

Corresponding states law for quantum liquids

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We propose a theory of non-degenerate quantum liquids which is insensitive to the kind of particle statistics and which is applied to condensed helium and hydrogen. We take explicitly into account the fact that the atomic mass and its polarizability are small. We take as the zeroth approximation a system of hard spheres while the attractive forces and the softness of the atom are taken into account as small effects. We show that for temperatures T which are larger than the degeneracy temperature, but less than the temperature at which the atoms are destroyed (ionized), the only characteristic energy scale of the liquid is the energy \bar{K}^0 of its zero point oscillations—the value of the mean kinetic energy of an atom at $T = 0$. “Quantum scaling” occurs, i.e., scale invariance of the thermodynamic and kinetic characteristics of the liquid under those changes in T and the density n which leave the reduced temperature $T^* = T/\bar{K}^0$ unchanged. Through a transformation of the scales of T and n one can determine the thermodynamic functions of other quantum liquids, using the known experimental data of He^4 . We obtain relations between the thermodynamic and kinetic characteristics of liquid He^3 and He^4 . Using the experimental data for He^4 and the isotopic law of corresponding states for quantum systems with a large value of the de Boer parameter we determine and tabulate all thermodynamic functions of liquid He^3 in those temperature and molar volume ranges where they have as yet not been measured. We propose a rough model for a quantum liquid which is based upon the assumption of a dominant contribution of diffusive excitations to the free energy of a dense condensed medium. We give a derivation of the equation of state of a quantum liquid. We find a relation between the equations of state of liquid He^3 and He^4 . We use experimental data for He^4 to determine the equation of state of hard sphere quantum liquids and compare it with similar equations obtained by computer simulations. We determine the ground state energy of spin-oriented condensed hydrogen isotopes.

1. CRITERION FOR QUANTUM NATURE OF A LIQUID

1. It was shown in Refs. 1–4, using liquid He^3 and He^4 as an example, that the quantum and exchange effects can be separated for dense condensed media at low temperatures T . For liquids, as for crystals, there exists a wide range of T which are so high that the effects of the particle statistics are still negligibly small, and so low that quantum effects are already pronounced. The aim of the present paper is to construct a quantitative theory of such quantum, but non-degenerate, liquids and apply it to condensed helium and hydrogen. Quantum liquids differ strongly in their crude properties both from slightly imperfect gases and from amorphous solids. Their uniqueness is determined by the concatenation of two factors: a small atomic mass M and a small atomic polarizability. The interaction potential $v(r)$ between helium atoms is purely peripheral, as the equilibrium between the strong close repulsive forces and the weak long-range attractive forces occurs at distances r which are much larger than the Bohr atomic diameter r_B . In other words, the effective atomic diameter r_0 for which $v(r_0) = 0$ is appreciably larger than r_B . For $r > r_B$ the rough structure of the potential $v(r)$ is given by the Buckingham formula⁵

$$v(r) = v_0 v^*(r^*), \quad v^* = \exp[\gamma(1-r^*)] - \frac{1}{r^{12}},$$

$$\gamma = \frac{r_0}{r_B} \approx 11, \quad r^* = \frac{r}{r_0}. \quad (1)$$

The thermodynamic and kinetic properties of helium are determined for $T < 10^3$ K by the ratio of r_0 and the mean intera-

tom distance a . In the whole range of densities $n = 1/a^3$ of interest for the theory, helium is a dense imperfect liquid: $a \gtrsim r_0$. On the other hand, since $a \gg r_B$ the optical properties of helium are determined by the characteristics of the isolated atom. The permittivity of helium is thus with good accuracy a linear function of its density n .

The de Boer parameter⁶ Λ^2 is a measure of the quantum nature of a medium; it is large for helium: $\Lambda^2 = h^2/Mr_0^2\varepsilon_0 \approx 10$, where ε_0 is the depth of the potential $v(r)$; $v_0 \approx \varepsilon_0 \approx 10$ K. The main idea which lies at the basis of the theory of quantum liquids consists in the choice of the zeroth approximation: $\Lambda^2 = \gamma = \infty$, where we first assume that $\gamma = \infty$ and then that $\Lambda^2 = \infty$; $\gamma^{-1} \ln \Lambda^2 = 0$. This approximation corresponds to a system of hard spheres:

$$v(r) = \infty \text{ for } r < r_0, \quad v(r) = 0 \text{ for } r > r_0. \quad (2)$$

The opposite limit, on the other hand, $\gamma = \Lambda^2 = \gamma^{-1} \ln \Lambda^2 = \infty$, corresponds to a perfect gas, as, if we put at once $\Lambda^2 = \infty$, i.e., $M = 0$ (or $\varepsilon_0 = 0$), the zero-point oscillations break up the atom. Therefore, in contrast to the traditional approaches based upon comparing a liquid with a gas or a solid, in the theory proposed here we take the specific nature of helium into account. A consistent theory of quantum liquids is based upon expanding the physical characteristics of the medium in series in the two small parameters $1/\gamma$ and $1/\Lambda^2$. Hence, the softness of the atom and its polarizability can be taken into account as small effects against the background of the zeroth, hard-sphere, approximation.

2. The approximation (2) is supplemented by a rather

general physical principle. As the main energy variables we choose not the temperature but a quantity which is measured in neutron scattering experiments—the mean kinetic energy $\bar{K}(n, T)$ of a single atom of the liquid. The energy \bar{K} is sensitive to quantum effects, as $\bar{K} = \frac{3}{2}T$, for a classical condensed medium even when we take its imperfectness into account. The parameter \bar{K} has the meaning of an effective temperature of the medium, i.e., it is its intrinsic natural characteristic. The extrinsic parameter T , on the other hand, characterizes not the liquid but the classical thermostat which is in statistical equilibrium with it. We note that without such a thermostat one cannot even define the concept of the temperature T . This choice of energy variable is justified by the simple functional dependence of the average atomic energy \bar{E} on \bar{K} :

$$\bar{E}(n^*, T) = [1 + \nu(n^*)] \bar{K}(n^*, T) + E^0(n^*). \quad (3)$$

For all condensed media there is a region where Eq. (3) can be applied. The parameters ν and E^0 depend on the reduced density $n^* = nr_0^3$, and they vanish in the limit $\gamma = \Lambda^2 = \infty$: $\nu \propto 1/\gamma$; $E^0 \propto \varepsilon_0$, so that $\bar{E} = \bar{K}$ in the hard sphere approximation (2). Expression (3) is the first approximation after the hard-sphere one in the expansion of \bar{E} in powers of $1/\gamma$ and $1/\Lambda^2$. For quasicrystalline media, (3) is the first approximation in the expansion of \bar{E} in powers of \bar{K}/ε_0 .

We show that the functions ν and E^0 are only weakly, logarithmically dependent on \bar{K} and that one can neglect this dependence when $1 < \bar{K}/\varepsilon_0 < e^{\gamma/3}$. To do this we relate the mean potential energy \bar{V} to the pair correlation functions $g(r)$

$$\bar{V}(\bar{K}, n) = \frac{n}{2} \int v(r) g(r, n, \bar{K}) d^3r, \quad \bar{E} = \bar{K} + \bar{V}. \quad (4)$$

We give a rough estimate for \bar{V} in the structureless-medium approximation, when $g = 1$ for $r > r_k$ and $g = 0$ for $r < r_k$. The turning point r_k is defined as that value of r for which the kinetic energy \bar{K} equals $v: \delta \bar{K} = v(r_k)$, where δ is a number of order unity which depends on n . This approximation corresponds to taking into account only those correlations between particles which are connected with their finite size. The calculation using the potential (1) leads to the result

$$\begin{aligned} \bar{V} = \nu(\bar{K}) \bar{K} + E^0(\bar{K}), \quad \nu(\bar{K}) &= \frac{2\pi n^* \delta}{\gamma} \left(x_k^2 + \frac{2x_k}{\gamma} + \frac{2}{\gamma^2} \right), \\ E^0(\bar{K}) &= -\frac{2\pi n^* v_0}{3x_k^3} \left(1 - \frac{3}{\gamma x_k} - \frac{6}{\gamma^2 x_k^2} - \frac{6}{\gamma^3 x_k^3} \right), \end{aligned} \quad (5)$$

where x_k is the solution of the equation

$$x_k = 1 - \frac{1}{\gamma} \ln \left(\frac{\delta \bar{K}}{v_0} + \frac{1}{x_k^6} \right). \quad (6)$$

When $1 < \bar{K}/v_0 < e^{\gamma/3}$ we get from (5) and (6), restricting ourselves to the first terms in the expansion of \bar{V} in powers of $1/\gamma$

$$\begin{aligned} \nu &= \frac{2\pi n^* \delta}{\gamma} \left(1 - \frac{2}{\gamma} \ln \frac{\delta \bar{K}}{v_0 e} \right) \approx \frac{2\pi n^* \delta}{\gamma} \left(\frac{v_0 e}{\delta \bar{K}} \right)^{2/\gamma}, \\ E^0 &= -\frac{2\pi n^* v_0}{3} \left(1 + \frac{3}{\gamma} \ln \frac{\delta \bar{K}}{v_0 e} \right) \approx -\frac{2\pi n^* v_0}{3} \left(\frac{\delta \bar{K}}{v_0 e} \right)^{3/\gamma}. \end{aligned} \quad (7)$$

We perform a similar calculation with the $m-6$ potential which is unphysical, but popular, in the theory of condensed media:

$$\begin{aligned} v = v_0 \left(\frac{1}{r^{m-6}} - \frac{1}{r^6} \right), \quad E^0 &= -\frac{2\pi n^* (m-6) v_0}{3(m-3)} \left(\frac{\delta \bar{K}}{v_0} \right)^{3/m}, \\ \nu &= \frac{2\pi n^* \delta}{m-3} \left(\frac{v_0}{\delta \bar{K}} \right)^{3/m}. \end{aligned} \quad (8)$$

Comparing (7) and (8) we verify that the potentials $m-6$ and (1) are indistinguishable in the range $1 < \bar{K}/v_0 < e^{\gamma/3}$ when $\gamma = m \gg 1$. The parameters r_0, v_0, m , and γ for the potentials $m-6$ and (1) are just in that \bar{K} range determined from a comparison between the theory and experiment in the limit of a low liquid density. The potential (1) with $\gamma \approx 11$ and the Lennard-Jones 12-6 potential⁸ therefore agree equally well with experiments for a broad class of condensed media.

Expressions (7) and (8) determine the structure of the functional $\bar{V} = \bar{V}(\bar{K})$ in the indicated \bar{K} range:

$$\begin{aligned} \bar{V} = \nu \bar{K} + E^0 - \nu_1 v_0 \ln \frac{\bar{K}}{v_0} - \nu_2 \bar{K} \ln \frac{\bar{K}}{v_0}, \\ \nu_1 \approx 1/\gamma, \quad \nu_2 \approx 1/\gamma^2. \end{aligned} \quad (9)$$

Of course, this expansion occurs also for a classical system with a low density n , when $\bar{K} = \frac{3}{2}T$ and $g = \exp(-v/T)$. When $T > v_0$ we have from (4) for the $m-6$ potential, changing the integration variable, $r = r(\varphi)$, where $\varphi = v/T$,

$$\begin{aligned} \nu &= \frac{4\pi n^*}{3m} \left(\frac{v_0}{T} \right)^{3/m} \Gamma \left(1 - \frac{3}{m} \right), \\ E^0 &= -\frac{2\pi n^* v_0 (m-3)}{3m} \left(\frac{T}{v_0} \right)^{3/m} \Gamma \left(1 + \frac{3}{m} \right). \end{aligned} \quad (10)$$

The comparison of (8) with (10) gives the value of the parameter δ in the limit of the low density n : $\delta = \frac{2}{3}$. The linear function of \bar{E} with \bar{K} and the force constant v_0 are thus a consequence of the stiffness of the atom $\gamma = m \gg 1$ and the neglect of the dependence of $g(r)$ on the attractive part of the potential $v(r)$, which is justified when $\bar{K} > v_0$. In that case the function $g(r)$ in (4) corresponds to a system of spheres of diameter r_0 that depends logarithmically on \bar{K} :

$$r_k = r_0 \left(1 - \frac{1}{\gamma} \ln \frac{\bar{K}}{v_0} \right) \approx r_0 \left(\frac{v_0}{\bar{K}} \right)^{1/\gamma}. \quad (6')$$

We emphasize that the spatial structure of the liquid, which already exists in the hard sphere approximation, is taken into account here. The n dependence of the functions ν and E^0 can be found, remaining within the framework of the quasiclassical approximation, by taking into account the next terms in the expansion of g in powers of n . In first approximation⁷

$$\begin{aligned} g=0 \quad \text{for} \quad r < r_k, \quad g=1 + \frac{4}{3} \pi n r_k^3 \left(1 - \frac{3}{4} \frac{r}{r_k} + \frac{r^3}{16r_k^3} \right) \\ \text{for} \quad r_k < r < 2r_k, \end{aligned}$$

$$\begin{aligned} g=1 \quad \text{for} \quad r > 2r_k, \quad \nu = \nu_0 (1 + a_1 n^*), \\ E^0 = E_0^0 (1 + a_2 n^*), \quad a_1 \approx a_2 \approx 1. \end{aligned}$$

Here ν_0 and E_0^0 are given by the result of the zeroth approximation (7). We give the numerical values of ν_0, E_0^0, a_1, a_2

found by comparing theory and experiment for liquid helium:

$$\nu_0 = 0.223n^*, \quad a_1 = 1.186, \quad a_2 = 1.014, \quad E_0^0 = 45.34n^*(K). \quad (11)$$

We also give the values of the equilibrium densities of liquid He³ and He⁴ for $T = 0$:

$$n_{03}^* = n_{03}r_0^3 = 0.273, \quad n_{04}^* = n_{04}r_0^3 = 0.365. \quad (12)$$

We took for the helium atom diameter the value $r_0 = 2.556$ Å. As a consequence of the smallness of the atomic masses of He³ and He⁴ the equilibrium densities n_{03}^* and n_{04}^* given here are much smaller than unity and the virial expansions are applicable for the parameters ν and E^0 , which are insensitive to quantum effects, and even for a pressure $P \approx 10^3$ bar. On the other hand, in the Frenkel' limit⁸ $\Lambda^2 \ll 1$, $\bar{K} \ll \nu_0$, so that the function $g(r)$ has a fine structure near the minimum of the potential $v(r)$ and attractive forces play a decisive role. There is also in this case a linear relation between \bar{E} and \bar{K} , but the expansion of \bar{E} is in the powers of \bar{K}/ν_0 and the parameter ν is close to unity. We can check this by considering the classical limit when $\bar{K} = \frac{3}{2}T$ and the specific heat per particle $\bar{C} = (1 + \nu)\frac{3}{2}$. For a true Frenkel' liquid which has clearly pronounced short-range order the specific heat is close to the value 3 for certain temperatures. Liquid helium does not have this feature, which is characteristic for quasicrystalline media, even at a pressure $P \approx 10^3$ bar. The maximum value of \bar{C} , measured by Dugdale and Franck,⁹ for He³ and He⁴ is equal to 1.59 which is close to the hard-sphere limit $\frac{3}{2}$. Hence, when we lower T from $T > \nu_0$ to $T < \nu_0$ there does not occur an appreciable restructuring of the helium correlation function. A strong temperature changes in $g(r)$ would at once have been observed experimentally, as the specific heat of a Frenkel' liquid drops in the region of $T \approx \nu_0$ from a value of 3 to $\frac{3}{2}$ owing to the destruction of the short-range order in the limit $T \gg \nu_0$. Comparison with experiments showed that the expansion (3) is applicable at least up to $\frac{3}{2}T \approx \bar{K} \approx 10^3$ K. However, there is no restriction on the low- T side, as the effective helium temperature \bar{K} does not fall below 10 K.

