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QUANTUM MECHANICAL CELL MODEL FOR THE THERMAL CONDUCTIVITY OF SIMPLE LIQUIDS*

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ABSTRACT

A model for calculating the thermal conductivity of simple liquids influenced by quantum effects is presented. The model is based on the cell theory of liquids. The prediction of the influence of quantum effects on the thermal conductivity, and its temperature, pressure, and volume derivaties, is qualitatively correct. Calculations of the thermal conductivity of liquid ^{4}He and ^{3}He are in fair agreement with experimental measurements.

I. INTRODUCTION

The thermal conductivity, η, of simple classical liquids, such as A, N_2, CH_4, and CO, generally follows the principle of corresponding states. When lighter species are included in the comparison, an increasing deviation from the classical behavior is observed in the series Ne, D_2, H_2, ^{4}He, and ^{3}He. This deviation from classicai behavior has been correlated with increasing quantum effects in the liquid[1]. As quantum effects become stronger η (in reduced units) decreases and $d\eta/dT$ changes from negative to positive. These changes can be predicted by modifying the classical cell model for the thermal conductivity of simple liquids as presented by McLaughlin[2–4]. The resulting quantum mechanical cell model contains the original model in the classical limit. Section II describes the classical model and Section III outlines the modifications required for the quantum mechanical case. Section IV discusses the resulting quantum mechanical expression for η and its derivatives while Section V presents the results of calculations of η of ^{3}He and ^{4}He, compared with some experimental results.

II. CLASSICAL MODEL

A model for calculating the thermal conductivity of simple classical liquids has been developed by McLaughlin[2–4]. This model is based on the cell theory of the

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liquid state of Lennard–Jones and Devonshire[5]. The structure of the liquid is assumed to be quasi-crystalline, *i.e.*, the available volume is divided into identical cells, at least one for each molecule, and the cells are located so that their centers form a regular lattice. Each molecule is confined to its cell by its nearest neighbors, and moves in a spherical potential field of all other molecules, located at the centers of their cells. In the cell theory of liquids the partition function, and thus the thermodynamic properties, can be evaluated from this picture. McLaughlin assumes this structure for a liquid and proceeds to develop expressions for two proposed mechanisms for the transport of heat down a temperature gradient. A vibrational contribution arises from the motion (vibration) of molecules within their individual cells, and a convective contribution arises from molecules which occasionally jump from their cells into adjacent vacant cells. The total thermal conductivity, η, is the sum of these two contributions.

With the cells located on a face-centered cubic (fcc) lattice, the vibrational contribution to the thermal conductivity, η_v, is given by

$$\eta_v = \sqrt{2}\, \nu C_v (1-f)/a$$

where ν is the frequency of vibration of the molecule in its cell, C_v is the heat capacity of the vibrating molecule, f is the fraction of vacant cells in the lattice, and a is the nearest neighbor separation, given by

$$a^3 = \sqrt{2}\, v/N, \tag{1}$$

with v the molar volume, and N Avogadro's number. McLaughlin assumed that $f \ll 1$, and that C_v was the heat capacity of a three dimensional harmonic oscillator in the classical limit,

$$C_v = 3\,k, \tag{2}$$

where k is Boltzmann's constant. The frequency, ν, is a function of the potential experienced by a molecule in its cell. McLaughlin assumed that ν could be calculated by expanding the potential in powers of r, the distance of a molecule from its equilibrium position in the cell, and keeping only the term in r^2(the harmonic approximation). The Lennard–Jones 6–12 potential function,

$$\phi(r') = 4\varepsilon[(\sigma/r')^{12} - (\sigma/r')^6] \tag{3}$$

was one form taken as the intermolecular potential, and summed over the first three shells of neighbors of a fcc lattice to obtain the potential experienced by a molecule in its cell[5]. In Eqn. (3), r' is the intermolecular distance of a pair of molecules, and ε and σ are a characteristic energy and distance. This results in

