

Temperature and pressure dependence of viscosity of quantum liquid ${}^4\text{He}$ according to significant structure theory

(transport phenomena/quantum effect/zero-point motion/low temperature)

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ABSTRACT Both solid-like and gas-like flow structures are considered in the calculation of viscosity of liquid ${}^4\text{He}$ using the significant structure theory of liquids. The predominance of quantum mechanical zero-point motion over that arising from thermal excitation is taken into account for the solid-like motion of molecules. The viscosity of liquid ${}^4\text{He}$ under its own vapor pressure calculated over its whole temperature range is in reasonably good agreement with experimental data. The pressure dependence of viscosity also was obtained. The calculation does not yield good results at high densities where the free jumping of molecules into the nearest neighboring vacancies through the kinetic zero-point motion is no longer plausible.

During the past four decades, it has been well known that liquid ${}^4\text{He}$ exhibits anomalous behavior in its transport properties. The viscosity of liquid ${}^4\text{He}$ measured by the oscillating disc method (1) decreases continuously with decreasing temperature below the λ point. On the other hand, measurements by the capillary flow method (2, 3) yield very small values for the viscosity below the λ point. This is not explained by classical hydrodynamics. This apparent contradiction between experimental methods leads directly to the so called two-fluid concept of He-II.

In ordinary liquids, the viscosity has a large negative temperature dependence. It is reasonably well defined by an Arrhenius type equation, $\eta = A e^{E_a/RT}$, indicating that the momentum transport in ordinary liquids is mainly affected by a thermal activation process. Such a dynamic type of viscosity can be explained by applying the significant structure theory of liquids (4, 5). In this theory, a liquid is described by using a quasi-lattice structure model in which the sites are occupied by molecules or fluidized vacancies of molecular size. It is considered that the molecules jump into adjacent vacancies as a result of a thermal activation of the lattice vibration, and thus the theory is based on the assumption of molecules having gas-like properties and solid-like properties. The overall viscosity is considered to be contributed by these two effects. The contribution of solid-like molecules is derived by using Eyring's rate theory; that of gas-like molecules is derived from the kinetic theory of gases. The theory has been applied to the viscosity of various liquids (4, 5). However, quite different from ordinary liquids, liquid ${}^4\text{He}$ shows a kinetic type of viscosity. It has a viscosity of the same order as He vapor in spite of the fact that it has a much larger density than the vapor. This almost temperature-independent kinetic type of viscosity observed in He-II was considered by many workers (6–8) as resulting from the large kinetic zero-point motion. The kinetic zero-point energy was taken into account also in our previous paper (9) in order to explain the thermodynamic properties and the surface tension of liquid ${}^4\text{He}$.

In this paper, the kinetic zero-point motion is considered to transport the ${}^4\text{He}$ molecules into their adjacent vacancies, together with the thermal activation of the quasi-lattice vibration. Hence, the viscosity contribution of solid-like molecules is significantly reduced over that found by assuming only the thermal activation process. This paper reports the study of the viscosity of liquid ${}^4\text{He}$ over the whole temperature range and under external pressures.

THEORY

Flow in the solid-like structure of liquid He

It is believed that, due to the quantum mechanical effect arising from the large zero-point energy, only He remains liquid down to absolute zero under pressures lower than 25 atm (2500 kPa). London (6) estimated the kinetic zero-point energy of liquid He by adopting a model of N hard-sphere molecules with diameter d confined in a given volume V :

$$K_0 = \frac{-151.3d}{(r - 0.8909d)^2(r + 0.7133d)} \text{ cal/mol (1 cal = 4.184 J)} \quad [1]$$

in which $r = (V/N)^{1/3}$, K_0 is the molar kinetic zero-point energy of liquid He, N is Avogadro's number, and r and d are expressed in angstroms. He first showed that the molar volume and the free energy of liquid He at 0 K can be explained by choosing a best-fitting value for the molecular diameter. Because the zero-point energy in Eq. 1 is the molar quantity obtained from the canonical ensemble for N molecules, one may consider that molecules at 0 K are executing kinetic motions which are expressed by

$$K_0 = \frac{1}{2} M \nu_0^2 \quad [2]$$

in which M is the atomic mass of ${}^4\text{He}$, and ν_0 is the average speed of ${}^4\text{He}$ molecules due to the kinetic zero-point motion.