3. It is convenient for a determination of the temperature dependence of the parameter \bar{K} to choose as a characteristic energy scale its value as $T \rightarrow 0$:

$$\bar{K}(n^*, T) = \bar{K}^0 \mathcal{K}^*(n^*, T^*), \quad T^* = T/\bar{K}^0, \quad \bar{K}^0 = \bar{K}(n^*, 0^+). \quad (13)$$

The limit $T = 0^+$ means that we must first put the temperature of the degenerate liquid equal to zero and then let T go to zero. The difference between $\bar{K}(0^+)$ and the true value $\bar{K}(0)$ determines the magnitude of the exchange effects against the background of the quantum effects. The effects of the particle statistics strongly affect only the T dependence of the derivatives of \bar{E} with respect to T for $T < 3$ K. The energy \bar{E} itself, and its derivatives with respect to the density n , depend very weakly on them for any T . For helium we have the strong inequality: $\bar{K}(0) - \bar{K}(0^+) \ll \bar{K}(0)$.

According to the usual terminology in the literature, the parameter \bar{K}^0 is the energy of the zero-point oscillations of the liquid. It is important that \bar{K}^0 is a strongly increasing function of n , whereas the degeneracy temperatures T_F and T_λ of liquid He³ and He⁴ decrease with increasing n . The

criteria for quantum behavior and for degeneracy thus contradict one another: the stronger the quantum nature of a liquid, the less it is degenerate. Indeed, for a dense condensed medium the average wavelength l of an atom is less than the average interatomic distance a (the degeneracy criterion $l \approx a$ is thus not satisfied):

$$\bar{l}^2 = \hbar^2/\bar{p}^2 = \hbar^2/2M\bar{K} \ll a^2 \quad \text{for} \quad \bar{p}^2/2M = \bar{K} \gg \hbar^2/Ma^2. \quad (14)$$

We emphasize that in accordance with the general principles of quantum mechanics the value of l is determined not by the temperature T , but by the average particle energy \bar{K} , and only in the classical limit $\bar{K} = \frac{3}{2}T$ is the length l the thermal de Broglie wavelength. This is the principle difference between quantum liquids and weakly imperfect gases. The motion of the atoms is quasiclassical even when $T = 0$, as the particle momenta are large and the occupation numbers n_p small. It is this which makes it possible to take into account quantum phenomena while neglecting exchange effects.

A qualitative explanation of the independence of the gross properties of condensed media of the particle statistics can be given by comparing the particle momentum distribution functions for liquid He³ and He⁴. For He⁴ the function n_p is determined by neutron scattering experiments. It is characterized by small occupation numbers n_p for all p , apart from a narrow region $p = 0$. The condensate particle density n_0 at $p = 0$ is so small that its exact value has so far not been determined. We can therefore to first approximation put $n_0 = 0$. There is therefore no longer any trace in the function n_p of the Bose nature of the liquid. The Fermi nature of the liquid for He³ manifests itself in a jump z in the function n_p at $p = p_F$.¹⁰ It is shown in Ref. 2 that the parameter z is small for He³ and a limit on its value is given there. At saturated vapor pressure $z < 0.13$ and at the pressure at which the liquid crystallizes $z < 0.05$. One can thus, as for He⁴, put $z = 0$. The function n_p has then no longer any trace of the Fermi nature of the liquid. Hence, for studying the gross features of liquid He³ and He⁴ we can use the same methods, even at $T = 0$. Liquid helium is thus almost structureless both in coordinate and in momentum space. The lack of coordinate structure is a consequence of the destruction of the Frenkel' short-range order in the quantum limit $\Lambda^2 \gg 1$. The lack of momentum structure is a consequence of the fact that the occupation numbers n_p are small and the Pauli principle is weakened. There exists for helium a broad temperature range $T_F, T_\lambda < T < \bar{K}^0$ where quantum effects are very pronounced, but exchange effects are small. The inequality $T < \bar{K}^0$ is the general criterion for the quantum nature of a condensed medium, and is applicable both to liquids and to crystals.

4. In connection with the crisis of the traditional "gas" methods for studying helium, a new trend has recently been strongly developed—the theory of almost solid quantum liquids. The basis of this theory is the assumption that there exists a strongly pronounced short-range order in a quantum liquid, which makes it possible to regard it for a certain class of phenomena as a system of particles which approximates in its properties an amorphous solid or a glass.¹¹⁻¹⁵ The quasicrystalline, lattice, and glass models of a liquid differ only in inessential details. They are, in fact, based upon premises of the molecular-kinetic theory of a liquid, developed by Fren-

kel'.⁸ Making a very strong statement about the localized structure of a liquid, the authors of Refs. 11–15 give a comparison of the theory with those experimental data which are insensitive to the nature of this structure, i.e., the existence of short-range order in helium is itself in fact postulated. On the other hand, there is an experiment critical for quasicrystalline models, on x-ray scattering in helium,¹⁶ in which the quantity most sensitive to local structure—the liquid pair correlation function $g(r)$ —is determined. The function $g(r)$ characterizes the degree of order of the liquid in coordinate space. For helium this order is minimal—it is a most disordered, most non-Frenkel'-like condensed medium. We note that in the history of the development of a theory of classical liquids there was a period when lattice and cell models were fashionable. However, the further development of the theory of the liquid state of matter showed that the degree of order in such models was too large⁷ and untypical not only for real liquids, but also for systems which could be modelled numerically with computers—computer liquids.

2. ROUGH MODEL OF A QUANTUM LIQUID

1. To explain the basic propositions of the rough model of a structureless quantum liquid we give the relation, obtained by Egelstaff,^{17,18} between the value of the binary autocorrelation function $\langle v(0)v(t) \rangle$ at $t = 0$ and the generalized frequency distribution $\bar{g}_k(\omega)$. The quantity \bar{v}^2 is proportional to the parameter \bar{K} :

$$2\bar{K} = M\bar{v}^2 = \int_0^\infty \omega g_k(\omega) \operatorname{cth} \frac{\omega}{2T} d\omega. \quad (15)$$

This expression is a consequence of the fluctuation-dissipation theorem. The function $g_k(\omega)$ is normalized by the condition $\bar{K} = \frac{3}{2}T$ as $T \rightarrow \infty$, i.e.,

$$\int g_k(\omega) d\omega = \frac{3}{2}. \quad (16)$$

The relation connecting the mean free energy \bar{F} , the mean energy \bar{E} , and the mean entropy \bar{S} with the frequency distribution (density of states) $g(\omega) = (1 + \nu)g_k(\omega)$ is valid with the same accuracy as of the linear relation (3) between \bar{E} and \bar{K} :

$$\begin{aligned} \bar{F}(T) - \bar{F}(0^+) &= T \int g(\omega) \ln(1 - e^{-\omega/T}) d\omega - T \ln g_{F,B}, \\ \bar{E}(T) - \bar{E}(0^+) &= \int g(\omega) n_B(\omega) \omega d\omega, \end{aligned} \quad (17)$$

$$\bar{S}(T) = \int g(\omega) \{ (1+n_B) \ln(1+n_B) - n_B \ln n_B \} d\omega + \ln g_{F,B}.$$

We separated in the entropy of He^3 the spin contribution $\ln 2$: $g_F = 2$; $g_B = 1$, which presupposes that exchange effects are small. Expressions (17) follow from (3) and from the definitions of \bar{F} , \bar{E} , and \bar{S} ; they are rather general and are applicable both to liquids and to crystals. The modeling of the liquid reduces, in fact, to determining the ω -dependence of the frequency distribution g , i.e., to finding the spectrum of the fluctuations of the square of the particle velocity \bar{v}^2 . For a maximally ordered Debye, liquid $\Lambda^2 \ll 1$, $1 - \nu \ll 1$, and the main contribution to $g_k(\omega)$ comes from the collective sound excitations with a characteristics frequency ω_D :

$$g_k = 9\omega^2/2\omega_D^3 \quad \text{for } \omega < \omega_D; \quad g_k = 0 \quad \text{for } \omega > \omega_D. \quad (18)$$

For a quantal maximally disordered liquid $\Lambda^2 \gg 1$, $\nu \ll 1$, and the main contribution to $g_k(\omega)$ comes from the diffusive excitations

$$g_k = 3\omega_0/\pi(\omega^2 + \omega_0^2) \quad \text{for } \omega < \omega_\infty; \quad g_k = 0 \quad \text{for } \omega > \omega_\infty. \quad (19)$$

The introduction of the parameter ω_∞ is necessary only in order to get the integral, determining the value of \bar{K}^0 ,

$$\bar{K}^0 = \bar{K}(0^+) = \int_0^\infty \frac{\omega}{2} g_k(\omega) d\omega \approx \frac{3\omega_0}{2\pi} \ln \frac{\omega_\infty}{\omega_0} \quad (20)$$

to converge. On the other hand, the convergence of the difference $\bar{K} - \bar{K}^0$ with an accuracy of exponentially small corrections is guaranteed by the factor $n_B(\omega)$:

$$\bar{K}(T) - \bar{K}(0^+) = \int_0^\infty \omega g_k(\omega) n_B(\omega) d\omega. \quad (21)$$

The zero-point oscillation energy \bar{K}^0 is, apart from a factor due to the cutoff, the same as the characteristic diffusion frequency ω_0 . The n and T dependences of the reduced kinetic energy K^* is, in fact, a single-parameter one: $K^* = K^*(T^*)$, i.e., K^* has no strong explicit dependence on the density n . Indeed, one can obtain from (21) a reduced, exact, unrenormalized expression for K^* :

$$K^*(n^*, T^*) = 1 + \int_0^\infty \omega^* g_k^*(\omega^*) n_B(\omega^*) d\omega^*, \quad (22)$$

where the reduced parameters are defined by the relations

$$\omega^* = \frac{\omega}{\bar{K}^0}, \quad n_B(\omega^*) = \frac{1}{e^{\omega^*/T^*} - 1}, \quad g_k^*(\omega^*) = \bar{K}^0 g_k(\omega = \bar{K}^0 \omega^*). \quad (23)$$

For the diffusion model we have from (19)

$$g_k^*(\omega^*) = \frac{3\omega_0^*}{\pi(\omega^{*2} + \omega_0^{*2})}, \quad \omega_0^* = \frac{\omega_0}{\bar{K}^0} = \frac{2\pi}{3 \ln(\omega_\infty/\omega_0)}. \quad (24)$$

Hence, if g_k^* and K^* depend on n^* , the dependence is logarithmic, connected with the dependence of the parameter ω_∞/ω_0 on the density n . This statement is not connected with the parametrization in the form (19) but is general in nature. It is only important that the T dependence of \bar{K} is determined by a single (arbitrary) kind of excitations. This is not the case for a Frenkel' liquid. At low frequencies $\omega\tau < 1$, where τ is the settling life time of an atom on the disordered lattice sites, the diffusion approximation (19) is applicable. For high frequencies, however, $\omega\tau > 1$, one can regard the liquid as an amorphous solid and the Debye approximation (18) holds. We note that even for classical argon the function $g_k(\omega)$ determined by Rahman¹⁹ by computer simulation agrees better with the diffusion than with the Debye model. It is therefore natural for helium in the limit $\Lambda^2 \gg 1$ to let the settling life time of an atom τ go to zero, i.e., to forget the Frenkel' ideas about the structure of the liquid. The considerations given above thus give us reasons

for assuming that we have quantum scaling for quantum liquids, i.e., that there is scale invariance of the properties of the medium relative to those changes in the temperature T , the density n , the coupling constant ϵ_0 , and the mass M which leave the reduced quantum temperature $T^* = T/\bar{K}^0$ unchanged. In the range of T higher than the degeneracy temperatures T_F and T_λ , but lower than the destruction (ionization) temperature T^∞ of an atom, the zero-point oscillation energy \bar{K}^0 is the only characteristic energy scale of the medium since we can put $T_F, T_\lambda = 0, T^\infty = \infty$ for such T . The properties of helium are indeed universal.⁴ In experiment one measures in fact the reduced dimensionless parameters K^*, C^*, S^* , and F^* defined by the relations

$$C^* = \partial K^* / \partial T^*, \quad F^* = K^* - T^* S^*, \quad S^* = -\partial F^* / \partial T^*. \quad (25)$$

The reduced parameters are connected with the observable quantities through expressions that follow from (3):

$$\begin{aligned} \bar{F}(T^*) &= (1+\nu)\bar{K}^0 F^*(T^*) + E^0 - T \ln g_{F,B}, \\ \bar{C}(T^*) &= (1+\nu)C^*(T^*), \quad \bar{K}(T^*) = \bar{K}^0 K^*(T^*), \\ \bar{E}(T^*) &= (1+\nu)\bar{K}^0 K^*(T^*) + E^0, \\ \bar{S}(T^*) &= (1+\nu)S^*(T^*) + \ln g_{F,B}. \end{aligned} \quad (26)$$

A detailed analysis of the experimental data has made it possible on the basis of these relations to determine the way the reduced parameters K^*, C^*, S^* , and F^* depend on the reduced density n^* and temperature T^* . We have thus determined the characteristics (26) of an idealized quantum system consisting of hard spheres for which $\nu = E^0 = 0$, using the properties of a real system for which the expansion (3) of \bar{E} in powers of γ^{-1} and Λ^{-2} holds.