$$\nu = \frac{1}{2\pi(m)^{\frac{1}{2}}}\left[\frac{24\varepsilon}{a^2}\left(\frac{L}{v^{*4}} - \frac{M}{v^{*2}}\right)\right]^{\frac{1}{2}} \tag{4}$$

where m is the molecular mass, L and M are constants associated with the fcc lattice ($L = 22.11$ and $M = 10.56$), and $v^* = v/N\sigma^3$. It should be pointed out that Eqn. (1) is only one of many expressions for ν that could be obtained depending on the form of the intermolecular potential function. In general, however, if the potential is a function only of the intermolecular spacing, ν will be a function of volume and not temperature, under the assumptions outlined here.

The convective contribution to the thermal conductivity, η_c, is given by

$$\eta_c = \sqrt{2}\omega C_v(1-f)/a$$

where ω is the frequency at which molecules jump into adjacent vacant cells. From rate theory ω was calculated as

$$\omega = \frac{f(kT/2\pi m)^{\frac{1}{2}}}{v_f^{\frac{1}{3}}} e^{-E/kT}$$

where v_f is the free volume of the liquid, E is the height of the potential barrier between cells, and T is the absolute temperature. McLaughlin estimated E and f from experimental values of η for argon at its normal boiling point, and showed that $\eta_c/\eta_v < 10^{-2}$. In subsequent discussions η_c was neglected and f was assumed negligible compared to 1, giving $\eta = \sqrt{2}\nu C_v/a$, or using Eqns. (1) and (2),

$$\eta = Z_c \, \nu/v^{1/3} \tag{5}$$

with $Z_c = (2\,N)^{1/3}\,3\,k$ as a constant.

The expression for the thermal conductivity developed here follows the principle of corresponding states. If Eqn. (5) is placed in reduced units,

$$\eta^* = 3(2)^{1/3}\ \nu^*/v^{*1/3} \tag{6}$$

where $\eta^* = (m^{1/2}\sigma^2/k\ \varepsilon^{1/2})\eta$, and $\nu^* = (\sigma m^{1/2}/\varepsilon^{1/2})\nu$. Using Eqn. (4) for ν results in $\eta^* = (3^{3/2}\ 2^{2/3}/\eta v^{*5/3})[(L/v^{*2}) - M]^{1/2}$. As was evident from Eqns. (4) and (5), the thermal conductivity is a function of volume only.

Using Eqn. (6) for the total thermal conductivity, the derivatives of η^* can be calculated as

$$(\partial\eta^*/\partial T^*)_P = \alpha^*\eta^*[-\tfrac{1}{3}-\gamma] \tag{7}$$

$$(\partial\eta^*/\partial P^*)_T = \beta_T^*\eta^*[\tfrac{1}{3}+\gamma] \tag{8}$$

$$(\partial\eta^*/\partial v^*)_T = (v^*)^{-1}\eta^*[-\tfrac{1}{3}-\gamma] \tag{9}$$

and

$$(\partial\eta^*/\partial T^*)_v = 0 \tag{10}$$

where $\alpha^* = (v^*)^{-1}(\partial v^*/\partial T^*)_P$, $\beta_T^* = -(v^*)^{-1}\,(\partial v^*/\partial P^*)_T$, $\gamma = -(\mathrm{d}\ln \nu^*/\mathrm{d}\ln v^*)$, $P^* = (\sigma^3/\varepsilon)P$, and $T^* = (k/\varepsilon)T$.

The quantity γ as defined here is analogous to Grüneisen's constant for solids. If Eqn. (4) is used to relate ν and v, then

$$\gamma = \frac{[(7L/3v^{*2}) - (4M/3)]}{[(L/v^{*2}) - M]} \tag{11}$$

From Eqn. (11), γ is positive and ranges from about 1 to 5 in the range of v^* appropriate to liquids. These values are in line with the analogy to Grüneisen's constant. Since α^*, β_T^* and γ are all positive quantities the model predicts that $(\partial\eta^*/\partial T^*)_P<0$, $(\partial\eta^*/\partial P^*)_T>0$, and $(\partial\eta^*/\partial v^*)_T<0$ for classical liquids. This is generally experimentally observed. Eqn. (10) does not hold exactly for real classical liquids but $(\partial\eta^*/\partial T^*)_v$ is generally found to be small compared to the other derivatives[6].