In order to move into a nearest-neighbor vacant site, the molecule must pass through a bottleneck due to an energy barrier formed by its nearest neighbors. Now, if we assume that the energy barrier between adjacent sites is very low compared with the zero-point energy, the molecules may be assumed to jump freely into their nearest-neighbor vacancies. This assumption stems from the large kinetic zero-point energy and the large distance, 3.8 Å (9), between adjacent sites compared with the shallow depth of free energy, -14.3 cal/mol, of liquid ${}^4\text{He}$ at 0 K. With this assumption, the average jumping frequency at which a molecule jumps into the neighboring site through the kinetic zero-point motion is approximately

$$k^0 = \frac{\lambda}{\nu_0} \cdot \frac{V - V_s}{V} \quad [3]$$

in which k^0 , V_s , and λ are the average jumping frequency when

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no external shear force is applied, the molar volume of the solid-like structure, and the distance between adjacent sites, respectively. Here, λ/ν_0 is the reciprocal of the time required to move a distance of λ to a neighboring vacant site. The distance λ can be obtained from the following expression, assuming a close-packed solid-like structure:

$$\lambda = \left(\frac{\sqrt{2}V_s}{N} \right)^{1/3} \quad [4]$$

Under an additional external shear stress, let k_{for}^0 and k_{rev}^0 be the frequencies of the forward and reverse directions with respect to the direction of the shear stress, respectively. Then, k_{for}^0 will be slightly increased while k_{rev}^0 is decreased because the shear stress favors the forward jumping motion over the reverse. The net jumping motion results in the flow of liquid ^4He in the direction of an external shear vector when summed over all molecules. Because of this motion, liquid He exhibits fluidity even at absolute zero. The superfluid component is treated as consisting of ground state molecules and is considered to flow only through this type of motion.

As the temperature increases, the thermal activation of the quasi-lattice vibration also becomes important. According to Eyring, the flow of ordinary liquids involves only one molecule at a time so that the rate processes are unimolecular, and the molecule must form an activated state in order to pass over the potential barrier. This leads to the following expression for the frequency of jumping through thermal activation:

$$k^{\text{ex}} = \kappa \frac{kT}{h} \frac{V - V_s}{V} f_s^{-1} \exp \frac{-a'E_s V_s}{(V - V_s)RT} \quad [5]$$

in which k^{ex} is the jump frequency when no external force is applied, f_s is the one-dimensional partition function of the solid-like vibration, T is the absolute temperature, and k , h , and R are the Boltzmann, Planck, and gas constants, respectively. κ is the transmission coefficient—that is, the probability that a process actually takes place once the system is in the activated state. In most well-behaved rate processes, κ varies between $1/2$ and 1. E_s is the potential energy of the quasi-lattice structure, and a' is a proportionality constant. For the superfluid component with no thermal excitation, k^{ex} becomes zero. When an external shear stress is applied, the rate of forward jump increases because the activation energy is lowered and the backward jump rate decreases. This type of jumping motion arising from thermal activation is quite different from the kinetic zero-point motion because the latter does not involve a potential barrier to be surmounted. We also assume that the two kinds of flowing motion in liquid ^4He occur independently so that the jumping processes are simply added together to give the total jumping rates. In the following section, the formulas for the viscosity coefficient of liquid ^4He will be derived by using the relationships between the external shear stress and the jump frequencies.