2. We now turn to a discussion of the diffusion model and determine the T^* dependence of K^* . We obtain first of all an interpolation formula by replacing in (22) the function n_B by its asymptotic expansion for $\omega < 2T$ and setting it equal to zero for $\omega > 2T$, where it is exponentially small:

$$n_B = \frac{T}{\omega} \left(1 - \frac{\omega}{2T} \right) \quad \text{for } \omega < 2T; \quad n_B = 0 \quad \text{for } \omega > 2T. \quad (27)$$

Evaluating the integral in (22) we find

$$K^* = 1 + \frac{3}{\pi} T^* \operatorname{arctg} \alpha T^* - \frac{3}{2\pi\alpha} \ln(1 + \alpha^2 T^{*2}), \quad (28)$$

where the parameter α is connected with the reduced diffusion frequency: $\alpha\omega_0^* = 2$. Using (28) and (25) we get expressions for the reduced specific heat C^* and entropy S^* :

$$C^*(T^*) = \frac{3}{\pi} \operatorname{arctg} \alpha T^*, \quad S^*(T^*) = \frac{3}{\pi} \int_0^{\alpha T^*} \frac{\operatorname{arctg} z}{z} dz. \quad (29)$$

The relations obtained suffice to determine the asymptotic behavior of K^*, C^* , and S^* for $T^* > 1$ and $T^* < 1$:

$$\begin{aligned} K^* &= \frac{3}{2} T^* + K_\infty^* - \tau_c \ln T^*, \quad C^* = \frac{3}{2} - \tau_c / T^* \quad \text{for } T^* > 1 \\ S^* &= \frac{3}{2} \ln T^* + S_\infty^* + \tau_c / T^* \\ K^* &= 1 + \Delta_1 T^{*2} - \Delta_2 T^{*4}, \quad C^* = 2\Delta_1 T^* - 4\Delta_2 T^{*3} \quad \text{for } T^* < 1 \\ S^* &= 2\Delta_1 T^{*3/2} - \frac{4}{3} \Delta_2 T^{*5/2}. \end{aligned} \quad (30)$$

where

$$K_\infty^* = 1 - \frac{3}{\pi} \ln \alpha \epsilon; \quad \tau_c = \frac{3}{\pi \alpha};$$

$$S_\infty^* = \frac{3}{2} \ln \alpha; \quad \Delta_1 = \frac{3\alpha}{2\pi}; \quad \Delta_2 = \frac{\alpha^3}{4\pi}.$$

The upper asymptotic ($T^* > 1$) is characteristic for all condensed media, i.e., it is not a specific feature of quantum liquids. It is only important that the potential v of (1) be an exponential function of r for small r . The attractive forces, on the other hand, can be neglected at high T . The lower asymptotic ($T^* < 1$) is characteristic for non-solid and non-superfluid media, i.e., for substances with a spectrum of low lying excitations which does not reduce to a phonon spectrum. Apart from small exchange effects the expansion of \bar{C} in powers of T starts for $T_F, T_\lambda < T < \bar{K}^0$ with a term $\propto T$ which is not forbidden by anything, as the value of the density of states g , in (17), is nonzero for $\omega = 0$. The inequality $T < \bar{K}^0$ can only be realized for condensed helium and hydrogen and the linear T dependence of \bar{C} can be discerned. At all other substances solidify at $T > \bar{K}^0$ and for them the liquid state is metastable at $T < \bar{K}^0$. As a consequence of the universality, i.e., the single-parameter dependence of the thermodynamic functions of helium on n and T , the parameters $K_\infty^*, S_\infty^*, \Delta_1, \Delta_2, \tau_c$ in (30) depend weakly on the liquid density:

$$K_\infty^* = 0.52 - 0.53, \quad S_\infty^* = 2.56, \quad \tau_c = 0.22 - 0.15, \quad (31)$$

$$\Delta_1 = 2.12, \quad \Delta_2 = 3.16.$$

We compare these empirical values with the analogous parameters obtained on the basis of the interpolation expressions (28) and (29). To do this, we fix the free parameter α by the condition $S_\infty^* = \frac{3}{2} \ln \alpha = 2.56$ from (31) and (30), i.e., $\alpha = 5.505$, and we get from (30)

$$K_\infty^* = 0.531, \quad \tau_c = 0.173, \quad \Delta_1 = 2.63, \quad \Delta_2 = 13.28. \quad (32)$$

It is interesting that the interpolation formulae (28), and (29) agree better with experiment than the exact expressions for K^*, S^* , and C^* obtained from (22) by numerical integration over ω :

$$\begin{aligned} K^* &= 1 + \frac{3}{2} T^* + \tau_c \{ \ln y - \Psi(1+y) \}, \quad y = \omega_0^* / 2\pi T^*, \\ C^* &= 3 \{ y^2 \Psi'(y) - y^{-1/2} \}, \\ S^* &= 3 \{ \ln \Gamma(y) + \frac{1}{2} \ln(y/2\pi e) - \Psi(y) y + y \}, \end{aligned} \quad (33)$$

where Γ is the gamma function, and Ψ and Ψ' are the first and second derivatives of the logarithm of that function with respect to the variable y . Determining the asymptotic expansions of (33) and comparing them with (30) we get

$$S_\infty^* = \frac{3}{2} \ln \frac{\alpha \epsilon}{2}, \quad K_\infty^* = 1 + \tau_c (\gamma_0 - \ln \pi \alpha), \quad (34)$$

$$\tau_c = 3/\pi \alpha, \quad \Delta_1 = \pi \alpha / 4, \quad \Delta_2 = \alpha^3 \pi^2 / 40, \quad \gamma_0 = 0.577.$$

We fix the value of α by the same condition $S_\infty^* = 2.56$, whence $\alpha = 4.049$, $\omega_0^* = 0.494$, and we get from (34)

$$K_\infty^* = 0.536, \quad \tau_c = 0.236, \quad \Delta_1 = 3.18, \quad \Delta_2 = 51.3. \quad (35)$$

A comparison of (31), (35), and (32) shows that the diffusion model with a single parameter ω_0^* agrees very well with experiments for high T . At low T , however, the correction

$\propto T^3$ to the linear T dependence (30) of \bar{C} differs from the empirical one by an order of magnitude, which may be connected with the fact that we have not taken into account the contribution from the long-wavelength sound excitations and have also neglected the temperature dependence (19) of the diffusion frequency ω_0^* . Because of the numerical factor 2π occurring in the definition (33) of the parameter ν , and appearing everywhere when we make the conversion $\omega \rightarrow T$, the high temperature asymptote of S^* , K^* , and C^* extends back to the region of low $T^* \approx 0.2$ almost down to the lines of the phase transitions of liquid He^4 into the superfluid and crystalline states. The low temperature limit $T \rightarrow 0$, where the diffusion approximation is no longer applicable, is thus practically inaccessible, for at low temperatures the question arises of taking exchange effects into account. The values of the parameters Δ_1 and Δ_2 in (30) are determined by separating the exchange contribution to K^* , C^* , S^* , i.e., they are obtained by an extrapolation of the functions (30) from the range $0.1 < T^* < 0.3$ to the low T region. The frequency distribution $g(\omega)$ can in principle be found using Eqs. (17) by considering them as integral equations with the functions \bar{F} , \bar{K} , and \bar{S} found experimentally. However, Lifshitz²⁰ has shown that such a problem is mathematically incorrect, as it is intrinsically unstable to small variations of the functions \bar{F} , \bar{K} , and \bar{S} . This problem is also physically incorrect, as $g(\omega)$ is T -dependent and cannot be determined without additional assumptions, apart from (17), about the properties of the liquid. One can, nevertheless, show that the combinatorial expression (17) for the entropy \bar{S} remains valid also after we take the T dependence of g into account, but in defining the specific heat \bar{C} we must differentiate not only the explicitly T dependent function n_B , but also $g(\omega, T)$. The diffusion Ansatz (19) for $g_k(\omega)$ was introduced from intuitive considerations based upon the assumption that the transition from the Debye approximation (18) to some other approximation, "orthogonal" to it, when the de Boer parameter Λ^2 increases from zero to infinity, is a continuous one. As there is a low frequency ω range where Eq. (19) holds, even when $\Lambda^2 \ll 1$, we have made the natural assumption that this other approximation can be obtained by a gradual broadening of the range of applicability of the diffusion approximation. The proposed model of a quantum liquid was considered only to illustrate the difference in principle between quantum and Frenkel' liquids and to corroborate the asymptotic expansions (30). The results below are not connected with the diffusion approximation, but are based upon the relations (26) which are a consequence of the linearity (3) of \bar{E} as a function of \bar{K} .

3. ISOTOPIC SCALING

1. To connect the properties of liquid He^3 and He^4 we need to find the way the zero-point oscillation energy \bar{K}^0 depends on the atomic mass M . This can be done on the basis of an identity which connects the mean kinetic energy \bar{K} with the derivative of the free energy per atom \bar{F} with respect to M ²¹:

$$\bar{K} = - \frac{\partial \bar{F}}{\partial M} M. \quad (36)$$

Using the M dependence of the parameter T^* , $T^* = T / \bar{K}^0(M)$, we can find from (36) and (26) an equation for $\bar{K}^0 = \bar{K}^0(M)$

$$-\bar{K}^0 = (1+\nu) \frac{\partial \bar{K}^0}{\partial M} M. \quad (37)$$

Hence \bar{K}^0 has a power law dependence on M :

$$\bar{K}^0 \propto M^{-1/(1+\nu)}. \quad (38)$$

Using (38) we can establish a connection between the zero-point oscillation energies \bar{K}_3^0 and \bar{K}_4^0 of liquid He^3 and He^4 for the same densities, $n_3 = n_4 = n$:

$$\bar{K}_4^0(n) = \lambda(n) \bar{K}_3^0(n), \quad \lambda(n) = (M_3/M_4)^{1/(1+\nu)}. \quad (39)$$

As the parameter ν is small for quantum liquids, the zero-point oscillation energy \bar{K}^0 is to a first approximation inversely proportional to the atomic mass M . This distinguishes a "good" quantum liquid from a "good" crystal for which $\bar{K}^0 \propto M^{-1/2}$. Using (26) and (39) we can obtain relations between the energies \bar{E}_3 and \bar{E}_4 , the free energies \bar{F}_3 and \bar{F}_4 , and the kinetic energies \bar{K}_3 , \bar{K}_4 per atom of liquid He^3 and He^4 for $n_3 = n_4 = n$:

$$\bar{E}_3(T) - \frac{1}{\lambda} \bar{E}_4(\lambda T) = E^0 \left(1 - \frac{1}{\lambda} \right), \quad \bar{K}_4(\lambda T) = \lambda \bar{K}_3(T), \quad (40)$$

$$\bar{F}_3(T) - \frac{1}{\lambda} \bar{F}_4(\lambda T) = E^0 \left(1 - \frac{1}{\lambda} \right) - T \ln 2.$$

Differentiating (40) with respect to T we get a relation between the specific heats \bar{C}_3 and \bar{C}_4 and the entropies \bar{S}_3 and \bar{S}_4 per atom of liquid He^3 and He^4 :

$$\bar{C}_3(T) = \bar{C}_4(\lambda T), \quad \bar{S}_3(T) - \bar{S}_4(\lambda T) = \ln 2. \quad (41)$$

Differentiating (40) with respect to n and using the dependence (39) of λ on n , we find the relation between the equations of state of liquid He^3 and He^4 , i.e., the n and T dependences of the pressures P_3 and P_4 :

$$P_3(n, T) - \frac{1}{\lambda} P_4(n, \lambda T) = P^-(n, T), \quad P \equiv \frac{\partial \bar{F}}{\partial n} n^2, \quad (42)$$

$$P^-(n, T) = \left(1 - \frac{1}{\lambda} \right) n^2 \frac{\partial E^0}{\partial n} + \ln \lambda \frac{\partial \nu}{\partial n} n^2 \bar{K}_3(n, T).$$

As the parameter ν is small, and the values of the masses M_3 and M_4 are nearly the same, the quantity P^- in (42) depends weakly on T . Using the expansions

$$\lambda \approx \lambda_0 \left(1 + \frac{\nu}{1+\nu} \ln \frac{1}{\lambda_0} \right), \quad \ln \frac{1}{\lambda_0} \approx \frac{1}{\lambda_0} - 1, \quad \lambda_0 = \frac{M_3}{M_4} \approx \frac{3}{4} \quad (43)$$

we can simplify Eq. (42):

$$P_3(n, T) - \frac{1}{\lambda_0} P_4(n, \lambda_0 T) = P_0^-(n, T), \quad (44)$$

$$P_0^-(n, T) = \left(1 - \frac{1}{\lambda_0} \right) n^2 \frac{\partial \bar{V}_3(n, T)}{\partial n}, \quad \bar{V}_3 = E^0 + \nu \bar{K}_3.$$

This equation is obtained from (42) by expanding in the small parameter $\lambda - \lambda_0$ and using the identity

$$P - \frac{\partial P}{\partial T} T = \frac{\partial \bar{E}}{\partial n} n^2. \quad (45)$$

Equations (40)–(42) are the physical content of the isotope law of corresponding states for quantum systems. It is satisfied up to exchange effects and applicable not only to liquids, but also to crystals, for which we must put $\nu = 1$ in (39). The derivation of Eqs. (40)–(42) is based only on the agreement of Eq. (26) for \bar{F} with the thermodynamic identity (36), without any modeling assumptions having been made about the properties of condensed media.

2. We can obtain another set of relations, if we bear in mind that the parameters F^* , K^* , C^* , and S^* depend weakly on n^* . It turns out to be possible to “convert” He^3 into He^4 at the same temperature $T = T_3 = T_4$, but at different densities n_3 and n_4 , such that the zero-point oscillation energies of the liquids are the same: $\bar{K}_3^0(n_3) = \bar{K}_4^0(n_4)$. In that case $T_3^* = T/\bar{K}_3^0 = T_4^* = T/\bar{K}_4^0$, and using (26) we get

$$\begin{aligned} \bar{K}_3(n_3, T) &= \bar{K}_4(n_4, T), & \bar{C}_3(n_3, T) &= \bar{C}_4(n_4, T) \kappa, \\ \bar{S}_3(n_3, T) - \bar{S}_4(n_4, T) &= \ln 2, & \kappa &= \frac{1+\nu(n_3)}{1+\nu(n_4)}. \end{aligned} \quad (46)$$

The parameter κ in (46) differs very little from unity, because ν is small and the values of n_3 and n_4 are nearly the same.

