Ab Initio Calculations for Helium: A Standard for Transport Property Measurements

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For helium, the accuracy of calculated transport properties and virial coefficients based on an accurate *ab initio* potential now exceeds that of the best measurements. The *ab initio* results should be used to calibrate measuring apparatus.

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Traditionally, accurate measurements of second virial coefficients and transport properties have, in part, been used to determine parameters in evermore-refined models for interatomic and intermolecular potentials [1–4]. It is the purpose of this Letter to point out that, in the case of helium, calculations of virial coefficients and transport properties based on an accurate state-of-the-art *ab initio* potential are now sufficiently accurate that the traditional practices can be usefully reversed. If the new theoretical results for helium are used to calibrate apparatus that are used to measure virial coefficients and transport properties, the accuracy of helium-based gas thermometry will be improved, as will measurements of the viscosity and thermal conductivity of gases of more complex atoms and molecules. The present suggestion resolves some controversy about the quality of data from different laboratories and it circumvents the unfortunate circumstance that the apparatus that was used to obtain the most accurate viscosity data for gases near ambient temperature is no longer in operation.

An *"ab initio"* standard is now possible because, after many years of effort, very accurate point-by-point *ab initio* values of the ground state potential have become available. First, van Mourik and van Lenthe [5] recently provided full configuration-interaction (FCI) calculations of the potential at separations of $4.0a_0$, $5.0a_0$, $5.6a_0$, $6.0a_0$, $6.5a_0$, $8.5a_0$, and $12.0a_0$ with very tight error bars. (a_0 = Bohr radius = 0.052 917 7249 nm.) Second, Ceperley and Partridge [6] have employed quantum Monte Carlo methods to determine the exact Born-Oppenheimer interaction energy of two helium atoms with separations between $1.0a_0$ and $3.0a_0$. Finally, accurate and self-consistent calculations of the dispersion coefficients have been provided by Thakkar [7] and Koide, Meath, and Allnatt [8] which define the long-range part of the potential.

We constructed an analytical representation of the potential using the HFD-B (Hartree-Fock-dispersion) form [3] and adjusted parameters so that the representation runs nearly through the *ab initio* points. (For example, the representation misses the FCI result by 0.073%, where ±0.052% is the standard uncertainty in the FCI result at $6a_0$. The corresponding values at $6.5a_0$ are −0.071% and ±0.029%.) In this way, we characterized the interaction energy *without* experimental input. The analytical HFD-B potential is dubbed the "HFD-B3-FCI1" and its parameters are presented in Table I. It is found to support a *very* weakly bound state with a binding energy E_b of 1.59 mK.

To calculate the viscosity and thermal conductivity, we used fourth-order Chapman-Cowling approximation expressions because fourth- and fifth-order calculations of the viscosity near ambient temperature differed by only 0.0005%. (If we had used the second-order Kihara approximation [1], the viscosity would have differed by only 0.027%.) The most important aspect in the calculation is the evaluation of accurate quantum collision integrals. Quantum temperature-dependent reduced cross sections are calculated using an adaptation [9] of the classical reduced collision integral program of O'Hara and Smith [10]. In this approach, a Chebyshev approximation is found for the quantal cross sections which are calculated using standard formulas [11] including the appropri-

TABLE I. Parameters for HFD-B3-FCI1 He-He potential. (Extra digits are displayed to avoid round off error.)

A^*	$1.869\,244\,04 \times 10^5$
α^*	10.571 7543
c_6	1.351 866 23
c_8	0.414 951 43
c_{10}	0.171 511 43
C_6 (J nm^6)	$1.398\,680\,78 \times 10^{-25}$
C_8 (J nm^8)	$3.782\,663\,73 \times 10^{-27}$
C_{10} (J nm^{10})	$1.377\,555\,54 \times 10^{-28}$
β^*	−2.077 587 79
β (nm^{-2})	−23.580 0000
D	1.438 000 00
ϵ/k_B (K)	10.956 0000
r_m (nm)	0.296 830 00
σ (nm)	0.264 138 13

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ate spin and statistical effects [12]. The required phase shifts are obtained using the quantal phase shift routine of LeRoy [13] which uses a numerical integration and a Gaussian quadrature of the WKB correction to the phase shift. The Clenshaw-Curtis [14] quadrature was used to perform the energy integration in the collision integrals to a specified uncertainty of 0.01%.