Equation of viscosity of liquid ^4He

According to the significant structure theory, the viscosity of a liquid, defined as the ratio of shear stress f to the shear rate s , is given by

$$\frac{V_s}{V} \eta_s + \frac{V - V_s}{V} \eta_g \quad [6]$$

in which η_s and η_g are the viscosities contributed by solid-like and gas-like structures, respectively. The rate of shear of a solid-like degree of freedom is equal to the viscosity with which one molecular layer slips over the next one divided by the distance λ_1 between the layers (Fig. 1) (10). We may write

$$s = \sum_{i=1}^z \frac{\lambda}{\lambda_1} \cos \theta_i k_i \quad [7]$$

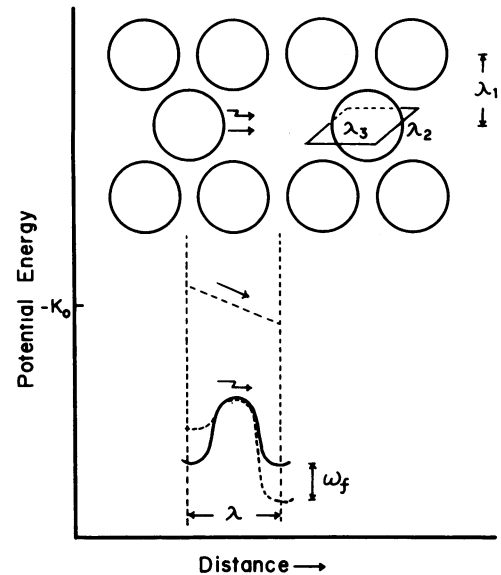


FIG. 1. Diagram of viscous shear, illustrating the flow processes in the solid-like structure of liquid ^4He . The area of a molecule in the shear plane is $\lambda_2\lambda_3$ and the distance between flowing layers is λ_1 .

in which the summation is over all z neighboring positions. The frequency is the net frequency at which the molecule jumps into the neighboring i th lattice position so that $k_i = 0$ when $f = 0$. θ_i is the angle between the displacement vector of the molecule jumping into the neighboring i th lattice site and the direction of the shear stress. If we pair each forward jump with the oppositely directed one, Eq. 7 becomes

$$\begin{aligned} s &= \sum_{i=1}^{z/2} \frac{\lambda}{\lambda_1} \cos \theta_i (k_{i,\text{for}} - k_{i,\text{rev}}) \\ &= \sum_{i=1}^{z/2} \frac{\lambda}{\lambda_1} \cos \theta_i [(k_{i,\text{for}}^0 + k_{i,\text{for}}^{\text{ex}}) - (k_{i,\text{rev}}^0 + k_{i,\text{rev}}^{\text{ex}})] \quad [8] \end{aligned}$$

in which $k_{i,\text{for}}^0$ s are the frequencies of the forward jump into the i th neighboring site and the $k_{i,\text{rev}}^0$ s are the reverse jump frequencies back from the i th site. The work done by f in moving the molecule a distance λ into the next position is written as $W_f = f\lambda_2\lambda_3\lambda \cos \theta_i$. For the thermal activation of the quasi-lattice vibration, the activation energies of the forward and reverse jumps are changed by the amount of the work $W_f/2$ for a symmetrical barrier. Thus, the frequencies $k_{i,\text{for}}^{\text{ex}}$ and $k_{i,\text{rev}}^{\text{ex}}$ may be written as

$$k_{i,\text{for}}^{\text{ex}} = k^{\text{ex}} e^{W_f/2kT} \quad [9]$$

$$k_{i,\text{rev}}^{\text{ex}} = k^{\text{ex}} e^{-W_f/2kT} \quad [10]$$

in which the same k^{ex} is assumed for every position i . Next, we have to obtain the expressions for $k_{i,\text{for}}^0$ and $k_{i,\text{rev}}^0$. Because the jump through the zero-point motion involves no activated state, we treat it as a reversible elementary process. The ratio of two rate coefficients is written as

$$\frac{k_{i,\text{for}}^0}{k_{i,\text{rev}}^0} = e^{W_f/kT} \quad [11]$$

From Eq. 11 and the condition that $k_{i,\text{for}}^0$ and $k_{i,\text{rev}}^0$ become k^0 when $f = 0$, we write the reversible elementary process as follows:

$$k_{i,\text{for}} = k^0 e^{W_f/2kT} \quad [12]$$

$$k_{i,\text{rev}} = k^0 e^{-W_f/2kT} \quad [13]$$

With Eqs. 9, 10, 12, and 13 and the condition $\lambda_2\lambda_3\lambda \cos \theta_i/2kT \ll 1$ for Newtonian flow, the exponentials are expanded and the rate of shear becomes