III. QUANTUM MECHANICAL MODIFICATIONS

A number of the assumptions that have gone into the classical model are no longer valid for liquids influenced by quantum effects. The two most significant changes involve new expressions for C_v and ν. For the classical model, the assumption was made that each molecule acted as a three dimensional harmonic oscillator to calculate C_v. Maintaining this general assumption, a quantum mechanical expression for C_v would use either the Debye or Einstein model to calculate C_v of a collection of harmonic oscillators influenced by quantum effects. The Einstein model was chosen here since it corresponds to the independent particle nature of the cell model. The resulting expression for the heat capacity is[7] $C_v = 3k\,g(T/\theta)$, where

$$g(T/\theta) = \frac{(\theta/T)^2\, e^{\theta/T}}{(e^{\theta/T}-1)^2}.$$

The quantity θ is a characteristic temperature called the Einstein temperature, and is related to the oscillator frequency, ν_E, by $\theta = h\nu_E/k$.

For the model to be useful for calculations, θ must be known. In the Einstein model of a three dimensional crystal, θ is related to the zero point energy, E_0, of the independently oscillating particles by

$$E_0 = (3/2)k\,\theta \tag{12}$$

Since the model of the liquid state used here consists of independently oscillating particles confined to specific cells, the same relation may be assumed. Now Levelt and Hurst have outlined the calculation of the zero point energy (as well as the higher energy levels) of a molecule in a cell. They used the results of the energy level calculations in their quantum mechanical cell model of liquids[8] (a quantum mechanical version of the Lennard–Jones and Devonshire cell theory) and for the estimation of zero point properties of crystals[9]. The zero point energy is obtained by numerical solution of the Schrödinger equation. Although many solutions of the Schrödinger equation have been obtained for simple potentials, such as a molecule confined to a cubical or spherical cell, Levelt and Hurst have succeeded in using the same potential as the classical cell theory, *i.e.*, the Lennard-Jones 6–12 intermolecular potential summed over a fcc lattice, to obtain the potential experienced by a molecule in its cell. A general result of the calculation is that E_0, and thus θ, are functions of volume only. Specific calculations of θ for ^{3}He and ^{4}He, and the relationship between θ and v, will be discussed in Section V. For the present it is sufficient to know that θ can be calculated and that it is a function of v only.

The second change required when quantum effects are important is in the calculation of the vibrational frequency of the molecule in its cell. The harmonic approximation is no longer valid[10]. The relatively large motion of the molecules about their equilibrium location (especially for ^{4}He and ^{3}He) due to the high zero point energy makes the harmonic approximation very poor. In fact, imaginary frequencies are obtained if this approximation is used with helium[9]. Since the molecule in its cell was considered as an oscillator for calculating C_v, a similar assumption will be made here. The vibrational frequency, ν, of the molecule in its cell will be equated to the oscillator frequency obtained from the Einstein model, $\nu = \nu_E = k\theta/h = (2/3)E_0/h$.

The two changes just discussed are sufficient to calculate the thermal conductivity if, following McLaughlin, the fraction of vacant cells, f, is assumed to be negligible compared to one, and the contribution of the convective mechanism is also assumed to be negligible. Any estimation of the fraction of vacant cells is a difficult problem. Two limiting approaches can be discussed. The use of the molar volume of the liquid for the calculation of the lattice spacing [Eqn. (1)] inherently assumes that the cell volume expands as the molar volume increases. The increase in the molar volume is thus assumed to be mainly due to an increase in cell volume, and not to an increase in the number of vacant cells. The value of f would remain very small in this case. The other extreme assumes that the cell volume remains constant at its value in the solid at melting as the molar volume increases. The increase in molar volume is accounted for by an increase in the number of vacant cells. In this second case the fraction of vacant cells is given by[11]

$$f = 1 - (v_s/v) \tag{13}$$

where v_s is the molar volume of the solid at melting. The lattice spacing is then calculated using v_s instead of v. It was decided here to follow the assumption that the increase in molar volume is associated with an increase in cell volume, and that $(1-f) \approx 1$. This assumption relates the model to the original cell theory where the presence of holes in the lattice was neglected.