3. On the basis of the relations given above and the experimental data for He^4 we have determined and tabulated (Sec. 10) the thermodynamic functions of liquid He^3 in that range of temperatures T and molar volumes V where they have not yet been found experimentally. The data for He^3 and He^4 which already exist agree well with these relations. In the range of high densities and pressures $P \approx 10^3$ bar the relation (41) between \bar{C}_3 , \bar{C}_4 and \bar{S}_3 , \bar{S}_4 agrees with the data of Dugdale and Franck⁹ (Fig. 1). The accuracy of the data for the quantities P_3 and P_4 is as yet insufficient to determine the n and T dependences of the parameter P^- . However, we can use (44) to find with an accuracy of 1% the n and T

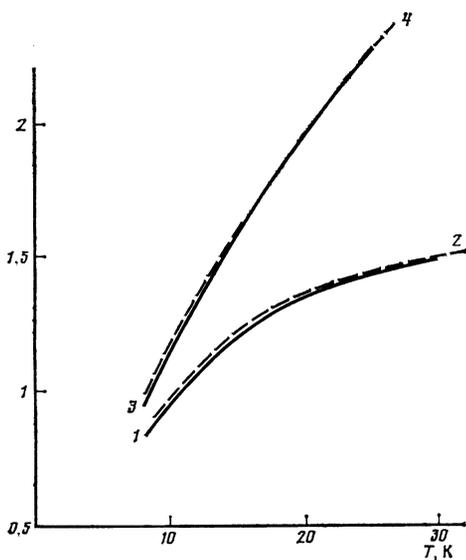


FIG. 1. Specific heat and entropy of liquid helium at constant volume $V = 16.25 \text{ cm}^3/\text{mole}$. Dugdale and Franck's data. 1—Specific heat $C_3(T)$ of He^3 , 2—specific heat $C_4(\lambda T)$ of He^4 , 3—Non-spin entropy $S_3(T) - \ln 2$ of He^3 , 4—entropy $S_4(\lambda T)$ of He^4 . The parameter λ is defined by Eq. (39).

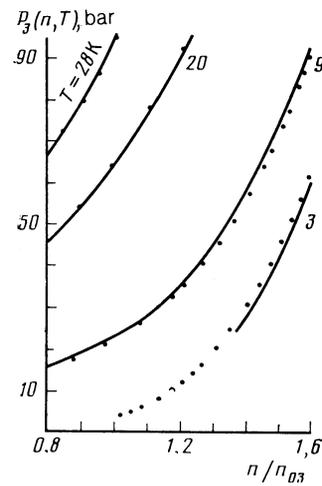


FIG. 2. The curves give the pressure $P_3(n, T)$ of He^3 as function of the liquid density n (n_{03} is the equilibrium density of He^3), determined using Eq. (47) and Hill and Lounasmaa's data²² for $P_4(n, T)$. The points are the results of measurements^{23,24} of $P_3(n, T)$.

dependences of P_3 for $T > 5$ K in the structureless-medium approximation when $\nu = 0$, $\lambda = \frac{3}{4}$, and $\bar{V}_3(n) = \bar{V}_3(n_{03})n/n_{03}$. In that case the parameter P^- is independent of T and is a quadratic function of n :

$$P_3(n, T) = \frac{4}{3} P_4\left(n, \frac{3}{4} T\right) + \frac{n^2}{n_{03}^2} \beta, \quad \beta = 11.72 \text{ bar}. \quad (47)$$

We give in Figs. 2 and 3 the function $P_3 = P_3(n, T)$ determined using (47) and Hill and Lounasmaa's data²² for $P_4(n, T)$. The points on these curves are the results of measurements of $P_3(n, T)$ by Bogoyavlenskii, Karnatsevich, and Konareva²³ and by Karnaus and Rudenko.²⁴ The difference between the measured and the calculated values of $P_3(n, T)$ for $T < 4$ K can be explained by the fact that exchange effects were neglected. However, for $8 < T < 14$ K this difference, which reaches 3%, is connected with the absence of a unique temperature scale for $T \approx 10$ K and is not the result of the assumption (47) of a structureless medium. The authors of Ref. 23 have themselves noted the systematic disagreement of data obtained in different laboratories in the world for $T \approx 10$ K. In the region $T \approx 10$ K there is in fact no good

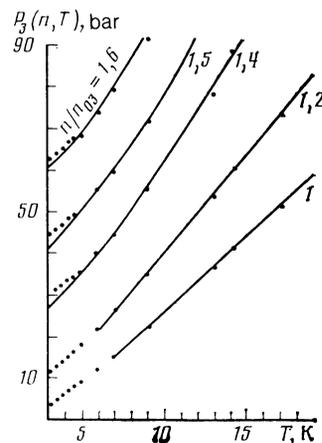


FIG. 3. The curves give the pressure $P_3(n, T)$ of He^3 as function of the temperature T , determined using (47) and data²² for $P_4(n, T)$. The points are data^{23,24} for $P_3(n, T)$.

thermometer. The pressure P and the density n are measured with a very great accuracy of $10^{-3}\%$, but the temperature T is measured with an accuracy of 1% which is low for present-day technique. Equation (47) holds also in the limit of a low liquid density where it is the relation between the virial coefficients B_3 and B_4 of liquid He^3 and He^4 :

$$B_3(T) - B_4(^3/4T) = \beta/n_0^2 T. \quad (48)$$

The values of B_3 and B_4 calculated by Kilpatrick *et al.*²⁵ on a computer agree with the parameter β in (48), which for $4 < T < 60$ K depends weakly on T :

$$\beta = 12(1 - T/T_\beta) \text{ bar}, \quad T_\beta \approx 260 \text{ K}. \quad (49)$$

The relation (39) between the zero-point oscillation energies \bar{K}_3^0 and \bar{K}_4^0 agrees with the variational computer calculations of these quantities by Manousakis, Fantoni, Pandharipande, and Usmani,^{26,27} as can be seen in Fig. 4 where we have given the values of \bar{K}_4^0 , $\lambda\bar{K}_3^0$, and $\lambda\bar{K}_{31}^0$ for polarized He^3 . The curve in that figure gives the n dependence of \bar{K}_4^0 determined below by using (3).

4. SPIN-ORIENTED HYDROGEN

Since all characteristics of the liquid depend on the dimensionless parameter $n^* = nr_0^3$ rather than on the dimensional density n , there is also coordinate scaling, i.e., a scale invariance of the properties of a medium to those changes in the size r_0 of the atom and in the density n for which the value of the reduced density n^* does not change. We give a formulation of the general law of corresponding states for quantum systems: those condensed media for which the potential v is determined by a single reduced function v^* of the reduced coordinate $r^* = r/r_0$, $v = \varepsilon_0 v^*(r^*)$, have the same reduced thermodynamic functions K^* , S^* , and C^* of the reduced density n^* and temperature T^* . On the other hand, the way the zero-point oscillation energy \bar{K}^0 depends on the force constant ε_0 is determined by matching the linear relation (3) between \bar{E} and \bar{K} to the thermodynamic identity which connects the average potential energy \bar{V} with the derivative of the free energy \bar{F} with respect to ε_0 :

$$\bar{V} = \frac{\partial \bar{F}}{\partial \varepsilon_0} \varepsilon_0, \quad \bar{V} = E^0 + \nu \bar{K}. \quad (50)$$

Since $E^0 \propto \varepsilon_0$, and ν is independent of ε_0 , we get from (50) and (26) an equation for $\bar{K}^0 = \bar{K}^0(\varepsilon_0)$:

$$\nu \bar{K}^0 = (1 + \nu) \frac{\partial \bar{K}^0}{\partial \varepsilon_0} \varepsilon_0. \quad (51)$$

The zero-point oscillation energy \bar{K}^0 has thus a power-law ε_0 dependence:

$$\bar{K}^0 \propto \varepsilon_0^{\nu/(1+\nu)}. \quad (52)$$

From (52) and (38) and a dimensionality analysis of the quantities h , r_0 , M , ε_0 , and n we find an expression for \bar{K}^0 as a function of those parameters:

$$\bar{K}^0 = f_k(n^*) \varepsilon_0^{\nu/(1+\nu)} \left(\frac{h^2}{Mr_0^2} \right)^{1/(1+\nu)} = f_k(n^*) \varepsilon_0 \Lambda^{2/(1+\nu)}, \quad (53)$$

where f_k is a dimensionless function of the reduced density

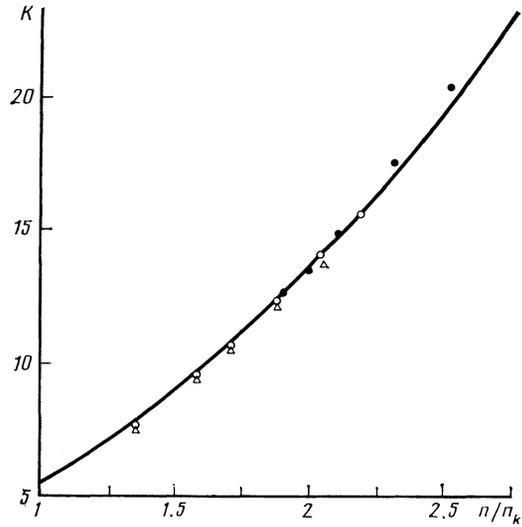


FIG. 4. The curve gives the parameter \bar{K}_4^0 of liquid He^4 as function of the density n , determined using (74) and (76); $n_k = 0.01035 \text{ \AA}^{-3}$. The points were obtained by variational calculation of the parameters of He^4 , He^3 , and polarized He^3 : ●: \bar{K}_4^0 , ○: $\lambda\bar{K}_3^0$, Δ: $\lambda\bar{K}_{31}^0$.^{26,27}

n^* , while Λ^2 is the de Boer parameter. We can thus determine the zero-point oscillation energy of other quantum liquids in terms of the value of the parameter \bar{K}_4^0 for liquid He^4 :

$$\bar{K}^0(n^*, \varepsilon_0, M, r_0) = \bar{K}_4^0 \left(\frac{\varepsilon_0}{\varepsilon_{0\text{He}}} \right)^{\nu/(1+\nu)} \left(\frac{M r_0^2 \text{He}}{M r_0^2} \right)^{1/(1+\nu)}, \quad (54)$$

where $r_{0\text{He}}$ and $\varepsilon_{0\text{He}}$ are the parameters of the interaction potential of helium atoms. As ν is small, the ε_0 dependence of \bar{K}^0 is very weak for quantum liquids.

As the parameter E^0 in (3) is proportional to ε_0 : $E^0 = \varepsilon_0 f_E$, where f_E depends only on n^* , we can determine it for all quantum liquids in terms of the value $E_3^0 = E_4^0$ for helium:

$$E^0(\varepsilon_0, n^*) = E_4^0(\varepsilon_{0\text{He}}, n^*) \frac{\varepsilon_0}{\varepsilon_{0\text{He}}}. \quad (55)$$

From (54), (55), and (3) we get an expression for the average energy \bar{E} :

$$\bar{E}(n^*, T^*)/\varepsilon_0 = \Lambda^{2/(1+\nu)} f_k(n^*) (1 + \nu) K^*(n^*, T^*) + f_E(n^*). \quad (56)$$

The dependence of \bar{E}/ε_0 on M , r_0 , h , ε_0 is thus a single-parameter one and is determined by the value of the de Boer parameter Λ^2 . It is convenient to eliminate the functions f_k and f_E from the considerations of (56) and to express \bar{E} in terms of directly observed quantities—the energies \bar{E}_3 and \bar{E}_4 of liquid He^3 and He^4 :

$$\bar{E}(n^*, T^*) \varepsilon_{0\text{He}}/\varepsilon_0 = \varphi_3 \bar{E}_3(n^*, T^*) + \varphi_4 \bar{E}_4(n^*, T^*); \quad (57)$$

the parameters φ_3 and φ_4 are defined by the expressions

$$\varphi_3 = \frac{\Lambda^{2/(1+\nu)} - \Lambda_1^{2/(1+\nu)}}{\Lambda_3^{2/(1+\nu)} - \Lambda_4^{2/(1+\nu)}}, \quad \varphi_4 = \frac{\Lambda^{2/(1+\nu)} - \Lambda_3^{2/(1+\nu)}}{\Lambda_1^{2/(1+\nu)} - \Lambda_3^{2/(1+\nu)}}. \quad (58)$$

TABLE I.

Substance	ϵ_0, K	$r_0, \text{\AA}$	Λ^2	$\varphi_3(\nu)$		$\varphi_4(\nu)$	
				$\nu=0$	$\nu=0.2$	$\nu=0$	$\nu=0.2$
H ₁	6.46	3.69	21.59	6.15	5.66	-5.15	-4.66
D ₁	6.46	3.69	10.82	1.56	1.54	-0.56	-0.54
T ₁	6.46	3.69	7.23	0.026	0.026	0.97	0.97
He ⁴	10.22	2.556	7.17	0	0	1	1
He ³	10.22	2.556	9.51	1	1	0	0

The n^* dependence of the parameter ν , determined from the classical value of the specific heat of helium $\bar{C} = (1 + \nu)^{3/2}$, was given earlier [see (11)]. As we did not use the smallness of ν in deriving Eq. (57), it also holds for quantum crystals where $\nu = 1$. For quantum liquids, the parameters φ_3 and φ_4 depend very weakly on n^* ($\nu \ll 1$).

We use the results to determine the ground-state energy behavior as $T \rightarrow 0$ for the spin-oriented condensed hydrogen isotopes H₁, D₁, and T₁. Nosanow²⁸ has written a survey the first papers on the properties of those media. It was shown in Refs. 29 and 30 that the interaction potential of the atoms of spin oriented H₁, D₁, and T₁ can be well approximated, as in the case of helium, by a Lennard-Jones 12-6 function. We give in Table I the parameters r_0 , ϵ_0 , Λ^2 for helium and hydrogen, and also the values of φ_3 and φ_4 given by (58) for $\nu = 0$ ($n^* = 0$) and $\nu = 0.2$ ($n^* = 0.55$). We show in Fig. 5 \bar{E}/ϵ_0 for helium and hydrogen as function of the reduced density n^* for $0.1 < n^* < 0.5$, determined from the experimental data for \bar{E}_3 and \bar{E}_4 , and from Eq. (57). It is clear that the light isotope H₁ has no minimum in the \bar{E} , n^* curve, whereas such minima exist for D₁ and T₁. The gaseous D₁ and T₁ therefore liquefy when the temperature is lowered, whereas H₁ can only exist in the gaseous state. As the values of the de Boer parameter for He⁴ and T₁ are nearly the same, their ground state energies in terms of reduced variables are practically the same (see Fig. 5). By transforming the scale of n and T on the basis of the experimental data

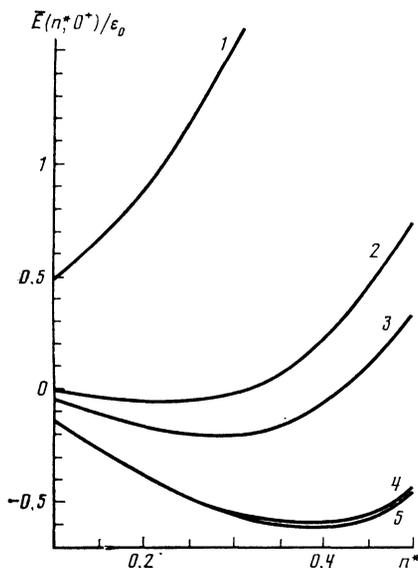


FIG. 5. The reduced ground state energy \bar{E}/ϵ_0 as a function of the reduced density n^* for helium and spin-oriented hydrogen: curve 1—H₁, 2—D₁, 3—T₁, 4—He⁴.

for helium we can thus determine the thermodynamic functions (57) of other quantum liquids.

