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Transport Properties of He^3 , He^4 , H_2 , D_2 , T_2 , and Ne

In the Liquid State

According to the Quantum Mechanical Principle
Of Corresponding States *

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ABSTRACT

The principle of corresponding states, in which the state variables have been reduced by the molecular parameters of the Lennard-Jones two-body interaction potential and the theory has been extended to account for quantum deviations from classical behavior, has been used to investigate the liquid state transport properties of He^3 , He^4 , H_2 , D_2 , T_2 , and Ne. The thermal conductivity and viscosity have been predicted for the liquid in equilibrium with the vapor along the coexistence curve up to the critical point. The measured positive temperature coefficients of thermal conductivity for the lighter species are consistent with this study. The heavier monatomic species, Ne and ^{Ar}Ar, as well as near-spherical molecules such as CH_4 are observed to deviate from the behavior of the diatomic molecules for both transport properties studied.

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Introduction

The principle of corresponding states provides a practical method for making use of the measured properties of one or more substances to predict the properties of other substances under conditions for which no data exist and no satisfactory theoretical treatments may be applied. This principle was originally formulated by van der Waals for classical systems and subsequently the concept of accounting for deviations caused by quantum effects, was suggested by Byk ⁽¹⁾. The further development of the quantum mechanical principle of corresponding states has been due primarily to de Boer and his collaborators ^(2,3,4). Early efforts were concerned with equation of state and vapor pressure correlations and predictions, the most successful of which was the prediction of the vapor pressure and the critical parameters of He³ prior to its liquefaction ⁽⁵⁾. Recognition of the applicability of the principle of corresponding states in quantum mechanics to transport properties has existed for some time. A good discussion is given in Hirschfelder et al. ⁽⁶⁾.

Theory

Provided that the total potential energy can be written as a sum of intermolecular pair potentials of the form $\varphi(r) = \epsilon \varphi^*(r/\sigma)$, where ϵ and σ are characteristic energy and distance parameters and φ^* is a universal function of the one variable r/σ , the transport properties may be written in

terms of the seven parameters v , T , m , k , σ , ϵ , and h . From dimensional arguments, the reduced transport coefficients of thermal conductivity and viscosity may be written as

$$\kappa^* = \kappa^*(v^*, T^*, \Lambda^*) \quad (1)$$

$$\eta^* = \eta^*(v^*, T^*, \Lambda^*) \quad (2)$$

in which the reduced temperature, volume, and Planck constant are

$$T^* = kT/\epsilon \quad (3)$$

$$v^* = v/\sigma^3 \quad (4)$$

$$\Lambda^* = h/\sigma \sqrt{m\epsilon} \quad (5)$$

The validity of these expressions has recently been confirmed by Helfand and Rice ⁽⁷⁾ by use of auto-correlation function expressions for the transport properties.

The values of ϵ/k and σ used herein are taken from Hirschfelder et al. ⁽⁸⁾ and are those obtained from second virial coefficients. These values were used as being the best consistent set and include values for the light gases from quantum mechanical formulae. It is believed that the use of this set does not significantly compromise the results obtained since in most cases the differences as compared with the values obtained from viscosity are small. A different consistent set might somewhat alter the nature of the intermediate constructions depicted in Figures 2 and 6.

When sufficient data become available it would seem more appropriate to use the molecular parameters derived uniformly from measured transport properties. The values for ϵ/k , σ , and Λ^* are given in Table I together with bibliographical reference notation.

The molecular parameters ϵ/k and σ are obtained from the Lennard-Jones 6-12 type molecular interaction potential

$$\varphi(r) = 4\epsilon \left[(\sigma/r)^{12} - (\sigma/r)^6 \right] \quad (6)$$

in which ϵ is the depth of the potential field and σ is the value of r for which $\varphi(\sigma) = 0$. The problems associated with the use of this type of potential function are discussed by de Boer ⁽⁹⁾.

Λ^* is the ratio of the de Broglie-wavelength of relative motion of two identical particles, when their mean relative kinetic energy is ϵ , to the parameter σ .

