

**A. F. Andreev.** *Thermodynamics of liquids below the Debye temperature.* According to the concepts developed by Frenkel<sup>1</sup>, a high vibration frequency  $\omega$  of the atoms near certain equilibrium positions as compared to the reciprocal lifetime  $\tau$  near the particular equilibrium position is a characteristic property of liquids. In the low-temperature quantum region, in which the vibrations of the atoms are basically zero-point vibrations and the time  $\tau$  is governed by quantum tunneling, the inequality  $\omega\tau \gg 1$  means that there are in the liquid two characteristic energies of quantum nature and of different orders of magnitude: the Debye temperature  $\Theta \sim \hbar\omega$  and the energy uncertainty  $T_d \sim \hbar/\tau$ , which is related to particle delocalization, and two physically different temperature ranges corresponding to the quantum fluid<sup>2</sup>: 1)  $T \ll T_d$  and 2)  $T_d \ll T \ll \Theta$ . Since  $T_d$  is of the same order of magnitude as the quantum degeneracy temperature (Fermi or Bose), it is clear that the first inequality actually obtains only for helium isotopes—ordinary quantum fluids. The number of quantum fluids of the second type is larger (this class includes the hydrogen isotopes as well as helium).

To prevent freezing of the liquid at  $T \ll \Theta$ , it is necessary that the amplitude of the zero-point vibrations be not too small compared to the distance between particles or, which is the same thing, that the Debye temperature  $\Theta$  not be too small compared to the characteristic interaction energy  $U$  of adjacent particles in the liquid. Actually,  $U$  is only a few times  $\Theta$  in helium and hydrogen. But since  $\omega\tau \sim \exp(U/\Theta)$ , this is quite sufficient to ensure satisfaction of the condition  $\omega\tau \gg 1$  (or  $T_d \ll \Theta$ ) for validity of the Frenkel<sup>1</sup> picture of the liquid.

It is found that the thermodynamic properties of quantum fluids in the range  $T_d \ll T \ll \Theta$  can generally be established theoretically. In fact, the condition

$T \gg T_d \sim \hbar/\tau$  makes it possible to treat the atoms of the liquid as localized near equilibrium positions in calculating the thermodynamic functions. Since the liquid lacks long-range order and the equilibrium positions are distributed quite irregularly in space, the liquid then becomes glasslike. Since practically no vibrations are excited at  $T \ll \Theta$ , the main contribution to the thermodynamics comes from a mechanism analogous to that proposed by Anderson, Halperin, and Varma<sup>3</sup> and Phillips<sup>4</sup> to explain the low-temperature properties of glasses. That is to say, we are dealing with disturbances corresponding to the transition of atoms to neighboring equilibrium positions with an energy increase  $\varepsilon \sim T$ . The difference from the case of glass consists in the fact that all energy barriers are penetrable in these liquids because of the high tunneling probability, so that the excitation density is low only because the temperature is low compared to the interaction energy  $U$ . Let  $\nu d\varepsilon$  be the probability that a certain atom has a neighboring vacant equilibrium position with an excitation energy between  $\varepsilon$  and  $\varepsilon + d\varepsilon$ . At  $\varepsilon \ll U$ , the level density does not depend on energy and its order of magnitude is that of  $z/U$ , where  $z$  is a certain effective number of neighboring vacant equilibrium positions. The free energy of the liquid per atom is

$$f(T) = -T \int_0^{\infty} \nu d\varepsilon \ln(1 + e^{-\varepsilon/T}) = -\frac{\pi^2}{12} \nu T^2,$$

from which we find the entropy and heat capacity

$$s(T) = c(T) = \frac{\pi^2}{6} \nu T. \quad (1)$$

The figure shows experimental plots<sup>5-7</sup> of the entropies of liquid He<sup>3</sup>, He<sup>4</sup>, and parahydrogen per atom against the ratio  $T/\Theta$ . The Debye temperature was calculated from the usual formula for solids, into which the mea-

