

AB INITIO CALCULATIONS FOR HELIUM-4 OF THERMODYNAMIC AND TRANSPORT PROPERTIES OF THE GAS AND THE GROUND STATE ENERGY OF THE LIQUID

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[Manuscript received 20 March 1972]

Abstract

A potential energy curve for the ^4He diatom obtained from a perturbation theory solution of the Schrödinger equation is used to calculate the viscosity, thermal conductivity, self-diffusion coefficient, and second virial coefficient of gaseous ^4He . In addition, the ground state energy of the zero-temperature liquid is obtained by a variation procedure using a trial wavefunction in conjunction with the Monte Carlo method. The results are in good agreement with experiment.

I. INTRODUCTION

During recent years a number of advances have been made towards the determination of accurate semi-empirical potential functions for the interactions between atoms of ^4He (Bruch and McGee 1967, 1970; Beck 1968). The number of *ab initio* determinations of the interaction potential has been smaller and these have been mainly confined to short-range repulsions (Phillipson 1962; Kestner and Sinanoglu 1966; Gilbert and Wahl 1967) and long-range multipole attractions (Bell 1965; Chan and Dalgarno 1965; Davidson 1966). The semi-empirical potentials have been generally determined by combining some suitable form for the bowl of the potential with these limiting forms, and then making adjustments to the bowl until the gas-phase thermodynamic and transport coefficients are satisfactorily represented. Although this method is capable of leading to potential functions that give good results both for other thermodynamic properties of helium (Murphy and Watts 1970; Murphy 1972) and for the other inert gases (Barker and Pompe 1968) it is, in the main, no more than a highly refined curve-fit to certain experimental data.

In this paper we report the results of using a potential function, derived solely from quantum mechanical calculations, to obtain some thermodynamic and transport properties of ^4He . The function was built up from the results of a calculation by Snook (1971) for the bowl of the potential using symmetry-adapted perturbation theory (Murrell and Shaw 1967) and also from the known short-range and long-range forms. In the following sections we give a brief description of the potential function and the results of using it to calculate the gas-phase thermodynamic properties and transport coefficients and also the ground state energy of the liquid at zero kelvin.

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II. INTERATOMIC POTENTIAL

The method by which the bowl of the potential was obtained and a discussion of the results is given elsewhere (Snook 1971; Snook and Spurling, in preparation). The values of the potential in kelvins for a number of distances between 2.1 and 5.3 Å were:

r (Å)	2.117	2.381	2.540	2.593	2.646	2.699	2.752	2.805	2.858	2.910
$\phi(r)/k$ (K)	287.7	54.94	11.29	3.663	-1.794	-5.600	-8.166	-9.803	-10.73	-11.20
r (Å)	2.963	3.016	3.069	3.122	3.175	3.440	3.704	4.233	4.762	5.292
$\phi(r)/k$ (K)	-11.28	-11.10	-10.75	-10.29	-10.11	-6.897	-4.875	-2.099	-1.001	-0.519

To obtain the full potential function used in this work it is necessary to combine the values given above with the curve-fit to the short-range results of Phillipson (1962) and Gilbert and Wahl (1967) given by Bruch and McGee (1967) and with the dipole-dipole and dipole-quadrupole coefficients given by Bell (1965), Chan and Dalgarno (1965), and Kestner and Sinanoglu (1966).

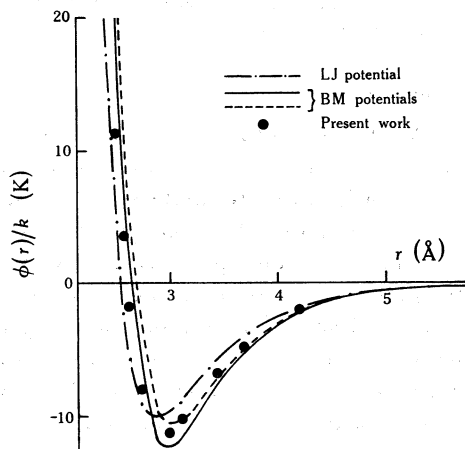


Fig. 1.—Comparison of values derived for the interatomic potential of ^4He from the present work with three semi-empirical potential functions:

LJ, Lennard-Jones (12, 6) potential;
BM, Bruch-McGee (1967, 1970).