The contribution from the convective mechanism cannot be calculated without an accurate estimate of f, since η_c is proportional to f. An upper limit estimate of f, in the sense of the model adopted here, is available in Eqn. (13), and ranges from 0.05 to 0.4. To complete the calculation of η_c estimates of E and v_f are needed. The height of the potential barrier between cells was estimated as $E = U_0 - E_0 = U_0 - (3/2)k\,\theta$ where U_0 is the lattice energy[12], $U_0 = 12\varepsilon\,[(1.2045/v^{*2}) - (0.5055/v^{*4})]$. The frequency, ω, was calculated as in the classical case. An estimate of the probability of tunnelling through the barrier indicates that tunnelling should not contribute significantly to the frequency of molecules escaping from their cells. The free volume was estimated from an approximate relation[12] $v_f = (4\sqrt{2}\pi/3N)[v^{1/3} - (N\sigma^3)^{1/3}]^3$, since values of the integrals required for a more exact calculation were not available at the low reduced temperatures encountered in this work. Using these estimates of f, E, and v_f, we find $\eta_c/\eta_v < 10^{-1}$.

Since the estimate of f may be orders of magnitude larger than the value appropriate to these calculations[13], the assumption that η_c is negligible seems justified. It should be pointed out that if calculations are carried through using Eqn. (13) to define f, the values of η obtained $(\eta_v + \eta_c)$ are only a very weak function of f, since as f increases from zero the contribution from η_c increases but the contribution from η_v decreases a similar amount.

The resulting expression for the total thermal conductivity is

$$\eta = Z\,\theta\, g(T/\theta)/v^{1/3} \tag{14}$$

where $Z = (2N)^{1/3}\, 3k^2/h$ is a constant. As with the classical model, Eqn. (14) can be placed in reduced units, giving

$$\eta^* = 3(2)^{1/3}\, \theta^*\, g(T^*/\theta^*)/v^{*1/3}\, \Lambda^* \tag{15}$$

where $\Lambda^* = h/\sigma\,(m\,\varepsilon)^{1/2}$, and $\theta^* = k\theta/\varepsilon$. To relate the quantum mechanical model to the classical model it should be noted that $C_v^* = 3\, g(T^*/\theta^*)$, and $v^* = \theta^*/\Lambda^*$.

IV. DISCUSSION

Although the thermal conductivity can be calculated directly from Eqn. (14), it is perhaps more instructive to examine the temperature, pressure and volume variation of η^* as predicted by the quantum mechanical model, and compared with the classical model. The qualitative influence of quantum effects on η^* can be demonstrated in this manner.

The influence of quantum effects on the magnitude of η^* can be seen from a comparison of Eqns. (6) and (15). The main difference is the additional factor $g(T^*/\varepsilon^*)$ in the quantum mechanical expression. This function is the well known Einstein specific heat function, approaching 1 for $T^* \gg \theta^*$ and approaching 0 exponentially for $T^* \ll \theta^*$. Thus $\eta_q^*/\eta_{cl}^* = g(T^*/\theta^*)$, where the subscripts indicate the quantum and classical expressions. At low temperatures $(T^* < \theta^*)$ η^* should begin to drop below the classical values, the deviation increasing with decreasing temperature. A second phenomenon shows up here in that the values of θ^* appropriate to different substances increase as quantum effects become important (with increasing value of Λ^*)[14]. Thus, the values of θ^* appropriate to ^{3}He are larger than those for A or N_2. This increase of θ^* with increasing Λ^* produces a larger quantum effect on η^* of ^{3}He ($\Lambda^* = 3.08$) than on η^* of ^{4}He ($\Lambda^* = 2.67$), even though both liquids exist in a similar temperature range. The effects described here have previously been experimentally observed[1], and correlated with the parameter Λ^*.