Table I: Force Constants, Λ^* , and References

Species	ϵ/k , °K	σ , Å	Λ^*	κ references	η references
He ³	10.22	2.556	3.08	(10)	(11)
He ⁴	10.22	2.556	2.67	(12)	(11)
H ₂	37.00	2.928	1.729	(13)	(14)
D ₂	37.00	2.928	1.223	(15)	----
T ₂	37.00	2.928	1.000	----	----
Ne	35.60	2.749	0.593	(15)	(17)
CH ₄	148.2	3.817	0.235	(18)	(19)
N ₂	95.05	3.698	0.226	(20)	(21)
CO	100.2	3.763	0.220	(18)	(22)
A	119.8	3.405	0.186	(23)	(24)
Kr	171	3.60	0.102	----	----

Liquid Thermal Conductivity

Figure 1 shows the measured thermal conductivities (smoothed solid lines) as a function of the reduced temperature. The positive temperature coefficient of the thermal conductivity is a result of large quantum effects. Quantum effects are also evident from the wide range of reduced conductivities obtained for the light species. The thermal conductivity of a liquid becomes more nearly gas-like both in magnitude and in its temperature dependence as the mass of the molecule decreases. This is due to the influence of the large zero point energies for light molecules in "blowing up" the liquid structure and making it effectively more gas-like. The conductivity curves were extrapolated in each case to the reduced triple point temperatures and the triple point locus was constructed for the diatomic species H_2 , D_2 , CO , and N_2 . Two branch triple point loci are also shown (broken lines) to indicate the nonconformity among the diatomic molecules, the monatomic molecules -Ne and Ar, and a light spherical molecule - CH_4 . Oxygen was also considered but has been rejected from this analysis since it was found to depart appreciably from the diatomic pattern for both thermal conductivity and viscosity, possibly because of complications arising from its paramagnetic character.

Success in correlating both thermal conductivity and viscosity by Thodos et al. (25, 26) for the heavier diatomic molecules provides

a basis for establishing the heavy molecule end of the critical point loci as nearly horizontal asymptotic lines. For the thermal conductivity no other good tie points exist and the critical point locus is more conjectural. It is believed that a single critical point locus will adequately include all types of molecules because of the lower density, and hence smaller interaction at the critical point in comparison with the liquid phase near the triple point.

Fortunately the effect of errors in locating the helium end of this locus is minimized in terms of predicting the behavior of the thermal conductivity for H_2 , D_2 , etc. The high temperature ends of the He^3 , He^4 , H_2 , D_2 , A, and N_2 thermal conductivity curves were extrapolated (broken lines) to their respective reduced temperatures. Figure 2 was then constructed from Figure 1 by cross plotting isotherms of reduced conductivity versus Λ^* . The CO thermal conductivity data were not used. Then from Figure 2 the values of η^* for tritium ($\Lambda^* = 1.00$) were obtained to predict the temperature dependence of the thermal conductivity of tritium along the vapor pressure curve as shown in Figure 1. Lastly, it may be pointed out that an extension of the Ne data of Löchtermann ⁽¹⁶⁾ to the critical temperature locus would appear to give some values of thermal conductivity which would be very near to those predicted for tritium and would also require an s-shaped curve which seems improbable in view of the value of T_c^* for Neon, i.e. 1.247. A predicted curve for the thermal conductivity of Neon predicated upon

behavior similar to argon and tritium is also shown. Derivation of the thermal conductivities of the unsymmetrical isotopic species of hydrogen - HT, HD, and DT - is a triviality and can easily be obtained from Figure 2. Note that de Boer's theory does not distinguish between the behavior of HT and D₂ (27).

Figure 2 again shows the nonconformity among the different types of species considered toward the heavy molecule terminus of the triple point loci. In addition the double valued thermal conductivity behavior is evident from the isotherms which lie above the diatomic molecule triple point locus. The crossover is seen to occur at reduced temperatures such that tritium should be the heaviest molecule exhibiting a thermal conductivity maximum along its vapor pressure curve.