We proceeded as follows. For distances less than 1.9 Å we used the form

$$\phi_{\text{sr}}(r) = 2.8456 \times 10^{-10} \exp(-3.6931 r - 0.07696 r^3) \text{ erg},$$

and for distances greater than 5.6 Å we used

$$\phi_{\text{lr}}(r) = -C_6 r^{-6} - C_8 r^{-8} \text{ erg},$$

where $C_6 = 1.41 \times 10^{-60} \text{ erg cm}^6$ and $C_8 = 3.82 \times 10^{-76} \text{ erg cm}^8$. At intermediate distances we obtained the potential energy of a pair of atoms separated by a distance r by using a four-point Lagrange interpolation formula fitted to those two points in the above tabulation which lay either side of r . At the extremities we constrained the Lagrange formula to give a curve that was continuous with $\phi_{\text{sr}}(r)$ and $\phi_{\text{lr}}(r)$. The resulting potential function is plotted for various values of r in Figure 1 and is compared with the well-known Lennard-Jones (12, 6) potential, for parameters $\epsilon/k = 10.22 \text{ K}$ and $\sigma = 2.556 \text{ Å}$, and with the two members of the Bruch-McGee

(1967, 1970) family of potentials used by Murphy and Watts (1970) in their study of the ground state energy of liquid ^4He . We see that although the potential is similar in form to the Bruch-McGee potentials it is softer than both. However, the well depth lies between the two semi-empirical potentials and has its minimum at a similar distance. It is clear from Figure 1 that the Lennard-Jones potential differs qualitatively from the other potentials.