The derivatives of η^* show even more interesting quantum effects. Using Eqn. (15) to define η^*, we have

$$(\partial\eta^*/\partial T^*)_P = \alpha^*\eta^*[-1/3-\gamma+G(T/\theta)(\gamma+(\alpha^* T^*)^{-1})] \tag{16}$$

$$(\partial\eta^*/\partial P^*)_T = \beta_T^*\eta^*[1/3+\gamma-\gamma G(T/\theta)] \tag{17}$$

$$(\partial\eta^*/\partial v^*)_T = (v^*)^{-1}\,\eta^*[-1/3-\gamma+\gamma G(T/\theta)] \tag{18}$$

and

$$(\partial\eta^*/\partial T^*)_v = (T^*)^{-1}\,\eta^*\,G(T/\theta) \tag{19}$$

where $G(T/\theta) = \dfrac{d\ln g(T/\theta)}{d\ln(T/\theta)} = G(T^*/\theta^*)$, and $\gamma = -(d\ln\theta^*/d\ln v^*)$ in light of the relation between θ^* and v^*. The function $G(x)$ has the following properties for $x>0$; $G(x)>0$, $\lim_{x\to\infty} G(x)=0$, and $\lim_{x\to 0} G(x) = +\infty$.

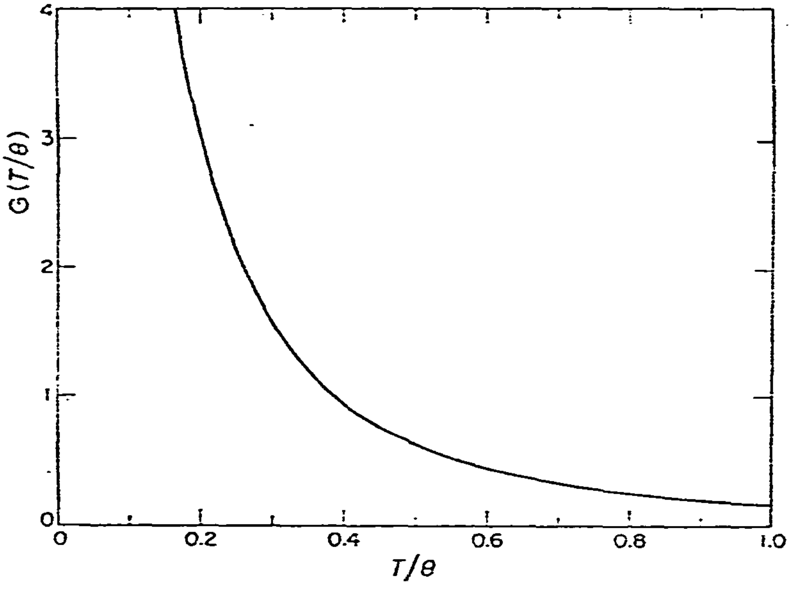

Fig. 1. The function $G(T/\theta)$ as a function of (T/θ).

Fig. 1 shows a plot of $G(T/\theta)$ as a function of (T/θ).

The quantum mechanical expressions for the derivatives [Eqns. (16)–(19)] all differ from their classical counterparts [Eqns. (7)–(10)] by terms proportional to $G(T/\theta)$. When (T/θ) is large $G(T/\theta)$ approaches zero, and the quantum mechanical expressions approach the classical expressions. As (T/θ) decreases the terms involving $G(T/\theta)$ can make significant contributions to the derivatives. Since $G(T/\theta)$ is positive, the quantum mechanical contributions to Eqns. (16)–(18) tend to change the sign of the derivatives, while for Eqn. (19) the quantum mechanical contribution increases the derivative from zero.