Curtiss maintains that bound state trajectories in both the bound and unbound regions lead to significant "corrections" to low-density transport properties. For gaseous argon he calculates corrections [15] on the order of 1% when $T^* = T/(\epsilon/k_B) = 1$. (Here, ϵ is the Lennard-Jones energy parameter.) However, at ambient temperature, where we recommend helium be used as a standard, $T^* \approx 29$ and the effects of bound states are negligible. Furthermore, in contrast with argon, helium has a *single* very weakly bound state ($E_b = 1.59 \times 10^{-3}$ K) and *no* quasibound states.

To check our evaluation of the quantal collision integrals, we used an independent procedure due to Hanson [16]. The results from the two procedures differed at most by 0.0025% of the collision integrals necessary for the evaluation of viscosity and thermal conductivity at 298.15 K.

For calibrations, Wakeham, Nagashima, and Sengers [17] recommend experimentally derived primary reference values for the thermal conductivity λ and viscosity η near ambient temperature and pressure. Thus, we shall pay particular attention to near-ambient conditions as we compare the *ab initio* results with experiments. Near 300 K, the computed values of λ and η are most sensitive to the value of the *ab initio* potential at $4.0a_0$, where $U(r)$ is known especially accurately: $U(4.0a_0) = 249.90 \pm 0.3$ K. The 0.3 K standard uncertainty in $U(r)$ propagated into a standard uncertainty of only $\pm 0.02\%$ in the values of λ and η and ± 0.004 cm^3 mol^{-1} in the value of the second virial coefficient B at 298.15 K. This uncertainty in the theoretical results was the dominant one affecting the properties near ambient temperature. Our results at 298.15 K are $\lambda = 154.81 \pm 0.08$ mW m^{-1} K^{-1} and $\eta = 19.800 \pm 0.010$ μPa s. For B, an additional possible uncertainty of 0.004 cm^3 mol^{-1} due to thermal averaging [18] is included. This results in $B = 11.846 \pm 0.008$ cm^3 mol^{-1}.

Probably the most accurate measurement of thermal conductivity is the hot-wire value of Assael *et al.* [19] at 308.15 K. Remarkably, this value is only 0.05% larger than the *ab initio* value and the difference is well within the experimental uncertainty of $\pm 0.2\%$. At nearly the same temperature (298.15 K), Kestin, Ro, and Wakeham [20] measured $\eta = 19.859 \pm 0.020$ μPa s. Their result exceeds the *ab initio* value by 0.059 μPa s or 0.3%, an amount that exceeds their estimated experimental uncertainty of $\pm 0.1\%$.

Recall that both λ and η depend on the same collision integral in the first-order Chapman-Cowling approximation and hence a potential which predicts an accurate value for one should also predict an accurate value for the other in fourth order. At 298.15 K, the *ab initio* value for the dimensionless Eucken ratio $\eta m/\lambda c_v = 1.0037$. This ratio is not sensitive to details of the potential. For hard spheres, $\eta m/\lambda c_v \equiv 1$. (Here m is the mass of a helium atom and c_v is constant-volume heat capacity per atom.) The Eucken ratio obtained by combining data from [19] and [20] is 1.0013 ± 0.0027. We conjecture that the uncertainty in the viscosity data from [20] was underestimated and that, perhaps by chance, the experimental value of λ is more accurate than the experimental value of η.

To further test the *ab initio* potential, we made extensive comparisons with thermophysical-properties data at other temperatures and with scattering data. Representative comparisons for η and λ are shown in Figs. 1 and 2 and representative comparisons for B are made in Tables II and III.