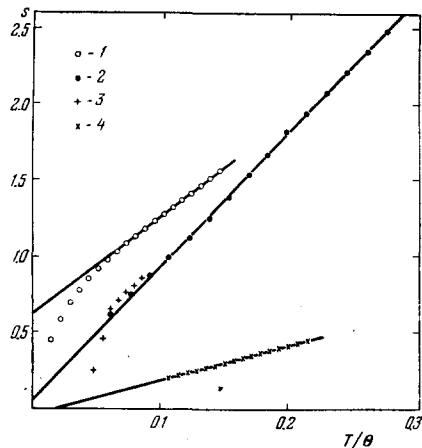


FIG. 1. Temperature dependence of entropy per atom. 1) He<sup>3</sup> at saturation vapor pressure<sup>5</sup>; 2) He<sup>4</sup> at 25 atm<sup>6</sup>; 3) He<sup>4</sup> at 25 atm<sup>5</sup>; 4) parahydrogen at 64.6 atm.<sup>7</sup>

sured sonic velocities and densities of the liquids at the pressures considered, i. e.,  $P=0$ ,  $P=25$  atm, and  $P=64.6$  atm for He<sup>3</sup>, He<sup>4</sup>, and H<sub>2</sub>, respectively, were substituted. The calculations give values of  $\Theta = 13.7$  °K,  $32.7$  °K, and  $155$  °K. In all cases, the linear law predicted by (1) is followed closely except at low temperatures for He<sup>3</sup> and He<sup>4</sup>, in which quantum degeneracy begins to appear. It is also important to note that the line drawn through the experimental points for He<sup>3</sup> extrapolates not to zero at  $T \rightarrow 0$  but, as it should, to the value  $s \approx 0.62$ , which is close to  $\ln 2$ , since the entropy of the disordered nuclear spins must be added in this case to the entropy determined from (1). Comparing the inclination angles of the lines in the figure to relation (1), we find the reciprocal level densities  $\nu^{-1}$  for He<sup>3</sup>, He<sup>4</sup>, and H<sub>2</sub>, respectively:  $3.5$  °K,  $6$  °K, and  $110$  °K, which seem quite reasonable.

The inequality  $T \ll \Theta$  is also conspicuously in evidence in the fully quantum range  $T \ll T_d$ . Analyzing the mag-

netic properties of liquid He<sup>3</sup> in the Fermi-liquid range, Castaing and Nozieres<sup>8</sup> noted that the inequality  $T_d \ll \Theta$  makes it possible to treat He<sup>3</sup> as a nearly solid-state system; this explains the relative weakness of the nuclear-spin exchange interaction and the associated anomalously large observed magnetic susceptibility. For liquid He<sup>4</sup>, the anomalously low density of the Bose-Einstein condensate is a manifestation of proximity to the solid state in the superfluid range. In addition, the experimentally observed positive velocity dispersion of phonons in He II<sup>9</sup> finds its natural explanation here. Actually, according to the general considerations advanced by Mandel'shtam and Leontovich,<sup>10</sup> any large relaxation time in a liquid (in this case  $\tau$ ) causes dispersion of sound, with the sonic velocity invariably increasing with frequency. A brief description of the study was published in Ref. 11.

<sup>1</sup>Ya. I. Frenkel', *Kineticheskaya teoriya zhidkostey* (Kinetic Theory of Liquids). USSR Academy of Sciences Press, Moscow-Leningrad, 1945.

<sup>2</sup>A. F. Andreev, *Zh. Eksp. Teor. Fiz.* **59**, 1819 (1970) [*Sov. Phys. JETP* **32**, 987 (1971)].

<sup>3</sup>P. W. Anderson, B. I. Halperin, and C. M. Varma, *Phil. Mag.*, 1972, Vol. 25, p. 1.

<sup>4</sup>W. A. Phillips, *J. Low Temp. Phys.* 1972, Vol. 7, p. 351.

<sup>5</sup>J. Wilks, *Liquid and Solid Helium* (Clarendon, Oxford, 1967).

<sup>6</sup>Thermophysical properties of Helium-4 from 2 to 1500 K with pressures to 1000 atmospheres [NBS Technical Note 631 (1972)].

<sup>7</sup>Thermophysical Properties of Parahydrogen from the Freezing Liquid Line to 5000 R for Pressures to 1000 Psia [NBS Technical Note 617 (1972)].

<sup>8</sup>B. Castaing and P. Nozieres, *J. de Phys.* (in press).

<sup>9</sup>H. J. Maris and W. E. Massey, *Phys. Rev. Lett.*, 1970, Vol. 25, p. 220.

<sup>10</sup>L. I. Mandel'shtam and M. A. Leontovich, *Zh. Eksp. Teor. Fiz.* **7**, 438 (1937).

<sup>11</sup>A. F. Andreev, *Pis'ma Zh. Eksp. Teor. Fiz.* **28**, 603 (1978) [*JETP Lett.* **28**, 556 (1978)].