$$\begin{aligned} \dot{s} &= \frac{\lambda}{\lambda_1} (k^0 + k^{\text{ex}}) \frac{f\lambda_2\lambda_3\lambda}{kT} \sum_{i=1}^{z/2} \cos^2\theta_i \\ &= \frac{\lambda^2\lambda_2\lambda_3}{\lambda_1 kT} (k^0 + k^{\text{ex}}) \frac{fz}{6}. \end{aligned} \quad [14]$$

The last equality in Eq. 14 follows because there are $z/2$ forward jumps for which the mean value of $\cos^2\theta_i$ is $1/3$. Using the relationships $\lambda_1 = \lambda_2 = \lambda_3$ and $\lambda^3 = \sqrt{2}V_s/N$ and putting Eqs. 8 and 10 into Eq. 14, we obtain the viscosity contributed by the solid-like structure

$$\begin{aligned} \eta_s &= \frac{f}{\dot{s}} \\ &= \frac{NkT}{z} \frac{V}{V_s} \frac{6}{\sqrt{2}} \frac{1}{V - V_s} \left(\kappa \frac{kT}{h} f_s^{-1} + \frac{\nu_0}{\lambda} \right)^{-1} \\ &= \frac{k^{\text{ex}}}{k^0 + k^{\text{ex}}} \left[\frac{Nh}{z} \frac{V}{V_s} \frac{6}{\sqrt{2}} \frac{1}{V - V_s} f_s \exp \left(\frac{a'E_s V_s}{(V - V_s)RT} \right) \right]. \end{aligned} \quad [15]$$

The term in the square bracket of Eq. 15 is the viscosity contributed by the solid-like structure that may be derived if we neglect the jump due to zero-point motion. The viscosity contributed by the solid-like structure of liquid ^4He is thus reduced to the fraction $k^{\text{ex}}/(k^0 + k^{\text{ex}})$ of the total viscosity.

The viscosity contributed by gas-like structure η_g is derived from the kinetic theory of gases. The quantum theory of transport phenomena in Bose-Einstein gases has been studied by Uehling (11). However, the classical kinetic theory can be used within the uncertainty of the experimental data because η_g is usually at most $\approx 2\%$ of the total viscosity. Then, we may write the expression for η_g of liquid ^4He

$$\begin{aligned} \eta_g &= X_n \eta_{g,n} + (1 - X_n) \eta_{g,s} \\ &= \frac{2}{3} \left(\frac{X_n}{d_n^2} + \frac{1 - X_n}{d_s^2} \right) \left(\frac{mkT}{\pi^3} \right)^{1/2} \end{aligned} \quad [16]$$

in which X_n is the mole fraction of the normal fluid component of He-II expressed by $X_n = (T/T_\lambda)^{5.6}$ below the transition temperature λ . T_λ and $\eta_{g,n}$ and $\eta_{g,s}$ are the contributions of the two fluid components, respectively. Here, m is the mass of a ^4He molecule. For the molecular diameters of the two components, $d_n = 2.073 \text{ \AA}$ and $d_s = 2.121 \text{ \AA}$ are used (9).

Under high pressures, the pressure effects also have been introduced into the expressions for V_s and η_s . Using Eqs. 6, 15, and 16 and considering the effect of pressure, we obtain

$$\begin{aligned} \eta &= X_n \frac{k^{\text{ex}}}{k^0 + k^{\text{ex}}} \left[\frac{Nh}{zK} \frac{6}{\sqrt{2}} \frac{1}{V - V_s} f_s \right. \\ &\quad \times \exp \left[\frac{a'E_s V_s}{(V - V_s)RT} \exp \frac{P(V - V_s)}{RT} \right] \\ &\quad \left. + \frac{V - V_s}{V} \left[\frac{2}{3} \left(\frac{X_n}{d_n^2} + \frac{1 - X_n}{d_s^2} \right) \left(\frac{mkT}{\pi^3} \right)^{1/2} \right] \right]. \end{aligned} \quad [17]$$

Here, the correction for V_s at pressure P is given by the equation

$$V_{sp} = V_s e^{-\beta\Delta\rho} \quad [18]$$

in which β is the coefficient of compressibility for the solid-like structure and V_{sp} is the solid-like volume under pressure P .