5. CLASSICAL LIMIT

1. When we determined the values of the zero point oscillation energies \bar{K}_3^0 and \bar{K}_4^0 by comparison of the theory with experiment, we encountered a complication which is connected with the fact that helium remains liquid down to zero temperature only in a narrow range of densities n_3, n_4 . At low densities there is a liquid-vapor phase transition, and at high densities a liquid-crystal phase transition. The parameters \bar{K}_3^0, \bar{K}_4^0 in the metastability region were found by the following physical device. By a comparison with experiment we found the density functions ν, T_s, T_c which characterize the asymptotic behavior of the entropy \bar{S}_4 and of the specific heat \bar{C}_4 per atom of liquid He⁴ for $T^* > 1$:

$$\bar{S}_4 = (1+\nu) \left(\frac{3}{2} \ln \frac{T}{T_s} + \frac{T_c}{T} \right), \quad \bar{C}_4 = (1+\nu) \left(\frac{3}{2} - \frac{T_c}{T} \right). \quad (59)$$

These expressions follow from (30): $\tau_c = T_c/\bar{K}^0, S_\infty^* = \frac{3}{2} \ln(\bar{K}^0/T_s)$. As the n and T dependence of the reduced thermodynamic functions S^* and C^* is single-parametric, the density functions T_s and \bar{K}^0 differ merely by the factor $\alpha = \bar{K}^0/T_s$ which depends weakly on n . The value of α is found in that range of n where helium remains liquid as $T \rightarrow 0$ and it is possible to determine the zero-point oscillation energy $\bar{K}^0: \alpha = 5.505$. Using the high-temperature asymptotic behavior of the entropy of any condensed medium we can find by the same method its characteristic energy scale. The entropy is the most important integral characteristic of a substance which cannot be determined from purely classical ideas, as there is no energy scale when Planck's constant h is zero and one can in no way make the temperature under the logarithm sign in (59) dimensionless. The general physical principle on the basis of which we must choose this scale, i.e., the system of units, consists in determining the reduced temperature $T^* = T/T_s$ and the reduced functions S^* and C^* whose n and T dependences are single-parametric:

$$\bar{S} = (1+\nu) S^*(T/T_s) + \ln g_{F, B} = (1+\nu) S^*(T/\bar{K}^0) + \ln g_{F, B}, \quad (60)$$

$$\bar{C} = (1+\nu) C^*(T/T_s) = (1+\nu) C^*(T/\bar{K}^0).$$

There are thus two equivalent ways of finding the characteristic scale. One consists in determining the zero-point oscillation energy \bar{K}^0 from low temperature experimental data, and the other in determining the parameter T_s using high-temperature data. The energies T_s and \bar{K}^0 have the same dependence, not only on the density n , but also on the atomic

mass M and the force constant ε_0 . This statement is based upon the agreement between the asymptotic expansions for \bar{F} , \bar{K} , and \bar{V} and the thermodynamic identities (36) and (50):

$$\begin{aligned}\bar{F} &= E^0 + (1+\nu) \left(K^\infty - \frac{3}{2} T \ln \frac{T}{T_s l} - T_c \ln T l \right) - T \ln g_{F,B}, \\ \bar{V} &= E^0 + \nu (K^\infty + \frac{3}{2} T - T_c \ln T) \quad \text{for } T > \bar{K}^0, \\ \bar{K} &= K^\infty + \frac{3}{2} T - T_c \ln T.\end{aligned}\quad (61)$$

2. The density functions T_c , T_s , and ν are determined by comparing expressions (59) and (61) with the data from Hill and Lounasmaa's paper²² where values are given, not only for \bar{E} , \bar{C} , \bar{S} , and \bar{F} , but also for P , $\partial P / \partial T$, and $\partial P / \partial n$ for liquid He⁴ at $2.5 < T < 20$ K and pressures $P < 100$ bar. It turned out that these very accurate experimental data in a narrow range of n and T are sufficient to find all thermodynamic functions of liquid helium up to $T \approx 10^3$ K and $P \approx 10^4$ bar using a scale transformation of n and T . Using the thermodynamic identities

$$P = \frac{\partial \bar{E}}{\partial n} n^2 - T n^2 \frac{\partial \bar{S}}{\partial n}, \quad \frac{\partial P}{\partial T} = - \frac{\partial \bar{S}}{\partial n} n^2 \quad (62)$$

and Eqs. (59) and (61) one determines the high temperature asymptotic equations of state $P = P(n, T)$ of quantum liquids:

$$\begin{aligned}P &= c_1 T + c_2 - c_3 T \ln T - c_4 \ln T, \\ c_1 &= \frac{3}{2} n^2 \frac{\partial \nu}{\partial n} + n^2 \frac{\partial S^\infty}{\partial n}, \quad c_2 = n^2 \frac{\partial}{\partial n} (E^\infty - T_c^0), \\ c_3 &= \frac{3}{2} n^2 \frac{\partial \nu}{\partial n}, \quad c_4 = \frac{\partial T_c^0}{\partial n} n^2.\end{aligned}\quad (63)$$

To simplify the formulae we introduced in (63) the notation

$$S^\infty = (1+\nu) \frac{3}{2} \ln T_s, \quad T_c^0 = (1+\nu) T_c, \quad E^\infty = E^0 + (1+\nu) K^\infty. \quad (64)$$

The asymptotic expression (63), with the density functions c_i found for $T < 20$ K, have been compared with the high temperature data of Tsiklis *et al.*³¹ and Mills *et al.*,³² for $75 < T < 420$ K and values of P given in the tables of Sychev *et al.*³³ It was made clear that the asymptotic expression (63) is a true and not an intermediate one and that the expansion (63) has an accuracy of 1% in the whole range $7 < T < 420$ K and an accuracy of 3% for $3 < T < 7$ K. There is an "extension" of the asymptotic expression (63) into the low temperature region which we mentioned earlier. This effect occurs for all thermodynamic functions except the specific heat \bar{C} : the high-temperature ($T^* > 1$) and low-temperature ($T^* < 1$) asymptotic expressions for P , \bar{S} , \bar{E} , and \bar{K} have a broad general range of applicability which makes the analysis of the experimental data considerably easier. A notable difference between (63) and the experimental values $P(n, T)$ occurs only in the n, T region close to the liquid-vapor phase transition line where the pressure P is low. On the other hand, near the liquid-crystal phase transition line there are no strong changes in the equation of state of liquid He⁴. When the density n increases, expression (63) does not lose its region of applicability, but the comparison between it and experiment is made difficult by the strong disagreement, which reaches 5%, between data in different papers on the measurement of the n and T dependence of P for liquid He⁴

at $T \approx 10$ K. Equation (63) exceeds in accuracy all known empirical equations of state of liquid helium. For instance, in the tables of Ref. 33 an equation of state is given with about 80 adjustable parameters, which is based upon an approximation of the T dependence of P by a power-series expansion in $1/T$:

$$P = b_1 T + b_2 + b_3 / T + b_4 / T^2 + \dots \quad (65)$$

In reality, however, the expansion is in powers of $\ln T$ and $T \ln T$. Therefore the functions $T \ln T$ and $\ln T$ which increase at high T are expanded in terms of decreasing powers of $1/T$, and this has led to a complication, unnatural for helium, of the equation of state given in Ref. 33. The unique nature of helium, its difference in principle from all other liquids, is that when one lowers T from room to helium (≈ 3 K) temperature there are no significant changes in the local properties of the liquid, i.e., of buildup of short-range order. For gaseous helium also we have (63) and not (65). The density functions c_1 and c_3 in (63) are independent of the mass M , i.e., they are the same for He³ and He⁴. One can check this by matching (61) and (63) with the identity

$$n^2 \frac{\partial \bar{K}}{\partial n} = - \frac{\partial P}{\partial M} M, \quad (66)$$

which follows after differentiating Eq. (36) with respect to n . We have thus an unique possibility to distinguish experimentally the classical and quantum contributions to the equation of state of helium, by measuring in one apparatus $P_3(n, T)$ and $P_4(n, T)$, and to determine the difference functions

$$P_3(n, T) - P_4(n, T) = \Delta P_{qu}, \quad (67)$$

$$P_3(n, T) - \frac{1}{\lambda} P_4(n, \lambda T) = P^-(n, T).$$

The function ΔP_{qu} is sensitive to quantum effects as P is independent of M for a classical system. However, the function $P^-(n, T)$ of (42) is sensitive to the classical contribution to P , as in the hard-sphere quantum limit $P^- = 0$. It is, indeed, useful to perform such an experiment, as the asymptotic expansions for P , \bar{C} , \bar{S} , and \bar{E} for $T^* > 1$ are more accurate than the linear relation (3) between \bar{E} and \bar{K} which we used to obtain them, and there exists the possibility of experimentally determining the logarithmic term in the relation (9) between \bar{V} and \bar{K} . Indeed, we determine \bar{C} using (9):

$$\bar{C} = \frac{\partial \bar{E}}{\partial T} = \frac{\partial \bar{E}}{\partial \bar{K}} \frac{\partial \bar{K}}{\partial T} = \frac{\partial \bar{K}}{\partial T} \left(1 + \nu - \nu_1 \frac{v_0}{\bar{K}} \right). \quad (68)$$

In the classical limit we get from (68) and (3)

$$\bar{C} = (1+\nu) \left(\frac{3}{2} - \frac{T_c}{T} \right), \quad T_c = T_c + \nu_1 v_0. \quad (69)$$

Hence taking the term with ν_1 into account in the expansion (9) of \bar{V} leads only to replacing T_c by \tilde{T}_c in Eqs. (59), (61), and (63). The parameter ν_1 is literally small, as it is proportional to $1/\gamma$ and vanishes in the rigid-atom limit, $\gamma = \infty$, but the parameter $T_c = \tau_c \bar{K}^0$ is numerically small, as the value of τ_c determined in the diffusion approximation is small [see (35)]. The correction $\propto 1/T$ to the classical \bar{C} and \bar{S} and the term $\propto \ln T$ in the equation of state (63)

contain therefore both a quantum contribution $\propto \bar{K}^0$ and a classical one $\propto v_0$. We can separate them only by using experimental data for He³ and He⁴ which have different dependences on the atomic mass, by measuring the difference functions (67) and ΔC_{qu} and C^- defined by the equations

$$C_3(T) - C_4(T) = \Delta C_{qu}, \quad C_3(T) - C_4(\lambda T) = C^-. \quad (70)$$

In the classical limit

$$\Delta C_{qu} = (1+\nu) \left(1 - \frac{1}{\lambda}\right) \frac{\bar{K}_4^0 \tau_c}{T}, \quad C^- = (1+\nu) \left(\frac{1}{\lambda} - 1\right) \frac{v_1 v_0}{T}.$$

As we are dealing with an experimental determination of a small contribution $\sim v_1 v_0 / T$ to a term $\sim T_c / T$ which itself is a correction to the classical \bar{C}_3 and \bar{C}_4 , the required accuracy of measurements of \bar{C}_3 , \bar{C}_4 , P_3 , and P_4 is 0.1%. The measurement of these quantities with less accuracy will, in fact, not give any information, since the thermodynamic functions of He³ are determined with an accuracy of 1% using the isotopic law of corresponding states and the experimental data for He⁴.

6. NUMERICAL RESULTS

1. We now give the numerical values of the He⁴ parameters determined using the data from Refs. 22 and 34 and using the set of units for the density n chosen by Hill and Lounasmaa²²: $\rho \equiv n/n_k$, where n_k is the density of He⁴ at the critical point of the liquid-vapor phase transitions, $n_k = 0.01035 \text{ \AA}^{-3}$. This value of n_k corresponds to a molar volume $V_k = 58.18 \text{ cm}^3/\text{mole}$ and an interatomic distance $a = 4.589 \text{ \AA}$. The density $n_0^3 = 1/r_0^3 = 5.787n_k$ is too large a scale for n for helium and all prominent quantum effects occur in the range $n_k < n < n_0^3$. In Ref. 22, which we chose as our standard, the thermodynamic functions of He⁴ are determined for $\rho < 3$. For such ρ we have for the quantities ν , E^0 , and \bar{T}_c the virial expansions:

$$\begin{aligned} \nu &= 0.0385\rho(1+0.205\rho), & \bar{T}_c &= 1.17\rho(1+0.055\rho)K, \\ -E^0 &= 7.835\rho(1+0.175\rho)K, \end{aligned} \quad (71)$$

in terms of which the functions c_3 and c_4 in (63) are determined. After separating the logarithmic terms in (63) we find the functions c_1 and c_2 . We give in Fig. 6 the behavior of the parameter $P^+ = P + c_3 T \ln T + c_4 \ln T = c_1 T + c_2$, constructed using the data of Refs. 22, 32, and 33. All existing experimental data for the equation of state of He⁴ agree with a linear T dependence of P^+ . In the n, T phase diagram of He⁴ there are "blank spots" where there are no data for P . We can easily remove them by extending the linear T dependence of P^+ (see Fig. 6). Due to the strong increase of the zero-point oscillation energy, which reaches 10^2 K , one cannot in the high density region $\rho \approx 6$ ($n^* \approx 1$) find the parameters \bar{T}_c and E^0 accurately, as they determine only small corrections to the equation of state (63). However, for such n one can use (26) to obtain an equation of state (63). However, for such n one can use (26) to obtain an equation of state, common to all T , by using the single-parameter character of dependence of F^* on n and T :

$$P = p_1(n^*) \bar{K}(n^*, T^*) + p_2(n^*) - p_3(n^*) T S^*(T^*), \quad (72)$$

where the parameters p_i are defined by the equations

$$p_1 = n^2 \left[(1+\nu) \frac{\partial \ln \bar{K}^0}{\partial n} + \frac{\partial \nu}{\partial n} \right]; \quad p_2 = n^2 \frac{\partial E^0}{\partial n}; \quad p_3 = \frac{\partial \nu}{\partial n} n^2. \quad (73)$$