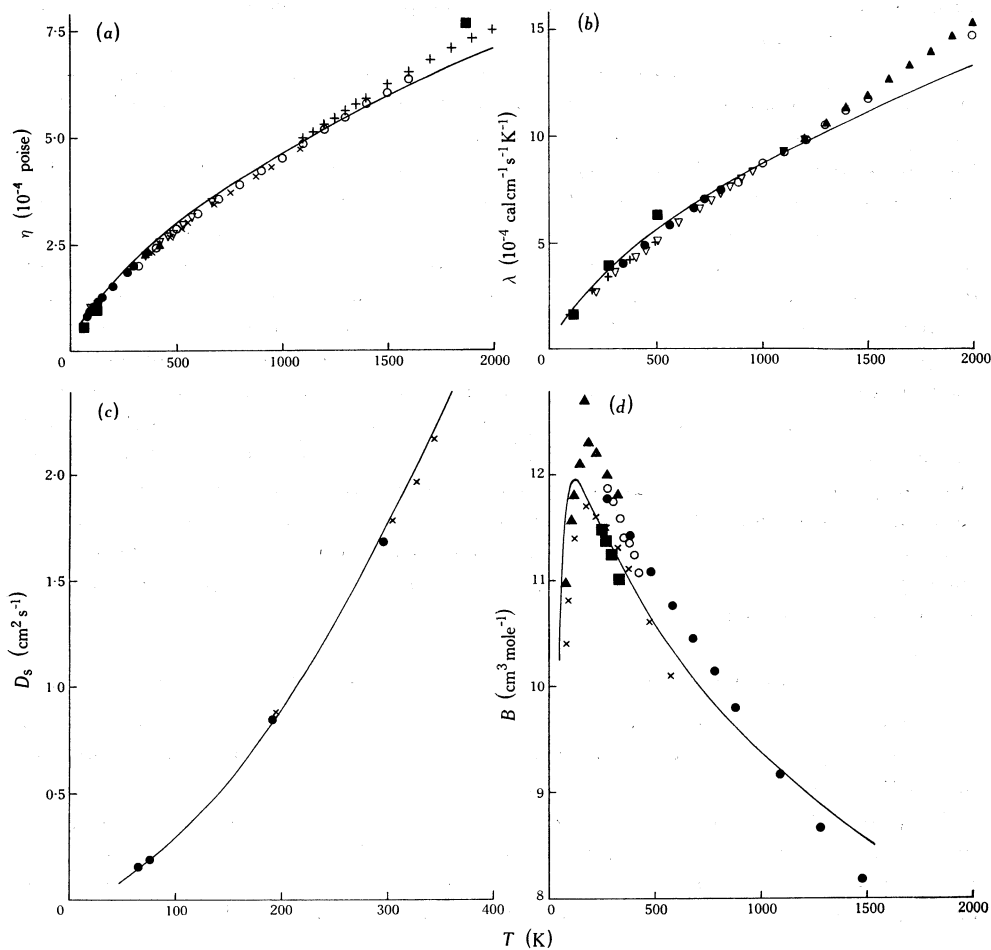


Fig. 2.—Theoretical curves for ^4He showing the variation with temperature T of (a) dilute gas viscosity η , (b) dilute gas thermal conductivity λ , (c) gaseous self-diffusion coefficient D_s , and (d) second virial coefficient B . The curves are compared with experimental data from: (a) Trautz and Binkele (1930); Trautz and Zink (1930); Trautz and Heberling (1934); Trautz and Hussein (1934); Wobser and Miller (1941); Johnston and Grilly (1942); Kestin and Leidenfrost (1959); Di Pippo and Kestin (1968); Guevara, McInteer, and Wageman (1969); Dawe and Smith (1970). (b) Trautz and Zink (1930); Kannuluick and Carman (1952); Blais and Mann (1960); Timrot and Umanskii (1965); Touloukian (1966); Gandhi and Saxena (1968); Liley (1968). (c) Bendt (1958); De Bro and Weissman (1970). (d) Michels and Wouters (1941); Keesom (1942); Schneider and Duffie (1949); Yntema and Schneider (1950); Stroud, Miller, and Brandt (1960); Blancett, Hall, and Canfield (1970); Hall and Canfield (1970); Provine and Canfield (1971).

III. GAS-PHASE PROPERTIES OF HELIUM-4

Figures 2(a)–2(d) contain the results for the viscosity, thermal conductivity, self-diffusion coefficient, and second virial coefficient of gaseous ^4He over the temperature range 100–2000 K. The calculations were carried out using methods developed by Barker, Fock, and Smith (1964) and used by Barker and Pompe (1968) and Bruch and McGee (1970) in their studies of argon and helium-4 respectively. From Figures 2(a) and 2(b) we see that at temperatures below about 1200 K the calculated and experimental values for the viscosity and thermal conductivity are in good agreement, although in both cases the calculated results are slightly higher. However, the high temperature calculations show systematic deviations from experiment, in both cases being rather low. If a detailed comparison is made between the Snook potential and the short-range form given by Bruch and McGee (1967) it is found that in the range 2.0 – 2.4 Å the former is about half of the latter. As this is a region where there could be significant errors in the perturbation calculations, it is reasonable to suggest that some of the high temperature discrepancies may be due to a poor representation of the potential in this region. The self-diffusion coefficient calculations are in good agreement with the experimental values over the temperature range considered here (see Fig. 2(c)), as is to be expected from the results for the viscosity and thermal conductivity. Finally, the comparison of experimental and calculated second virial coefficients given in Figure 2(d) is similar to that found in the work of Bruch and McGee (1967, 1970), who used semi-empirical potentials. Obviously there is not good agreement between the various experimental determinations, and the calculated results fall within the range of the experimental scatter. However, the calculations seem to suggest somewhat lower values than the bulk of the experimental data and it would appear that the errors in the repulsive region are again having an important effect.