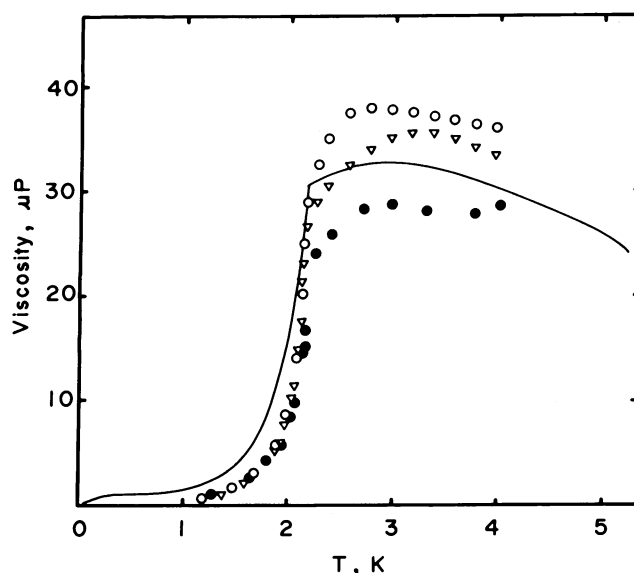


FIG. 2. Viscosity of liquid ^4He under its saturated vapor pressure. ●, de Troyer *et al.* (13); ○, Dean Taylor and Dash (14); ▽, Welber (15); —, our calculation.

CALCULATION

The viscosity of liquid ^4He is calculated from Eq. 17. The parametric values of $\kappa = 0.5$, $a' = 0.001$, and $\beta = 3.897 \times 10^{-3} \text{ atm}^{-1}$ are used for the calculation, and all other parameters are taken from our previous paper (9). The calculated molar volumes (9) are then introduced into Eq. 17 to yield the viscosity under vapor pressures above 0.3 K. These input data for molar volume deviate at most by 2% from the experimental values up to 3.5 K. The maximum deviation is 6.6% at 4.9 K. Below 0.3 K, the experimental molar volume is used in the calculation because the volume was not calculated at this extremely low temperature. In order to examine the pressure dependence of viscosity, the viscosities are calculated up to 4 K at constant densities of $\rho = 0.145, 0.161, 0.171, \text{ and } 0.180 \text{ g/cm}^3$. The pressures taken from the experimental PVT relationships are introduced into Eq. 18 where $\Delta P = P - P_s$. For the saturated vapor pressure, P_s , the calculated values (9) are used.

The one-dimensional partition function of the solid-like vibration, f_s , must be derived from a one-dimensional crystal of length L and consisted of N molecules by treating them as a continuum with only longitudinal displacement allowed (12).

Table 1. Calculated viscosity of liquid ^4He under its saturated vapor pressure

$T, \text{ K}$	$K_0, \text{ cal/mol}$	Φ^*	$\eta, \mu\text{P}$
0.1	22.11	1.785×10^{-11}	0.39
0.4	22.08	4.120×10^{-7}	0.78
0.8	21.99	4.627×10^{-5}	1.15
1.2	21.80	7.058×10^{-4}	1.90
1.6	21.50	4.829×10^{-3}	4.92
2.0	21.17	2.126×10^{-2}	16.80
2.177	21.10	3.702×10^{-2}	30.52
2.4	20.75	4.123×10^{-2}	31.66
2.8	20.00	4.891×10^{-2}	32.74
3.4	18.43	6.115×10^{-2}	32.24
4.0	16.28	7.493×10^{-2}	30.26
4.6	13.44	9.193×10^{-2}	27.84
5.2	8.71	1.227×10^{-1}	24.78
5.258	6.95	1.365×10^{-1}	23.77

* $\Phi = X_n [k^{\text{ex}}/(k^0 + k^{\text{ex}})]$.