In the classical limit $T^* \gg 1$, Eq. (72) goes over into (63) if we take into account the asymptotic expansions (30) for K^* and S^* . For high T , (63) is a more accurate formula, as the single-parameter dependences of F^* on n and T imposes restrictions on the parameters K^∞ and T_c in (64): $K^\infty = K_\infty^* / \bar{K}^0$, $T_c = \tau_c \bar{K}^0$, where K_∞^* and τ_c are independent of n . However, when n increases, these restrictions become unimportant, as the classical correction (69) to T_c becomes small compared to the background of the large quantum contribution $\tau_c \bar{K}^0$. The less accurate expression (72) has a wider range of applicability and also holds for $T = 0$ because of the small exchange contribution to P . Taking into account the virial expansions (71) for the classical quantities ν and E^0 , and the T^* dependences of K^* and S^* , obtained in the framework of the diffusion model (33), Eq. (72) contains only one density function $p_1(n^*)$ which can be determined by comparison with experiments. If one knows this function one finds the n dependence of the derivative of the logarithm of the zero-point oscillation energy $\bar{K}^0 = \alpha T_s$. Another direct way to determine $\ln \bar{K}^0$ consists in comparing the asymptotic behavior (59) of the entropy with experiments for $\rho < 5$.^{22,9} The two different methods gave, at first glance, different results. The direct method determined very accurately the virial expansions for \bar{K}_4^0 which occurs only for low $\rho < 1.6$:

$$\bar{K}_4^0 = 3.76\rho^{0.3}(1+0.41\rho+0.097\rho^2). \quad (74)$$

The value of the first term $\propto n^{2/3}$ is fixed by the magnitude of the entropy of a classical perfect gas. The n dependence of \bar{K}_4^0 agrees for $\rho > 1.6$ well with the "mean free path" approximation which corresponds to a dimensional quantum-mechanical estimate for \bar{K}^0 :

$$\bar{K}^0 \propto h^2 / M l^2, \quad l = a - a_c, \quad (75)$$

where l is the wavelength of the atom, a the interatomic distance, and a_c a phenomenological parameter which is of the order of the size of an atom r_0 ,

$$\begin{aligned} \bar{K}_4^0 &= \varepsilon_k^\infty \frac{\eta^3}{(1-\eta^{1/4})^2}, & \eta &= \frac{a_c^3}{a^3} = \frac{n^*}{n_c} = \frac{\rho}{\rho_c}, \\ n_c &= 1.95, & \rho_c &= 11.3 \end{aligned} \quad (76)$$

$$\varepsilon_k^\infty = 8.266 \text{ K}, \quad a_c = 2.045 \text{ \AA}.$$

However, an indirect method gave for $\rho < 4$ a very good result [compare with (74)]

$$\begin{aligned} \bar{K}_4^0 &= 3.76\rho^{0.3} \exp(0.41\rho) = \varepsilon_k^0 \eta^{0.3} \exp(\xi \eta), \\ \varepsilon_k^0 &= 18.93 \text{ K}, & \xi &= 4.633. \end{aligned} \quad (77)$$

The physical (76) and empirical (77) approximations for \bar{K}_4^0 have a very wide range of n where they do not differ and

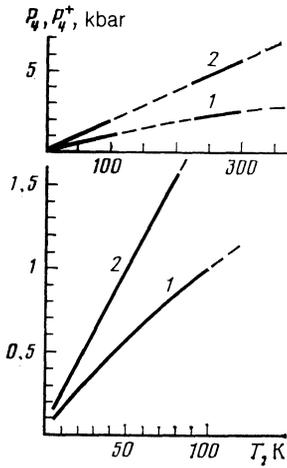


FIG. 6. The parameters $P_4(n, T)$ (curve 1) and $P_4^+(n, T)$ (curve 2) of He^4 as functions of the temperature T for a fixed value of the liquid density $n = 3n_k$ ($n_k = 0.01035 \text{ \AA}^{-3}$). The solid curves are the data of Refs. 22, 32, and 33, and the dashed curves are calculated using Eq. (63).

there exists a relation between the parameters ε_k^∞ , ε_k^0 , and $\xi: \ln(\varepsilon_k^0/\varepsilon_k^\infty) = \delta_2$, and $\xi = \delta_1$, where δ_1 and δ_2 are the coefficients in the relation

$$-2 \ln(1-\eta^{1/3}) = \delta_1 \eta + \delta_2; \quad \delta_2 = 0.829; \quad \delta_1 = 4.633. \quad (78)$$

which holds for $0.1 < \eta < 0.6$. There exists thus a range of average densities $n_k < n < n_0^0$ where the mean free path approximation (76) holds for He^4 .

2. We now consider a quantum hard-sphere system for which $\nu = E^0 = 0$ in (72):

$$P = n^2 \frac{\partial \ln \bar{K}^0}{\partial n} \bar{K}(n^*, T^*). \quad (79)$$

This equation is a consequence of the universality of quantum liquids for in deriving (72) we assumed that the n and T dependence of K^* were single-parametric. This is clearly the case if the diffusion approximation is applicable. Allowing for the model T^* dependence (33) of K^* and the empirical n dependences (76) and (77) of \bar{K}^0 , we find that Eq. (79) is the experimentally obtained equation of state of the simplest quantum liquid consisting of hard spheres. At high n and T this equation has the form

$$P = \frac{2}{3} n \frac{\bar{K}(n^* T^*)}{1-\eta^{1/3}} \approx \frac{nT}{1-\eta^{1/3}}, \quad \eta = \frac{n^*}{n_c}. \quad (80)$$

Since in the classical limit $K^* = \frac{3}{2} T^*$ and K^* is not explicitly dependent on n^* , Eq. (80) is based solely on Eq. (76) for $T^* \gg 1$. However, the single-parameter n and T dependences of K^* allow us to use the classical limit to determine the T dependence of P for all T , replacing T by $\frac{2}{3} \bar{K}$. Expression (80) differs from all known classical equations of state for a hard sphere system. We give two of them:

$$P = nT \frac{1+2\eta+3\eta^2}{(1-\eta)^2}, \quad P = nT \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}, \quad \eta = \frac{\pi n^*}{6}. \quad (81)$$

The left-hand expression was obtained by Wertheim³⁵ and

Thiele³⁶ using the exact solution of the Percus–Yevick equation. The right-hand formula, obtained empirically by Carnahan and Stirling,³⁷ reproduces the first six virial coefficients found by numerical simulation of a hard-sphere system. The value of the limiting density $n_c = 6/\pi \approx 1.91$, Eq. [(81)], is close to the value 1.95 found empirically [see (76)], but the n dependence of P is completely different. On the other hand, the n dependence (76) of \bar{K}_4^0 agrees very well with the variational calculation for $T = 0$; see Fig. 4. The resolution of the contradiction is that Eq. (81) has no quantum analog. In other words, the classical limit of the equation of state of a quantum hard-sphere system is not the same as Eqs. (81). The fact is that a classical system of spheres has no energy scale at all as its potential v is either zero or infinite. For this system there is no expansion of the free energy in powers of \hbar^2 (Ref. 21), and without solving first the quantum problem it is impossible to determine even the values of T starting from which the system reaches its classical limit. To show this we consider the limit of a low-density n and determine the virial coefficient B for a soft potential v , and in the final answer make it rigid, which is the hard-sphere limit. We start from the known expression²¹ for B taking the first quantum correction, $\propto \hbar^2$ into account:

$$B(T) = \frac{1}{2} \int (1 - e^{-v/r}) d^3r + \frac{\pi \hbar^2}{6MT} \int \left(\frac{\partial v}{\partial r} \right)^2 e^{-v/r} r^2 dr. \quad (82)$$

For the potential $v = v_0 \exp[\gamma(1 - r/r_0)]$, we get from (82) for $\gamma \gg 1$

$$B(T) = \frac{2\pi r_0^3}{3} \left(\frac{v_0}{T} \right)^{3/\gamma} \Gamma\left(1 - \frac{3}{\gamma}\right) + \frac{\pi \hbar^2 r_0 \gamma}{6MT} \left(\frac{v_0}{T} \right)^{2/\gamma} \Gamma\left(1 - \frac{2}{\gamma}\right). \quad (83)$$

In the limit of a rigid potential ($\gamma \rightarrow \infty$) we have from (83)

$$B(T) = B_{cl} \left(1 + \frac{\hbar^2 \gamma}{4M r_0^2 T} \right), \quad B_{cl} = \frac{2\pi r_0^3}{3}. \quad (84)$$

If we put at once $T = \infty$, B is the same as B_{cl} . However, if we first put $\gamma = \infty$ it is impossible to take into account the next terms in the expansion of B in powers of \hbar^2 . We must thus solve the quantum problem for $\gamma = \infty$ and only afterwards go to the classical limit. Expression (79) is the experimentally found solution of this quantum problem. A similar hard sphere anomaly occurs also in scattering theory: the high energy limit of the total cross section for scattering by a quantum sphere is twice that for a classical sphere (Massey effect).

7. GROUND-STATE ENERGY

1. We consider the quantum limit $T^* \ll 1$ and compare the true ground state energies of He^3 and He^4 at $T = 0$: $\bar{E}_3(0)$, $\bar{E}_4(0)$ with the values $\bar{E}_3(0^+)$, $\bar{E}_4(0^+)$ determined neglecting exchange effects. One can easily find the parameter $\bar{E}_4(0^+)$ for He^4 from experimental data²² for $T > T_\lambda$ and the low temperature asymptotic expression of the energy $\bar{E}_4(n, T)$ obtained in the framework of the diffusion model (30):

$$\bar{E}_i(n, T) = \bar{E}_i(n, 0^+) + \frac{\gamma_i}{2} T^2 - \frac{\beta_i}{4} T^4 + E_{\lambda_i}, \quad (85)$$

where E_λ is the small contribution from the critical fluctuations near the point of the phase transition of He^4 to the superfluid state. Similar expansions hold for $T_\lambda < T < \bar{K}_4^0$ for the entropy \bar{S}_4 and specific heat \bar{C}_4 :

$$\bar{S}_i = \gamma_i T - \beta_i T^3/3 + S_\lambda, \quad \bar{C}_i = \gamma_i T - \beta_i T^3 + C_\lambda. \quad (86)$$

In contrast to E_λ and S_λ the parameter C_λ is large near T_λ so that one must find the rough quantum characteristics $\bar{E}_4(0^+)$, γ_4 , and β_4 of the liquid from the asymptotic behavior of \bar{E} and \bar{S} for $T > T_\lambda$. Using (85) and the data of Ref. 22 we determined six values of $\bar{E}_4(n, 0^+)$; see the points in Fig. 7. On the other hand, we can find parameter $\bar{E}_4(0^+)$ from Eq. (3) as $T \rightarrow 0$:

$$\bar{E}_i(n, 0^+) = (1+\nu)\bar{K}_i^0 + E^0, \quad \bar{K}_i^0 = \alpha T_s. \quad (87)$$

We know all density functions, ν , T_s , E^0 , $\bar{E}(0^+)$ in this expression and this makes it possible to determine the value of the parameter α introduced earlier. It is important that in a broad range of densities $2 < n/n_k < 3$ where, on the one hand, we have data for \bar{E}_4 ,²² and, on the other hand, the asymptotic expansions (85) and (86) hold, the parameter α is independent of n with an accuracy of a fraction of a percent. We can therefore use (87), and expressions (71) for E^0 and (76) for \bar{K}_4^0 in the metastability region of He^4 to find the n dependence for $\bar{E}_4(n, 0^+)$ —the curve $\bar{E}_4(0^+)$ in Fig. 7. As there are no experimental data for \bar{E}_3 for $T > 2.5$ K for liquid He^3 it is impossible to determine directly the parameters $\bar{E}_3(n, 0^+)$, γ_3 and β_3 in an expansion like (85) for $\bar{E}_3(n, T)$. However, one can find the n dependence of $\bar{E}_3(n, 0^+)$ using the law of corresponding states (39)—the curve $\bar{E}_3(0^+)$ in Fig. 7:

$$\bar{E}_3(n, 0^+) = (1+\nu)\bar{K}_3^0 + E^0, \quad \bar{K}_3^0 = \frac{1}{\lambda}\bar{K}_4^0. \quad (88)$$

We have thus used the experimental data for He^4 at $T > T_\lambda$ to find the two quantities $\bar{E}_4(n, 0^+)$ and $\bar{E}_3(n, 0^+)$ as functions of n_4 and n_3 i.e., we know the ground state energies of helium when exchange effects are neglected.