As shown in Fig. 1, Vogel's viscosity results [21] track the temperature dependence of the *ab initio* results with extraordinary precision ($\pm 0.05\%$ from 298 to 623 K). However, Vogel's viscometer [21] was calibrated with the primary data of Kestin, Ro, and Wakeham [20]. This accounts for most of the 0.22% deviation of Vogel's results from the *ab initio* results at 298 K. The data of Clarke and Smith [22] and of Johnston and Grilly [23] agree with the *ab initio* results within their respective experimental uncertainties. As published, the low tem-

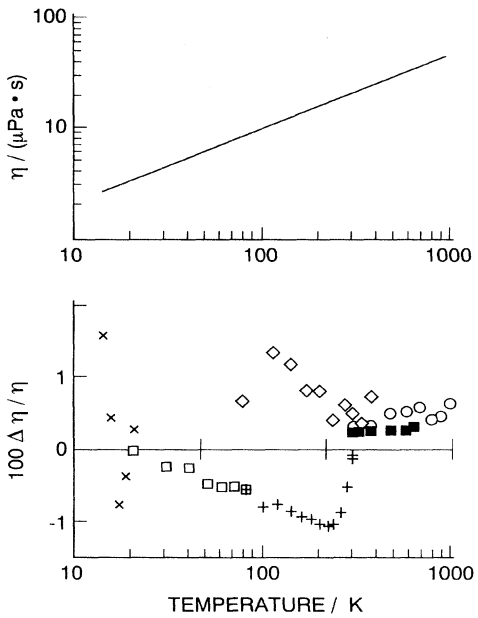

FIG. 1. *Ab initio* viscosity η and deviations of the measured η from the *ab initio* η. Data sources: × Becker and Misenta [25] rescaled at 77.2 K; □ Coremans *et al.* [24] rescaled at 20.4 K; + Johnston and Grilly [23]; ◇ Clarke and Smith [22]; ■ Vogel [21]; ○ Kestin, Ro, and Wakeham [20].

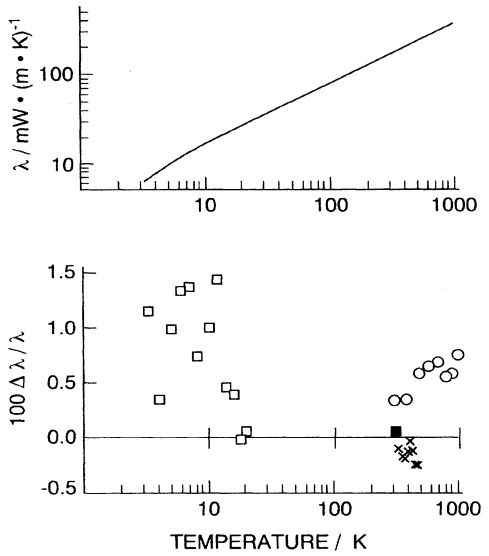

FIG. 2. *Ab initio* thermal conductivity λ and deviations of the measured λ from the *ab initio* λ. Data sources: □ Acton and Kellner [27]; ■ Assael *et al.* [19]; × Haarman [26]; ○ Wakeham, Nagashima, and Sengers [17].

perature results of Coremans *et al.* [24] and of Becker and Misenta [25] disagree with the *ab initio* results. However, both groups used calibration data that must be questioned. Thus, prior to plotting the data from [24], we scaled them to the *ab initio* results at 20.4 K. Similarly, we rescaled the data from [25] at 77.2 K. After rescaling, these data parallel the *ab initio* results within their uncertainties.

Figure 2 displays the thermal conductivity data recommended by Wakeham, Nagashima, and Sengers [17] and the data of Haarman [26], of Assael *et al.* [19], and of Acton and Kellner [27]. In all of these cases, the data and the *ab initio* results are in satisfactory agreement.

Tables II and III compare the *ab initio* results with the accurate second virial coefficient data from the various standards laboratories. The data were painstakingly acquired to account for the nonideality of the helium used in the gas thermometers that are used to define the ITS-90 temperature scale from 3.0 to 24.5561 K. The method of calculating B (taking into account the binding energy contribution in the case of ^{4}He) is described in Aziz and Slaman [3]. The theoretical potential predicts the ^{3}He second virials of Matacotta *et al.* [28] (third virial corrected) to 0.1 $cm^3\,mol^{-1}$ and Berry's smoothed ^{4}He virials [29] within ± 0.3 $cm^3\,mol^{-1}$. Almost all of the *measured* values of Kemp *et al.* [30] are predicted to within their combined random and systematic experimental uncertainties even after ignoring the influence of the systematic uncertainty due to the chosen reference point (Berry's value at 20.271 K). All the Gammon [31] points from 123 to 423 K are predicted to within ± 0.04 $cm^3\,mol^{-1}$. The data of Blancett, Hall, and Canfield [32] and the data of Kell, McLaurin, and Whalley [33] at 298.15 and 623 K are predicted within experimental uncertainty.