IV. GROUND STATE ENERGY OF LIQUID HELIUM-4

The short-range correlations in liquid ^4He are commonly treated by assuming that the many-body wavefunction may be written as a Jastrow function, a product of pair functions. This is the simplest form that can be made to satisfy simultaneously the requirement that the wavefunction obey Bose–Einstein statistics and the requirement, imposed by the strong repulsion of the pair potential, that the wavefunction vanish when any two particles are close together. We make the assumption that the ground state wavefunction may be written (Murphy and Watts 1970)

$$\psi(r_1, \dots, r_N) = \exp\left(-\sum_{i < j} u(r_{ij})\right),$$

where $u(r) = (\alpha/r)^5$, α being a variational parameter. It is then straightforward to show that the ground state energy of the liquid is given by

$$E_0 = \frac{1}{2}N\rho \int \tilde{\phi}(r)g(r) \, dr,$$

where

$$\tilde{\phi}(r) = \phi(r) + (\hbar^2/2m)\nabla^2 u(r)$$

and $g(r)$ is the radial distribution function. With the form for the wavefunction assumed here, it is evident that $g(r)$ is equal to the radial distribution function of a fictitious classical gas at density ρ and temperature T_{eff} interacting through a pair potential

$$V(r) = 2kT_{\text{eff}} u(r).$$

Consequently it is possible to use the Monte Carlo method (Metropolis *et al.* 1953) to generate the $g(r)$ for many combinations of ρ and α and then to determine the ground state energy by the requirement that, at a particular density, α is such that E_0 is a minimum. Proceeding in this way we obtained the results given in Table 1. We have also included in this table the results for the Lennard-Jones potential, two

TABLE 1
COMPARISON OF RESULTS FOR GROUND STATE ENERGY OF LIQUID HELIUM-4

Potential	Ground state energy (K)					
	$\rho = 0.018$	0.020	0.021	0.022	0.023	$0.024 \text{ \AA}^{-3}$
Lennard-Jones	-5.86	-5.96	-5.83	-5.70	-5.47	-5.19
Bruch-McGee (BM1)	-6.97	-7.10	-7.07	-6.95	-6.69	-6.44
Bruch-McGee (BM2)	-5.67	-5.62	-5.33	-5.06	-4.65	-4.24
Present work	-6.89	-7.09	-7.05	-6.98	-6.73	-6.52
Three-body	0.06	0.07	0.09	0.10	0.12	0.14
Experimental results*				-7.21	-7.15	-7.05

* From Boghosian and Meyer (1966).

semi-empirical potentials (Murphy and Watts 1970), and the small contribution from the Axilrod-Teller triple dipole potential (Murphy and Barker 1971). It can be seen that the present potential gives results that are in very good agreement with the experimental ground state energy of liquid ^4He but that the calculated density dependence is not as good. It is probable that much of the remaining difference is due to the inadequacy of the trial wavefunction rather than of the pair potential. This conclusion is reinforced by the poor radial distribution functions reported for the Jastrow function by Murphy and Watts (1970). The observation that the calculated energies are a little higher than the experimental energies is fortunate, as any improvement in the wavefunction used will tend to lower the ground state energy.

V. CONCLUSIONS

Although the calculated bulk properties reported here are not in very good agreement with their corresponding experimental values over the entire temperature range considered, the results are on the whole satisfactory. The agreement with the dilute gas data in the temperature range 100–500 K, particularly for the transport properties, is extremely good. This indicates that the potential is quite adequate in the region of the bowl. It is obvious that more refined calculations of the potential are needed for the repulsive region. Once these are made, the high temperature behaviour should be particularly improved and the potential would then be expected

to be at least as good as the semi-empirical potentials used previously by Bruch and McGee (1967, 1970) and Beck (1968). Nevertheless in its present form the potential has many satisfying features, among them being close resemblance with the Bruch-McGee family and good predictions for the transport coefficients of the dilute gas. Work is now in progress both towards improving the calculations of Snook (1971) and towards extending the calculations reported here to the low-temperature region where quantum statistical mechanics must be used (Kilpatrick *et al.* 1954). In addition we hope to use the more refined potential to calculate molecular beam scattering cross sections and other thermodynamic properties.

VI. ACKNOWLEDGMENTS

The authors are grateful to Dr. I. J. McGee for supplying many of the computer programs used to calculate the gas-phase properties. They also thank Dr. R. D. Murphy for useful discussions.

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