2. We now turn to the determination of the dependence of the true energies \bar{E}_3, \bar{E}_4 on the liquid density for $T = 0$. To

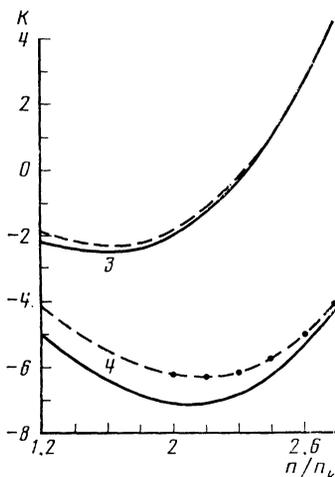


FIG. 7. The ground-state energies of helium as functions of the density n : 3—for He^3 , 4—for He^4 . The solid curves take exchange effects into account: $\bar{E}_3(0)$ and $\bar{E}_4(0)$, and the dashed curves neglect them: $\bar{E}_3(0^+)$ and $\bar{E}_4(0^+)$. The points are the values of $\bar{E}_4(0^+)$ determined using Eq. (85) and the data of Ref. 22.

do this we integrate the thermodynamic identity connecting \bar{E} , the chemical potential μ , and the sound velocity u :

$$\mu = \bar{E} + n \frac{\partial \bar{E}}{\partial n}, \quad Mu^2 = n \frac{\partial \mu}{\partial n}. \quad (89)$$

The sound velocities u_3 and u_4 for He^3 and He^4 are measured with an accuracy of 10^{-5} , which makes it possible to find five coefficients in the expansion of E near the equilibrium density n_0 in the parameter $x = n/n_0 - 1$:

$$\bar{E}(n, 0) - \bar{E}(n_0, 0) = \frac{Mu_0^2}{2}(x^2 + \lambda_3 x^3 + \lambda_4 x^4 + \lambda_5 x^5), \quad (90)$$

where n_0 is the value of the sound velocity for $n = n_0$, and $\bar{E}(n_0)$ the energy \bar{E} for $n = n_0$. The functions $\bar{E}_3(n, 0)$, $\bar{E}_4(n, 0)$ from (90) are plotted in Fig. 7. It is clear that $\bar{E}(0)$ and $\bar{E}(0^+)$ differ little, even at the equilibrium densities n_{03} and n_{04} , and that with increasing n_3 and n_4 the difference between $\bar{E}(0)$ and $\bar{E}(0^+)$ vanishes completely, i.e., the exchange contribution to \bar{E} is small even for $T = 0$. The first coefficients λ_i in (90) can thus be determined with good accuracy without turning to experiments about measuring the way the sound velocity depends on the liquid density, but imposing the obvious boundary conditions $\bar{E}(0, 0) = 0$ and $\bar{E}(2n_0, 0) = \bar{E}(2n_0, 0^+)$. In other words, instead of an expansion of \bar{E} in powers of $n/n_0 - 1$ we can construct a virial series in powers of n , requiring that when we double the equilibrium density there is no difference between $\bar{E}(0)$ and $\bar{E}(0^+)$. Or, what comes to the same, imposing boundary conditions on the expansion (90) at $x = -1$ and $x = 1$:

$$\bar{E}(0, 0) = 0 = \bar{E}(n_0, 0) + \frac{Mu_0^2}{2}(1 - \lambda_3 + \lambda_4 - \lambda_5), \quad (91)$$

$$\bar{E}(2n_0, 0^+) = \bar{E}(n_0, 0) + \frac{Mu_0^2}{2}(1 + \lambda_3 + \lambda_4 + \lambda_5).$$

As in reality the expansion of \bar{E} is in powers of $n^* = nr_0^3$ while the equilibrium densities n_{03} and n_{04} are much less than $1/r_0^3$ [see (12)], the virial series for \bar{E} converges rapidly. We can check this by substituting in (91) the numerical values of the parameters $\bar{E}(n_0)$, u_0 , $\bar{E}(2n_0)$, and M :

$$\text{He}^4: 0.478 = \lambda_3 - \lambda_4 + \lambda_5, \quad 0.535 = \lambda_3 + \lambda_4 + \lambda_5; \quad (92)$$

$$\text{He}^3: 0.585 = \lambda_3 - \lambda_4 + \lambda_5, \quad 0.461 = \lambda_3 + \lambda_4 + \lambda_5.$$

The boundary condition (91) for $x = 1$ turns out in fact to be superfluous, for when the main correction $\sim \lambda_3 x^3$ is determined it merely repeats the boundary condition (91) for $x = -1$. Similarly, with an accuracy of 1% it is sufficient to retain only two terms in the expansion of the square of the sound velocity in powers of the parameter x :

$$u^2/u_0^2 = 1 + x(4 + 3\lambda_3) + x^2(3 + 10\lambda_3 + 6\lambda_4). \quad (93)$$

3. We can, apart from small exchange corrections, obtain a relation between the coefficients in the expansion (90) of \bar{E} for He^3 and He^4 using the law of corresponding states. We substitute these expansions into (40) and obtain in the rigid-atom approximation $\nu = 0$ and $\lambda = M_3/M_4$

$$\frac{M_3}{M_4} \bar{E}_3(n, 0) - \bar{E}_4(n, 0) = \left(\frac{M_3}{M_4} - 1 \right) E^0(n). \quad (94)$$

As the virial expansion (71) for $E^0(n)$ converges very rapid-

ly and has only two terms, while we take into account three terms in the expansions of \bar{E}_3 and \bar{E}_4 , we have from (94) and (90)

$$M_3^2 u_{03}^2 n_{04}^3 \lambda_{33} / M_4^2 u_{04}^2 n_{03}^3 \lambda_{34} = 1. \quad (95)$$

Substituting in (95) the numerical values of the parameters, we get 0.97 instead of 1. This three percent difference between the numbers is connected with the neglect of small exchange effects. We have thus once again verified that the theory of a structureless quantum liquid is applicable to liquid helium. Determining the parameters T_s , E^0 , and ν at high (room) temperatures T , where helium is undoubtedly structureless, we were able to calculate the characteristics of helium at $T = 0$.

8. MIXTURES OF QUANTUM LIQUIDS

The universality of quantum phenomena holds also for isotopic mixtures of quantum liquids, but the scaling is two-parametric. When we fix the density n and temperature T of a mixture of liquid He^3 and He^4 , their thermodynamic functions are additive. The energy of the mixture \bar{E}_{34} , its kinetic energy \bar{K}_{34} , specific heat \bar{C}_{34} , and equation of state P_{34} depend linearly on the concentrations x_3 and x_4 ($x_3 + x_4 = 1$):

$$\begin{aligned} \bar{C}_{34}(n, T) &= \bar{C}_3(n, T)x_3 + \bar{C}_4(n, T)x_4, \\ P_{34}(n, T) &= P_3(n, T)x_3 + P_4(n, T)x_4, \\ \bar{E}_{34}(n, T) &= \bar{E}_3(n, T)x_3 + \bar{E}_4(n, T)x_4. \end{aligned} \quad (96)$$

These equations are a consequence of the fact that helium has no structure, i.e., the fact that the zero-point oscillation of an atom \bar{K}^0 and its wavefunction are independent of the isotopic composition of the atoms which make up its surroundings. The value (75) of \bar{K}^0 is determined only by the mass M of the atom itself and its wavelength, i.e., by the liquid density. Equations (96) agree with all experimental data one can find in the literature for He^3 and He^4 mixtures, and their accuracy increases when n and T increase. Experimenters traditionally compare their results with the theory of excess molar volumes of quantum isotopic systems which was developed by Prigogine³⁸:

$$V_{34}(P, T) = V_3(P, T)x_3 + V_4(P, T)x_4 + \Delta V. \quad (97)$$

This equation gives less information than Eq. (96) for P_{34} , since the excess molar volume ΔV is sensitive to quantum effects even in the zeroth approximation: when $\Delta V = 0$ the relation (97) holds only for classical mixtures. On the other hand, Eqs. (96) are violated only after one takes exchange effects into account, so that they are applicable both for classical and for quantum mixtures. Moreover, for liquid helium there are in the n, T phase diagram no regions where the molar volumes V_3 and V_4 differ greatly, so that the parameter V_{34} is only a weak function of the concentrations x_3 and x_4 . On the other hand, for the pressures P_3 and P_4 there is an n, T region where they have different orders of magnitude; nonetheless, the parameter $P_{34}(n, T, x_3)$ depends with good accuracy linearly on x_3 . This is clear from Fig. 8., where we show the x_3 dependence of P_{34} for one value of n and several values of T , constructed using the data from refs. 39 and 40.

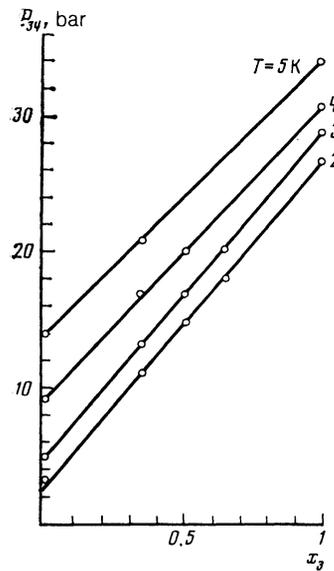


FIG. 8. The pressure P_{34} of a He^3 - He^4 mixture as a function of the He^3 concentration x_3 for a molar volume $V = 26.45 \text{ cm}^3/\text{mole}$. The straight lines are the functions (96), the points the data of Refs. 39 and 40, and the numbers the values of the temperature T in K.

9. THERMAL CONDUCTIVITY AND VISCOSITY OF QUANTUM LIQUIDS

1. Not only the thermodynamic, but also the kinetic properties of helium are universal in those n, T regions where we can neglect exchange effects. We consider first of all a hard-sphere system for which the natural energy scale is the quantum parameter $\epsilon_k = h^2/Mr_0^2$, and we define the dimensionless reduced viscosity η^* and thermal conductivity κ^* by the relations

$$\eta(n, T) = \eta^* \left(n^*, \frac{T}{\epsilon_k} \right) \frac{h}{r_0^3}, \quad \kappa(n, T) = \kappa^* \left(n^*, \frac{T}{\epsilon_k} \right) \frac{h}{r_0^3 M}. \quad (98)$$

We can check that η^* and κ^* are, indeed, dimensionless by using the elementary gas kinetic relations which connect κ , η , \bar{v} , the characteristic particle velocity \bar{v} , and the mean free paths l_κ and l_η :

$$\kappa \propto \bar{C} n \bar{v} l_\kappa, \quad \eta \propto M n \bar{v} l_\eta. \quad (99)$$

One can justify these relations rigorously only in the limit of low density n , when the parameters l_κ and l_η are, indeed, mean free paths. For high n one must consider the relations (99) as a formal definition of l_κ and l_η , as it is clear that when n increases the dimensionality of the parameters occurring in (99) cannot change. By choosing the scale of T we establish from (98) relations between the thermal conductivities κ_3, κ_4 and the viscosities η_3 and η_4 of liquid He^3 and He^4 when they have the same density, in the hard-sphere approximation:

$$\kappa_s(n, T) = \frac{1}{\lambda_0} \kappa_s(n, \lambda_0 T), \quad \eta_s(n, T) = \eta_s(n, \lambda_0 T), \quad \lambda_0 = \frac{M_s}{M_4}. \quad (100)$$

We present qualitative arguments that enable us to go be-

yond the framework of the hard-sphere approximation, making in (100) the substitution $\lambda_0 \rightarrow \lambda$, where the parameter λ is defined by Eq. (39). Indeed, the lengths l_κ and l_η in (99) depend only weakly logarithmically on T , owing to the weak dependence of the particle scattering cross section σ on their energy which is $\approx \bar{K}$. In the low n limit (6')

$$l_{\kappa,\eta} \sim 1/n\sigma, \quad \sigma \sim r_0^2(\bar{K}) = r_0^2 \left(1 - \frac{2}{\gamma} \ln \frac{\bar{K}}{\epsilon_0} \right). \quad (101)$$

However, we have shown above that the specific heat \bar{C} and the particle velocity \bar{v} have a universal reduced temperature T^* dependence. Hence, κ and η also have a universal T^* dependence apart from the weak non-universal \bar{K}/ϵ_0 dependence (101) of l_κ and l_η . The value of the mean particle velocity \bar{v} can be expressed in terms of the parameter \bar{K} [Eq. (15)]:

$$\bar{v}^2 \sim \bar{v}^2 = 2\bar{K}/M, \quad \bar{K} = \bar{K}^0 K^*(T^*). \quad (102)$$

It is convenient to eliminate the lengths l_κ and l_η from (99), normalizing κ and η by their value at some $T = T_0$, where T_0 is an arbitrary value of T in the range $T_F, T_\lambda < T < \epsilon_0 \exp(\gamma/3)$ where the expansion (3) in terms of the parameter $1/\gamma$ is valid:

$$\kappa(n, T) = \kappa(n, T_0) \frac{\bar{C}(T)}{\bar{C}(T_0)} \left(\frac{\bar{K}(T)}{\bar{K}(T_0)} \right)^{1/4}, \quad (103)$$

$$\eta(n, T) = \eta(n, T_0) \left(\frac{\bar{K}(T)}{\bar{K}(T_0)} \right)^{1/4}.$$

To determine the temperature dependence of κ and η in a wide range of n and T it is thus sufficient to perform a control measurement of κ and η for a single value $T = T_0$. The n and T dependence of \bar{C} and \bar{K} , on the other hand, were determined earlier. Equations (103) hold when $T_F, T_\lambda < T < 10^3$ K.

2. There are surprisingly few experimental data for κ and η for helium in the quantum regions of n and T . There are none at all for $4 < T < 20$ K. The preferred values of κ and η for He^4 given in the tables of Refs. 41, 42 are based upon empirical expressions which are not confirmed for high n by direct measurements of the kinetic coefficients of helium. In the range $T < 4$ K, the relation (100) between κ_3 and κ_4 agrees with Kerrisk and Keller's data.⁴³ We show in Fig. 9 the n dependence of κ_3 ($T=4$), κ_3 ($T=3$) and $\frac{4}{3}\kappa_4$ ($T=3$), $\frac{4}{3}\kappa_4$ ($T=2.25$). When n increases, the relation (100) between κ_3 and κ_4 becomes asymptotically exact. We show in Fig. 10 the T dependences of $\eta_3(T)$ and $\eta(\frac{3}{4}T)$ for one value of n , constructed using Betts and Marshall's data⁴⁴ for He^3 at $1.2 < T < 3$ K and the $\eta_4(n, T)$ values given in the tables of Ref. 41. It is clear that the relation (100) holds also between η_3 and η_4 .

3. It follows from (99) that in the scaleless quantum region $T_F, T_\lambda < T < \bar{K}^0$ the thermal conductivity of quantum liquids is proportional to the temperature, while the viscosity is independent of it:

$$\bar{C} \sim \frac{T}{\bar{K}^0}, \quad \bar{K}^0 \sim \frac{\hbar^2}{M l_0^2}, \quad \kappa \sim T \frac{l_\kappa l_0}{\hbar a^2}, \quad \eta \sim \frac{\hbar l_\eta}{a^2 l_0}. \quad (104)$$

In the limit as $\bar{K}^0 \rightarrow \infty$, i.e., $M \rightarrow 0$, the atomic mass M does

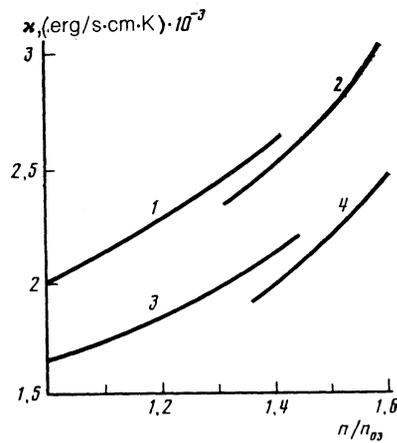


FIG. 9. The thermal conductivity of helium as function of its density n (n_{03} is the equilibrium density of He^3): 1— $\kappa_3(n, T=4)$, 2— $\frac{4}{3}\kappa_4(n, T=3)$, 3— $\kappa_3(n, T=3)$, 4— $\frac{4}{3}\kappa_4(n, T=2.25)$. The data are from Ref. 43.

not occur in the expressions for κ and η ; the kinetic coefficients of helium can be expressed solely in terms of geometric quantities—the lengths l_κ and l_η , the interatomic distance a , and the wavelength of the atom at $T=0$. The asymptotic form (104) agrees with experiments.^{43,44} It is interesting that in a paper by Andreev and Kosevich¹² the same linear law (104) was found for κ in the framework of the glass model of a liquid. However, for the viscosity η another expression was given in Ref. 12:

$$\eta = \bar{\epsilon} \hbar / T, \quad (105)$$

where the parameter $\bar{\epsilon}$ is independent of T and has the dimensions of energy per unit volume. In our opinion, regardless of how it was derived and what were the modeling ideas, Eq. (105) contradicts the dimensionality analysis of the observed quantities. Indeed, in the scaleless T region, which was considered in Ref. 12, the only quantity which has the dimensions of energy is the temperature T itself. One must therefore replace $\bar{\epsilon}$ in (105) by T/a^3 and in that case (105) is the same as (104).