Experimentally, $(\partial\eta^*/\partial T^*)_P$ is negative for classical liquids but becomes increasingly positive[1] through the series D_2, H_2, ^{4}He, and ^{3}He. The model presented here predicts just this behavior; since the range of liquid state temperatures becomes lower through this series of materials, the range of values of $G(T/\theta)$ appropriate to each material increases through the series, making $(\partial\eta^*/\partial T^*)_P$ increasingly positive.

Experimentally, $(\partial\eta^*/\partial P^*)_T$ is positive for classical liquids, and in most cases, for liquids influenced by quantum effects. Eqn. (17) predicts that $(\partial\eta^*/\partial P^*)_T$ should be positive for classical liquids, but decreases with increasing quantum effects, finally becoming negative. McLaughlin has shown that $(\beta_T^*\eta^*)^{-1}(\partial\eta^*/\partial P^*)_T$ has a value in the order of 2.2 for classical liquids[4], while experimental data for liquid ^{3}He give this quantity values from about 1/2 to 1 between 1.5 K and 3 K[16]. At very low temperatures, the experimental $(\partial\eta^*/\partial P^*)_T$ of liquid ^{3}He does become negative[15]. Although the qualitative predictions of Eqn. (17) are followed, it will be seen in Section V that calculations for liquid ^{4}He and ^{3}He give negative values of $(\partial\eta^*/\partial P^*)_T$ in a higher temperature range than they are observed experimentally.

The behavior of $(\partial\eta^*/\partial v^*)_T$ should be very similar to $(\partial\eta^*/\partial P^*)_T$ since they are related by $(\partial\eta^*/\partial P^*)_T = \beta_T^* v^*(\partial\eta^*/\partial v^*)_T$. Thus, the same statements that have been made in the preceding paragraph carry through for $(\partial\eta^*/\partial v^*)_T$.

The quantity $(\partial\eta^*/\partial T^*)_v$ is not extensively known for liquids. Data taken on liquid ammonia indicate that, within experimental error, it is zero[17]. Data on various classical high density gases indicate that it is a small positive quantity[6]. Experimental data on liquid ^{4}He and ^{3}He show that $(\partial\eta^*/\partial T^*)_v$ is positive and increases as the temperature decreases, in line with the prediction of Eqn. (19)[16].

A point about the "anomalous" regions of thermal conductivity of liquid ^{4}He and ^{3}He should be made. As the λ-transition is approached, η of liquid ^{4}He goes through a minimum and increases sharply. Below the transition, helium II exhibits properties such that the usual definition of thermal conductivity is not valid. At very low temperatures (below 1 K) η of liquid ^{3}He goes through a minimum and increases with decreasing temperature as T^{-1}. Both of these phenomena are related to a quantum statistical behavior of a collection of bosons (^{4}He) or fermions (^{3}He). The model presented here ignores the statistics of the molecules, treating them as a collection of independent particles. The value of this treatment lies mainly in the intermediate region, where quantum mass effects are becoming important, but before the quantum statistics of the molecules begin to influence their behavior.

In summary, the model of liquid thermal conductivities presented here predicts that with increasing quantum effects, changes in the magnitude of η^*, and in the magnitude and possibly the sign of its derivatives, should occur. Quantum effects were mainly introduced through a quantum expression for the heat capacity of a molecule vibrating in its cell. The expression involves a characteristic temperature, θ. Quantum effects are important when the temperature is small compared to θ, and are unimportant when the temperature is large compared to θ. The predictions of the model are qualitatively in line with experimental behavior.

V. CALCULATIONS

The thermal conductivity of liquid ^{4}He and ^{3}He has been measured[16] between 1.5 K and 4 K, and at pressures up to 34 atm. Values of η for both liquids were calculated using Eqn. (14), to determine if the model quantatively predicts the correct thermal conductivities.