TABLE II. The measured second virial coefficient B_{expt} of ^{4}He, its uncertainty ΔB, and the difference between the experimental and calculated values in units of $cm^3\,mol^{-1}$.

T(K)	B_{expt}	ΔB	$B_{expt} - B_{calc}$	Ref.
2.600	−142.295	1.0	0.053	[29]
2.750	−133.230	0.7	0.002	[29]
3.330	−106.118	0.7	0.060	[29]
4.220	−79.392	0.5	0.254	[29]
7.200	−38.764	0.7	0.344	[29]
13.800	−11.830	0.4	0.076	[29]
20.271	−2.472	0.2	−0.003	[29]
27.100	2.505	0.2	0.041	[29]
27.097	2.470	0.06[a] 0.26[b]	0.008	[30]
43.794	7.800	0.11[a] 0.31[b]	0.029	[30]
54.358	9.280	0.07[a] 0.27[b]	−0.024	[30]
63.150	10.010	0.09[a] 0.29[b]	−0.117	[30]
83.804	11.130	0.11[a] 0.31[b]	−0.108	[30]
172.011	12.150	0.14[a] 0.26[b]	−0.062	[30]
98.15	11.522	0.05	−0.128	[31]
123.15	11.984	0.05	−0.041	[31]
148.15	12.174	0.05	−0.002	[31]
173.15	12.228	0.05	0.016	[31]
198.15	12.209	0.05	0.024	[31]
223.15	12.148	0.05	0.025	[31]
248.15	12.065	0.05	0.024	[31]
273.15	11.968	0.05	0.021	[31]
298.15	11.863	0.05	0.018	[31]
323.15	11.756	0.05	0.014	[31]
348.15	11.647	0.05	0.010	[31]
373.15	11.539	0.05	0.007	[31]
398.15	11.433	0.05	0.003	[31]
423.15	11.329	0.05	0.001	[31]
223.15	12.16	0.03	0.037	[32]
273.15	11.94	0.03	−0.006	[32]
323.15	11.76	0.03	0.018	[32]
298.15	11.83	0.03	−0.016	[33]
623.15	10.61	0.01	0.012	[33]
3.00	−120.522	1.0	−0.314	[39]
4.00	−85.200	0.7	−0.126	[39]
5.00	−64.316	0.7	−0.002	[39]
8.00	−33.283	0.5	0.112	[39]
10.00	−23.020	0.7	0.104	[39]
15.00	−9.435	0.4	0.050	[39]
20.00	−2.723	0.2	0.014	[39]
27.00	2.412	0.3	0.001	[39]

[a]Random and systematic uncertainties only.
[b]Random, systematic, and reference point uncertainties.

It is reassuring that the HFD-B3-FCI1 potential, which had no experimental input, is able to predict the "standard" ^{3}He and ^{4}He virials with significantly smaller deviations than any of the recent "experimental" or model potentials [3,4,9,34–36].

We have verified that the *ab initio* results reproduce both the total [37] and differential [38] ^{4}He-^{4}He scatter-

TABLE III. The measured second virial coefficient B_{expt} of ^{3}He, its uncertainty ΔB, and the difference between the experimental and calculated values in units of $cm^3\,mol^{-1}$.

T (K)	B_{expt}	ΔB	$B_{expt} - B_{calc}$	Ref.
1.47	−173.58	0.5	−0.021	[28]
1.50	−170.54	0.5	−0.008	[28]
1.55	−165.68	0.5	0.004	[28]
1.73	−149.99	0.4	0.051	[28]
1.90	−137.37	0.4	0.081	[28]
2.20	−119.12	0.5	0.076	[28]
3.00	−86.31	0.5	0.010	[28]
4.30	−57.15	0.4	−0.021	[28]
9.00	−19.75	0.3	−0.008	[28]
13.80	−7.33	0.2	−0.079	[28]
20.30	0.24	0.2	−0.125	[28]

ing cross section data as well as or better than the model or semiempirical potentials that have been used in the past [4,9]. These comparisons will be discussed elsewhere.

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