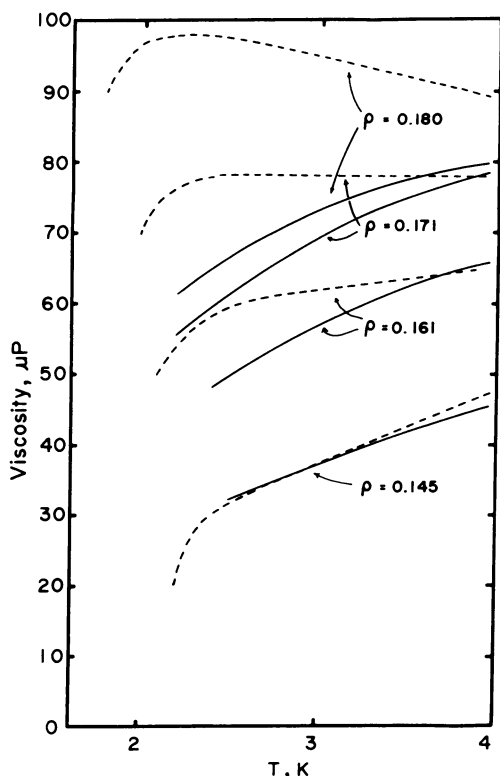


FIG. 3. Viscosity of liquid ${}^4\text{He}$ at constant density. —, Our calculation; ---, Tjerkstra's experiment (16).

However, for simplicity, the one-third power of the three-dimensional Debye partition function is used because $f_s \cong 1$ at liquid helium temperature.

RESULTS AND DISCUSSION

In Fig. 2, the calculated viscosities subject to the system vapor pressures are compared with the available experimental values as measured with the oscillating disc method (13–15). The calculation yields a viscosity maximum at about 3 K and shows a satisfactory agreement with experimental data, especially for He-I. The somewhat larger viscosity obtained for He-II shows that we need a more realistic treatment of the gas-like contribution of the superfluid component.

For ordinary liquids, the viscosities are very sensitive to the transmission coefficient κ and the proportionality constant a' , and these parameters are chosen so that the calculations yield the best fit to the experimental data. However, the present calculation for liquid ${}^4\text{He}$ shows only 5% of the common dependence expected for ordinary liquids on these parameters. This small dependence of viscosity values on κ and a' is due to the large contribution of zero-point motion to flow in the solid-like structure, as shown in Table 1: $k^0 \gg k^{\text{ex}}$. Eq. 15 reduces to the equation for the solid-like viscosity of other simple liquids where the zero-point motion may be neglected.

In Fig. 3, the calculated viscosities at constant densities are compared with Tjerkstra's experimental data (16). The calculation shows good agreement with experiment at $\rho = 0.145$ g/cm 3 , but the temperature dependence of viscosities at higher densities is not satisfactory. He shows large values of the compressibility coefficient: $\beta = 2.6 \times 10^{-3}$ and 3.3×10^{-3} atm $^{-1}$ for α and γ solids, respectively, according to the measurement near the melting curve and the λ line (17). Hence, the value $\beta = 3.897 \times 10^{-3}$ atm $^{-1}$ for the solid-like structure is acceptable. The discrepancies in the viscosity between calculation and experiment at the higher densities arises from neglect of the energy barriers between molecules. As the density increases, the molecular separation becomes less and the energy barrier between adjacent sites increases steeply compared with the average value of the kinetic zero-point energy. It is necessary to consider the fluctuation of the zero-point energy of molecules in order to discuss further explanations of the viscosity of liquid ${}^4\text{He}$ at high densities.

Liquid ${}^4\text{He}$ thus shows a kinetic type of viscosity, but this does not mean that the liquid is similar to a gas. And the fact that the measured temperature coefficient of viscosity of He-I changes its sign from positive to negative as the density increases is to be explained not as a result of difference in characteristics of a gas and a normal liquid but rather as a result of a decrease in the quantum effect due to an increase in the energy barrier. The gas-like contribution of viscosity is only 5.8% of the total at the λ -point.

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