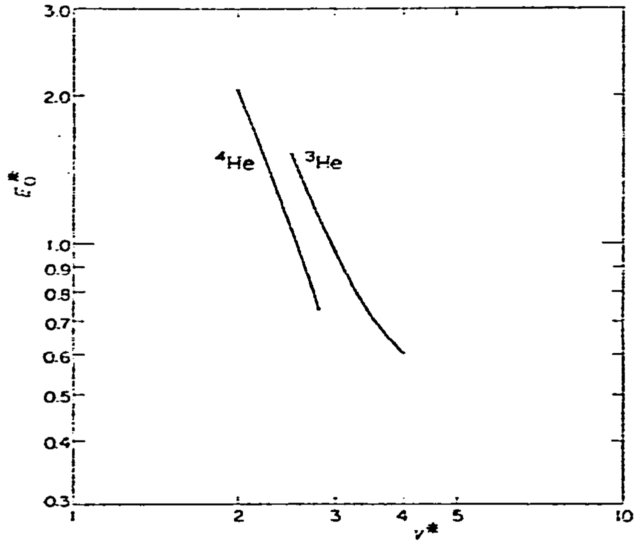

Fig. 2. Reduced zero point energy of liquid ^{3}He and ^{4}He as a function of reduced molar volume.

The first order of business is the calculation of θ, or equivalently, E_0, since Eqn. (12) relates the two quantities. As stated in Section III, Levelt and Hurst have provided a procedure for calculating E_0 by a numerical solution of the Schrödinger equation with a potential obtained from summing the Lennard–Jones 6–12 intermolecular potential over a number of shells of nearest neighbors. They calculated E_0 of ^{4}He for a range of values of v^*. In this work, values of E_0 were calculated for liquid ^{3}He and ^{4}He using the potential obtained from the first ten shells of nearest neighbors. The values of the parameters in the Lennard–Jones potential were $(\varepsilon/k) = 10.22$ K, and $\sigma = 2.556$ Å, resulting in $\Lambda^* = 2.677$ for ^{4}He and $\Lambda^* = 3.084$ for ^{3}He. Table I contains the values of $E_0^* = E_0/\varepsilon$ obtained in this manner, and Fig. 2 shows a plot of E_0^* as a function of v^*. To facilitate the use of the calculated data, values of E_0^* were fitted by a least squares method to the function

$$E_0^* = A(v^*)^{-l} \exp(nv^*). \qquad (20)$$

Table II contains the values of the parameters obtained. A function of this form results in $\gamma = -(\mathrm{d} \ln \theta^*/\mathrm{d} \ln v^*)$ being $\gamma = l - nv^*$.

Since the measurements of η were made as a function of pressure and not volume, values of v coresponding to the pressure and temperature of the measured η were

TABLE I

CALCULATED ZERO POINT ENERGY OF ^{3}He AND ^{4}He

v^*	E_0^*		
	^3He	^4He	$^4He^a$
2.0		2.065	2.053
2.1		1.793	
2.2		1.563	1.552
2.3		1.367	
2.4		1.199	1.190
2.5	1.519	1.055	
2.6	1.373	0.932	
2.7	1.247	0.826	
2.8	1.139	0.734	
2.9	1.045		
3.0	0.966		
3.1	0.897		
3.2	0.839		
3.3	0.789		
3.4	0.747		
3.5	0.711		
3.6	0.681		
3.7	0.656		
3.8	0.634		
3.9	0.617		
4.0	0.602		

[a] Values obtained by Hurst and Levelt (Ref. 9).

TABLE II

VALUES OF THE PARAMETERS IN EQUATION (20)

Parameter	^3He	^4He
A	15.597	21.098
l	5.699	1.804
n	1.159	-0.537

necessary. The density data of Sherman and Edeskuty[18] were used for ^{3}He, and the density data of Elwell and Meyer[19] for ^{4}He. Table III shows a comparison of the experimental and calculated values of η for ^{3}He, while Table IV shows the same comparison for ^{4}He. The values of v used are included. In neither case is the agreement good. At constant pressure the calculated η generally increases with increasing temperature, following the experimental behavior. At constant temperature, the calculated η increases with increasing pressure at the higher temperatures, but decreases with increasing pressure at the lower temperatures. Thus, the calculations indicate that $(\partial\eta/\partial P)_T$ changes from positive to negative as the temperature decreases in this range. This is contrary to the experimental behavior which shows a positive $(\partial\eta/\partial P)_T$ over the