4. There is a combination of κ , η , and \bar{C} which does not contain the quantum parameters of the liquid:

$$M \frac{\kappa}{\bar{C}\eta} = \frac{l_\kappa}{l_\eta} \sim \frac{5}{2} \quad \text{as } n \rightarrow 0. \quad (106)$$

This relation has the following remarkable properties: it is not renormalized when the helium density increases, i.e., in the n region where the virial expansions for κ and η are

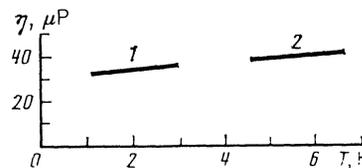


FIG. 10. The viscosity of helium as a function of the temperature T for a given density $n = 2n_k$: 1— $\eta_3(T)$, 2— $\eta_4(\lambda T)$. The data are from Refs. 41 and 44, $n_k = 0.01035 \text{ \AA}^{-3}$.

TABLE II. Mean kinetic energy per atom (in K) of liquid He³ and He⁴; $\bar{K}_3(V_3, T) = \bar{K}_4(V_4, T)$.

T, K	V ₄ — Molar volume of liquid He ³ , cm ³ /mole									
	48.48	41.56	36.36	32.32	29.09	26.45	24.24	22.38	20.78	19.39
2.5	8.593	9.770	11.07	12.69	14.50	16.46	18.77	21.32	24.14	27.26
3.0	9.149	10.31	11.57	13.14	14.90	16.85	19.09	21.59	24.38	27.47
3.5	9.721	10.87	12.11	13.63	15.34	17.26	19.44	21.90	24.66	27.72
4.0	10.31	11.43	12.67	14.17	15.83	17.70	19.84	22.25	24.97	28.00
4.5	10.94	12.01	13.24	14.72	16.34	18.17	20.26	22.64	25.32	28.31
5.0	11.49	12.61	13.85	15.28	16.87	18.66	20.71	23.05	25.69	28.65
5.5	12.07	13.16	14.44	15.84	17.41	19.17	21.19	23.49	26.09	29.01
6.0	12.66	13.79	15.04	16.42	17.96	19.70	21.68	23.95	26.52	29.40
6.5	13.32	14.43	15.66	17.01	18.53	20.24	22.19	24.43	26.96	29.81
7.0	13.99	15.07	16.28	17.61	19.10	20.79	22.72	24.93	27.43	30.24
7.5	14.66	15.72	16.91	18.22	19.69	21.35	23.26	25.44	27.92	30.70
8.0	15.33	16.38	17.54	18.84	20.28	21.92	23.81	25.97	28.42	31.17
9.0	16.68	17.70	18.83	20.08	21.50	23.10	24.94	27.06	29.46	32.16
10.0	18.03	19.03	20.12	21.35	22.73	24.30	26.11	28.19	30.56	33.22
12.0	20.77	21.71	22.76	23.94	25.26	26.78	28.54	30.57	32.87	35.47
14.0	23.54	24.44	25.45	26.58	27.86	29.34	31.06	33.04	35.30	37.85
16.0	26.33	27.21	28.17	29.27	30.52	31.95	33.64	35.57	37.80	40.31
18.0	29.17	30.01	30.94	32.01	33.22	34.62	36.26	38.17	40.36	42.83
20.0	32.02	32.83	33.74	34.78	35.95	37.33	38.93	40.81	42.96	45.41
30.0	46.41	47.20	47.98	48.83	49.89	51.10	52.64	54.43	56.45	58.74
50.0	75.64	76.35	76.98	77.65	78.57	79.62	81.03	82.67	84.54	86.66
	62.20	52.39	45.24	39.26	34.74	31.30	28.45	26.04	23.99	22.23

V₃ — Molar volume of liquid He³, cm³/mole.

inapplicable, we have such a combination of observable quantities that one can find its value in the low n limit in the hard sphere model, when κ and η are independent of n and the mean free path is $\propto 1/n$. This means that the number $\frac{5}{2}$ in (106) is of purely combinatorial origin and the lengths l_κ and l_η which have the meaning of a mean free path only for low n change in the same way when n changes, i.e., as follows:

$$l_\kappa(n)/l_\kappa(n^0) = l_\eta(n)/l_\eta(n^0),$$

where n^0 is any value $n < 1/r_0^3$.

Therefore, we have between the kinetic coefficients of helium the relations (100), (103), (106) which one can use to determine κ and η in a broad n, T range, where the particle-statistics effects are negligibly small.

10. TABLES

We give in the form of Tables II–V for $2.5 < T < 50$ K the average kinetic energies of liquid He⁴ and He³, $\bar{K}_4(n, T)$ and $\bar{K}_3(n, T)$, and the thermodynamic functions of He³; $\bar{C}_3(n, T)$, $\bar{S}_3(n, T)$, and $\bar{E}_3(n, T)$, determined using the isotopic law of corresponding states (Sec. 3) and Hill and Lounasmaa's experimental data²² for He⁴. These quantities have not been measured experimentally in a broad range of densities n_3 for $T > 2.5$ K. The low temperature data of Greywall,⁴⁵ and of Pandorf *et al.*⁴⁶ for $\bar{C}_3(n, T)$ and $\bar{S}_3(n, T)$ agree with an accuracy $\approx 1\%$ with the corresponding states law for $T \approx 2.5$ K. The parameter \bar{K}_4 for He⁴ is found in neutron scattering experiments only in the region of low $T < 4$ K at the saturated vapor pressure, and for He³ the determination of \bar{K}_3 entails considerable difficulties⁴⁷ because of

TABLE III. Energy $\bar{E}_3(V_3, T)$ per particle (in K) of liquid He³.

T, K	V ₃ — molar volume cm ³ /mole									
	62.20	52.39	45.24	39.26	34.74	31.30	28.45	26.04	23.99	22.23
2.5	1.634	-0.110	-0.580	-1.000	-1.240	-1.220	-0.902	-0.358	0.445	1.580
3.0	2.213	0.456	-0.052	-0.519	-0.781	-0.792	-0.543	-0.055	0.718	1.822
3.5	2.810	1.042	0.523	0.017	-0.298	-0.337	-0.148	0.298	1.037	2.110
4.0	3.424	1.634	1.114	0.593	0.231	0.147	0.293	0.688	1.391	2.434
4.5	3.585	2.251	1.695	1.185	0.785	0.659	0.760	1.127	1.790	2.792
5.0	4.653	2.884	2.372	1.787	1.361	1.197	1.261	1.588	2.211	3.185
5.5	5.264	3.453	2.999	2.388	1.948	1.758	1.788	2.084	2.667	3.601
6.0	5.874	4.121	3.637	3.012	2.545	2.335	2.338	2.601	3.157	4.051
6.5	6.568	4.795	4.295	3.646	3.165	2.934	2.906	3.142	3.659	4.525
7.0	7.262	5.468	4.954	4.290	3.784	3.538	3.491	3.699	4.195	5.021
7.5	7.963	6.152	5.624	4.946	4.425	4.155	4.090	4.278	4.753	5.552
8.0	8.656	6.847	6.293	5.612	5.066	4.780	4.704	4.875	5.323	6.095
9.0	10.07	8.239	7.664	6.944	6.392	6.077	5.963	6.101	6.509	7.239
10.0	11.47	9.636	9.035	8.308	7.728	7.395	7.261	7.374	7.762	8.463
12.0	14.34	12.45	11.84	11.09	10.48	10.12	9.966	10.05	10.40	11.06
14.0	17.22	15.33	14.70	13.93	13.30	12.93	12.76	12.83	13.16	13.81
16.0	20.13	18.25	17.59	16.82	16.19	15.80	15.63	15.68	16.01	16.65
18.0	23.09	21.19	20.53	19.76	19.13	18.74	18.54	18.60	18.94	19.56
20.0	26.06	24.16	23.51	22.74	22.10	21.71	21.52	21.58	21.90	22.54
30.0	41.07	39.28	38.64	37.83	37.24	36.85	36.77	36.89	37.27	37.94
50.0	71.56	69.96	69.46	68.80	68.41	68.20	68.34	68.68	69.29	70.18

TABLE IV. Entropy $\bar{S}_3(V_3, T)$ per particle of liquid He³.

T, K	V_3 — molar volume cm ³ /mole									
	62.20	52.39	45.24	39.26	34.74	31.30	28.45	26.04	23.99	22.23
3.0	2.500	2.305	2.139	1.979	1.840	1.722	1.623	1.533	1.447	1.361
3.5	2.685	2.485	2.308	2.140	1.991	1.861	1.745	1.640	1.544	1.453
4.0	2.853	2.644	2.466	2.288	2.133	1.990	1.861	1.745	1.639	1.540
4.5	3.003	2.793	2.607	2.427	2.262	2.110	1.973	1.847	1.731	1.624
5.0	3.138	2.925	2.731	2.552	2.383	2.225	2.078	1.944	1.821	1.706
5.5	3.266	3.050	2.851	2.669	2.495	2.331	2.179	2.038	1.907	1.786
6.0	3.382	3.161	2.963	2.778	2.600	2.431	2.274	2.128	1.992	1.863
6.5	3.488	3.270	3.068	2.879	2.698	2.524	2.364	2.216	2.074	1.939
7.0	3.591	3.370	3.166	2.975	2.792	2.615	2.451	2.297	2.152	2.014
7.5	3.688	3.464	3.258	3.064	2.878	2.701	2.535	2.378	2.229	2.086
8.0	3.778	3.554	3.346	3.149	2.963	2.783	2.614	2.454	2.302	2.157
9.0	3.943	3.717	3.506	3.308	3.117	2.934	2.762	2.599	2.443	2.291
10.0	4.093	3.863	3.651	3.452	3.259	3.073	2.899	2.733	2.574	2.420
12.0	4.353	4.120	3.906	3.700	3.510	3.322	3.145	2.976	2.815	2.658
14.0	4.576	4.342	4.127	3.922	3.727	3.538	3.360	3.191	3.028	2.870
16.0	4.770	4.537	4.320	4.116	3.920	3.730	3.551	3.381	3.218	3.059
18.0	4.944	4.711	4.493	4.290	4.092	3.903	3.723	3.553	3.390	3.231
20.0	5.101	4.867	4.650	4.446	4.249	4.060	3.879	3.709	3.546	3.387
30.0	5.705	5.471	5.264	5.058	4.862	4.676	4.498	4.327	4.163	4.003
50.0	6.484	6.254	6.051	5.848	5.657	5.476	5.303	5.138	4.979	4.825

TABLE V. Specific heat $\bar{C}_3(V_3, T)$ per particle of liquid He³.

T, K	V_3 — molar volume cm ³ /mole						
	39.26	34.74	31.30	28.45	26.04	23.99	22.23
3.0	—	—	0.871	0.747	0.655	0.593	0.548
3.5	—	1.039	0.934	0.833	0.744	0.673	0.616
4.0	—	1.085	0.999	0.911	0.826	0.749	0.681
4.5	1.182	1.125	1.054	0.975	0.897	0.819	0.746
5.0	1.208	1.159	1.098	1.030	0.958	0.884	0.808
5.5	1.233	1.190	1.137	1.077	1.012	0.941	0.866
6.0	1.257	1.218	1.171	1.118	1.060	0.994	0.921
7.0	1.300	1.265	1.227	1.185	1.138	1.085	1.023
8.0	1.329	1.300	1.270	1.238	1.202	1.160	1.111
9.0	1.352	1.330	1.307	1.281	1.255	1.224	1.187
10.0	1.370	1.355	1.336	1.318	1.298	1.276	1.252
12.0	1.405	1.395	1.386	1.375	1.365	1.355	1.345
14.0	1.434	1.429	1.423	1.417	1.412	1.408	1.404
16.0	1.458	1.455	1.451	1.449	1.446	1.443	1.441
18.0	1.478	1.477	1.476	1.475	1.473	1.472	1.472
20.0	1.494	1.495	1.495	1.495	1.495	1.496	1.496
25.0	1.513	1.517	1.521	1.528	1.533	1.539	1.545
30.0	1.529	1.536	1.542	1.551	1.559	1.567	1.576
40.0	1.550	1.560	1.569	1.580	1.591	1.603	1.615
50.0	1.562	1.574	1.585	1.598	1.611	1.624	1.638

TABLE VI. The parameters $\bar{K}_4^0, E^0, \nu, K_\infty^*, \tau_c, \lambda$ as functions of the molar volume $V_4, \rho_4 = n_4/n_k$ is the reduced density, $n_k = 0.01035 \text{ \AA}^{-3}$.

ρ_4	1.0	1.2	1.4	1.6	1.8
$V_4, \text{cm}^3/\text{mole}$	58.18	48.48	41.56	36.36	32.32
\bar{K}_4^0, K	5.669	6.929	8.310	9.796	11.58
$-E^0, \text{K}$	9.207	11.38	13.66	16.05	18.55
ν	0.0464	0.0576	0.0694	0.0818	0.0949
K_∞^*	0.514	0.518	0.521	0.527	0.520
τ_c	0.221	0.215	0.200	0.199	0.199
λ	0.763	0.765	0.768	0.770	0.772

ρ_4	2.0	2.2	2.4	2.6	2.8	3.0
$V_4, \text{cm}^3/\text{mole}$	29.09	26.45	24.24	22.38	20.78	19.39
\bar{K}_4^0, K	13.55	15.71	18.09	20.70	23.59	26.75
$-E^0, \text{K}$	21.16	23.88	26.71	29.65	32.70	35.86
ν	0.1086	0.1229	0.1379	0.1535	0.1697	0.1866
K_∞^*	0.513	0.507	0.511	0.517	0.524	0.531
τ_c	0.191	0.184	0.174	0.166	0.159	0.152
λ	0.775	0.777	0.780	0.782	0.785	0.788

the strong absorption of neutrons by this liquid. Table VI gives numerical values of the parameters ν , E^0 , \bar{K}_4^0 , λ , τ_c , and K_∞^* defined in (3), (13), (30), and (39).

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