Liquid Viscosity

The quantum effects upon liquid viscosity are manifested primarily by the wide range of values of reduced viscosity as may be seen in Figure 3. The viscosity of He⁴ shows a lambda point precursor behavior with the dropping of the viscosity appreciably above the lambda point temperature. The triple point loci for the heavier molecules were constructed in a manner similar to that discussed for the thermal conductivity. Again, the solid lines exhibit experimental data. One data value for viscosity of super-cooled CH₄ was available. The justification for locating the heavy

molecule end of the critical point locus is similar to that advanced in the discussion of the thermal conductivity. Taylor and Dash (11) measured the viscosity of both liquid and vapor He^3 just below and above the critical temperature ($T_c = 3.34^\circ\text{K}$) at 3.338°K and 3.35°K respectively. These and one single N_2 viscosity value are shown as x's.

Figure 4 is a linear extrapolation of the work of Tjerkstra (28) to the critical temperature of He^4 . The viscosity values thus obtained were then plotted versus density on semi-log paper and extrapolated (shown in Figure 5) to the critical density as reported by Edwards and Woodbury (29). A critical point viscosity for He^4 of $31.2(10)^{-6}$ g/cm-sec was obtained. The critical point locus of Figure 3 was constructed through the He^3 and He^4 viscosity values and the N_2 and CO limits obtained by Thodos. The hydrogen, nitrogen, and helium viscosity curves were then extrapolated (broken lines) to their respective critical temperatures. Figure 6 was constructed in the same fashion described for the thermal conductivity, i.e. Figure 2. The isotherms for T^* between 0.5 and 0.7 were determined from Figure 3 with several points and the balance with fewer "fixes" from Figure 3 were constructed to give a reasonable pattern. Values of reduced viscosity at $\Lambda^* = 1.00$ and 1.22 were then taken from Figure 6 to predict the respective viscosities of tritium and deuterium (broken lines of Figure 3). The viscosity curves of Ne and CO closely parallel those of A and N_2 respectively.

The values of the reduced temperatures at the critical points and the triple points as used herein for the various species were obtained from the N.B.S. compilation (23) and are listed in Table II.

Table II: Reduced Critical and Triple Point Temperatures

Species	T_c^*	T_{TP}^*
He ³	0.326	-----
He ⁴	0.509	-----
H ₂	0.895	0.377
D ₂	1.034	0.506
T ₂	1.181	0.557
Ne	1.247	0.689
CH ₄	1.286	0.598
N ₂	1.329	0.665
CO	1.326	0.678
A	1.259	0.700
Kr	-----	0.697

Discussion and Results

In lieu of experimental data, the principle of corresponding states in quantum mechanics has been applied to the light molecular species to predict the liquid state thermal conductivities and viscosities along their coexistence curves. The positive temperature coefficient of thermal conductivity for He^3 , He^4 , H_2 , and D_2 is shown to be part of a consistent pattern of quantum deviations. This effect is also predicted for tritium. The existing data for Ne thermal conductivity does not follow the expected pattern of this analysis. On the heavy molecule end of the triple point loci (reduced thermal conductivity and/or viscosity versus reduced temperature) differences are observed among the diatomic molecules, the monatomic molecules, light spherical molecules, and oxygen.

The prediction of the liquid viscosities was facilitated by extrapolation of the data of Tjerkstra for He^4 . The viscosity of He^4 at its critical point was estimated to be $31.2(10)^{-6}$ g/cm-sec. This value greatly facilitated the construction of the viscosity critical point locus. Values for those transport properties at the critical temperatures believed to be well predicted are given in Table III.

The nature of this study is an empirical analysis based upon the principle of corresponding states in quantum mechanics. Extrapolations of the transport properties and a method of cross plotting data in coordinates reduced by molecular parameters have

Table III: Transport Properties at the Critical Point

Species	κ_c , cal/sec-cm-°K, (10) ^a	η_c , g/cm-sec, (10) ^a
He ³	-----	18.69
He ⁴	-----	31.2
H ₂	252	43.8
D ₂	200	64.8
T ₂	179	82.2
Ne	110	168
N ₂	(85.5)*	(182)
CO	(86.1)	(186)
A	94.3	285

* Values in parentheses are from references 25 and 26.

been used for predicting the transport properties of other molecules. The techniques used will be greatly strengthened as more data become available. A very few values of thermal conductivity and viscosity nearer to the critical condition for the several molecular species will considerably enhance the accuracy of the predictions.

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FIGURE I