TABLE III

COMPARISON OF EXPERIMENTAL AND CALCULATED THERMAL CONDUCTIVITIES OF LIQUID ^3He

T(K)	*P (atm)*	*v (cc/mole)*	$\eta \times 10^{-4}$ *(watts/cm K)*	
			Exp.	*Calc.*
1.50	4	33.30	1.10	0.58
	10	30.27	1.13	0.48
	16	28.45	1.14	0.38
	22	27.36	1.17	0.31
	28	26.16	1.18	0.22
	34	25.32	1.21	0.16
2.00	4	33.80	1.33	0.86
	10	30.25	1.37	0.85
	16	28.59	1.44	0.79
	22	27.23	1.50	0.70
	28	26.23	1.53	0.61
	34	25.41	1.57	0.52
2.53	4	34.60	1.53	1.03
	10	30.84	1.60	1.13
	16	28.80	1.72	1.14
	22	27.42	1.78	1.11
	28	26.36	1.85	1.05
	34	25.51	1.91	0.97
3.00	4	35.85	1.69	1.07
	10	31.34	1.82	1.27
	16	29.14	1.96	1.36
	22	27.64	2.04	1.38
	28	26.53	2.10	1.38
	34	25.64	2.18	1.34
3.50	4	37.94	1.80	1.05
	10	32.07	2.01	1.34
	16	29.56	2.15	1.49
	22	27.94	2.24	1.59
	28	26.75	2.33	1.64
	34	25.82	2.40	1.65
3.95	4	40.76	1.88	0.98
	10	33.00	2.10	1.34
	16	30.08	2.29	1.55
	22	28.34	2.42	1.70
	28	27.05	2.55	1.79
	34	26.07	2.64	1.85

entire range, although it does decrease with decreasing temperature. The calculated values are all below the experimental values.

Although the agreement between the calculated and experimental values of η is only fair, it should be pointed out that the model has no constants which can be

TABLE IV

COMPARISON OF EXPERIMENTAL AND CALCULATED THERMAL CONDUCTIVITIES OF LIQUID ^{4}He

T(K)	*P (atm)*	*v (cc/mole)*	$\eta \times 10^{-4}$ *(watts/cm K)*	
			Exp.	*Calc.*
2.42	1	27.15	1.50	1.12
	10	24.81	1.72	1.12
	18	23.54	1.86	1.03
	26	22.63	1.96	0.92
	34	21.97	1.99	0.82
2.62	1	27.40	1.60	1.17
	10	24.95	1.82	1.24
	18	23.63	1.99	1.19
	26	22.69	2.09	1.10
	34	22.02	2.15	1.01
2.82	1	27.66	1.68	1.21
	10	25.06	1.96	1.35
	18	23.73	2.11	1.33
	26	22.77	2.21	1.27
	34	22.09	2.30	1.19
3.01	1	27.93	1.73	1.22
	10	25.19	2.03	1.43
	18	23.80	2.18	1.45
	26	22.85	2.32	1.41
	34	22.18	2.40	1.35
3.60	1	29.28	1.89	1.16
	10	25.72	2.26	1.57
	18	24.18	2.46	1.72
	26	23.12	2.60	1.77
	34	22.37	2.75	1.77
3.95	1	30.55	2.04	1.03
	10	26.13	2.37	1.59
	18	24.43	2.61	1.81
	26	23.32	2.80	1.91
	34	22.54	2.91	1.96

adjusted to bring the calculations into line with the experimental results. It may be possible to use θ as an adjustable parameter to correlate the measurements of η of liquid ^{4}He and ^{3}He. That procedure was not attempted here, since the purpose of this work was to outline the model for liquid thermal conductivities and to compare it with existing experimental data.

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