and  $f$  is a generalized force that varies  $q$  can be determined in the following manner. We write down the Hamiltonian of the system with two states 1 and 2 in the form

$$H = \varepsilon_1 a_1^\dagger a_1 + \varepsilon_2 a_2^\dagger a_2 + J(a_1^\dagger a_2 + a_2^\dagger a_1),$$

where  $a_{1,2}^\dagger$  and  $a_{1,2}$  are the creation and annihilation operators of (for the sake of argument, Fermi) particles in the excited positions 1 and 2, and  $J$  is the overlap integral of the wave functions of the considered state. The total Hamiltonian can be represented as the sum  $H = H_1 + H_2$  of the operators

$$H_1 = \varepsilon_1 a_1^\dagger a_1 + \frac{1}{2} J(a_1^\dagger a_2 + a_2^\dagger a_1),$$

$$H_2 = \varepsilon_2 a_2^\dagger a_2 + \frac{1}{2} J(a_1^\dagger a_2 + a_2^\dagger a_1),$$

which assume the role of the energy operators at the points 1 and 2, respectively. The energy flux  $q$  is defined as

$$q = \dot{H}_1 = \frac{i}{\hbar} [H, H_1]$$

$$= \frac{i}{\hbar} J \frac{\varepsilon_1 + \varepsilon_2}{2} (a_2^\dagger a_1 - a_1^\dagger a_2).$$

The matrix elements of the operator  $q$  are thus

$$q_{21} = -q_{12} = \frac{i}{\hbar} J \frac{\varepsilon_1 + \varepsilon_2}{2}.$$

The energy dissipation at  $\hbar\omega \ll T$  is defined by an

equation similar to (2):

$$\dot{\epsilon} = \frac{\pi \hbar \omega^2}{2T} |f|^2 |q_{12}|^2 w_1 \delta(\epsilon_2 - \epsilon_1 - \hbar \omega), \quad (6)$$

where

$$w_1 = e^{-\epsilon_1/T} / (1 + e^{-\epsilon_1/T} + e^{-\epsilon_2/T})$$

is the probability of finding the considered particle with two close excited equilibrium positions in the excited state 1 with the lower energy  $\epsilon_1$ .

The meaning of the generalized force  $f$  is clear from the known thermodynamic equation for the energy dissipation  $q\delta T/T$  when an energy  $q$  is transferred between bodies whose temperatures differ by  $\delta T$ , and from the general formula<sup>7</sup> for the dissipation  $-fq$  under the action of a perturbation of the considered type. We have

$$j = -i\omega f = -\frac{\delta T}{T} = -\frac{\nabla T}{T} \mathbf{a},$$

where  $\mathbf{a}$  is the space vector that joins the equilibrium positions 1 and 2, and  $\nabla T$  is the macroscopic temperature gradient and varies with time at a frequency  $\omega$ .

From (6) we get

$$\dot{\epsilon} = \frac{\pi J^2}{8\hbar T^3} |\nabla T \mathbf{a}|^2 (\epsilon_1 + \epsilon_2)^2 \frac{e^{-\epsilon_1/T}}{1 + e^{-\epsilon_1/T} + e^{-\epsilon_2/T}} \delta(\epsilon_2 - \epsilon_1 - \hbar \omega),$$

from which we find, by averaging with allowance for the inequality  $\hbar \omega \ll T$ , the energy dissipation per unit volume of the liquid:

$$\dot{E} = \frac{\pi}{6\hbar T^3} \langle J^2 a^2 \rangle |\nabla T|^2 \rho n \int_0^\infty \frac{\epsilon^2 e^{-\epsilon/T}}{1 + 2e^{-\epsilon/T}} d\epsilon = 0.87 \frac{\langle J^2 a^2 \rangle}{\hbar} \rho n |\nabla T|^2.$$

In accord with the definition of the thermal-conductivity coefficient, the dissipation is equal to  $(\kappa/2T)|\nabla T|^2$ . As a result we get

$$\kappa_0 \sim \kappa_\infty = 1.74 \frac{T}{\hbar} \rho n \langle J^2 a^2 \rangle. \quad (7)$$

The thermal conductivity coefficient of a semiquantum liquid is thus proportional to the temperature.

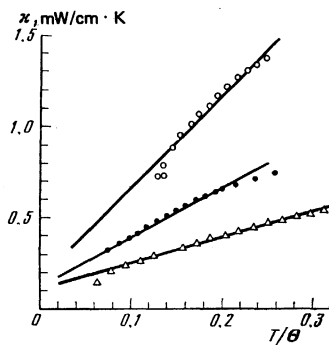


FIG. 2. Temperature dependence of the thermal conductivity of liquid hydrogen and helium at constant density:  $\circ$ —hydrogen, density 0.0769 g/cm<sup>3</sup>,  $\bullet$ —He<sup>4</sup>, density 0.200 g/cm<sup>3</sup>,  $\triangle$ —He<sup>4</sup>, density 0.176 g/cm<sup>3</sup>.

Figure 2 shows the experimental data<sup>8,9</sup> on the temperature dependence of the thermal conductivity of hydrogen and helium at constant density. The linearity of the thermal conductivity is thus quite well confirmed.

We are grateful to I. M. Lifshitz for a helpful discussion.

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