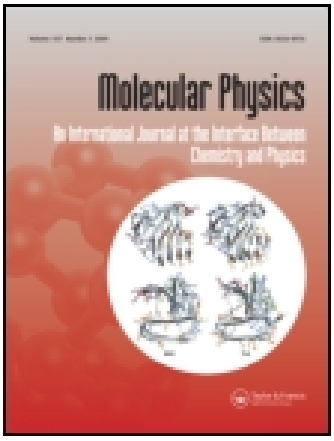

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A new interatomic potential function for helium

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A new interatomic potential function for helium

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A new interatomic potential for helium is proposed of the form:

$$v(r)=A\exp(-\alpha r-\beta r^6)-\frac{0\cdot869}{(r^2+a^2)^3}\left(1+\frac{2\cdot709+3a^2}{r^2+a^2}\right),$$

with $a=0\cdot675$ Å, $\alpha=4\cdot390$ Å^{-1}, $\beta=3\cdot746\times10^{-4}$ Å^{-6} and $A=398\cdot7$ ev. The long-range attraction has the correct theoretical dependence on the separation with the terms having the coefficients as calculated by Dalgarno and Kingston and by Davison. The short-range repulsive part of the potential was fitted to the calculated potential energy values of Phillipson and the experimentally determined values of Amdur and his co-workers. In addition the parameters were adjusted so that the potential reproduces the experimentally determined second virial coefficient for helium.

Recent investigations have provided direct knowledge about the interatomic potential for two helium atoms. The short-range repulsive part of the potential has been studied experimentally by Amdur and his co-workers [1] and many authors [2–4] have performed quantum mechanical calculations for this part of the potential. The repulsive part of the potential has also been studied by inverse Laplace transformation of the high temperature virial coefficient [5]. The long-range part of the potential is known to have the form:

$$v(r)\underset{r\to\infty}{\to}-\frac{C_6}{r^6}-\frac{C_8}{r^8}+O\left(\frac{1}{r^{10}}\right), \tag{1}$$

where the coefficients C_6 and C_8 are positive. These coefficients have been calculated [6–8], and C_6 as calculated by Dalgarno and Kingston [6] has an absolute error of less than 10 per cent [9].

The calculations of Phillipson [2], and Dalgarno and Kingston [6] are very accurate and future calculations are likely to produce only small refinements, hence Bernstein and Morse [10] proposed a He–He potential (the PMD potential) which was constructed by joining Phillipson's short-range repulsion via a Morse function to a C_6/r^6 attractive term where C_6 is given by the calculation of Dalgarno and Kingston. They chose a well depth of $\epsilon=8\cdot739\times10^{-4}$ ev for the Morse function leaving the position of the minimum and connecting points to be determined by slope matching. However, Bruch and McGee [11] in their study of helium potentials found a discontinuity in the slope for this potential at the matching point between the Phillipson piece and the Morse function. Also the

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second virial coefficient, $B(T)$, for helium calculated using the PMD potential [12] was found to be significantly higher than the experimentally determined coefficient for temperatures from 50 to 150°K.

The considerations which led Bernstein and Morse to propose the PMD potential are certainly correct [13], and these considerations have led us to construct a potential which agreed with the directly determined potential [1–8] and the second virial coefficient data [14–16]. Yntema and Schneider [17] used a single functional form for the complete range of the interaction and obtained a smooth potential function. It was not possible to adjust the parameters in their potential to fit all of the data available and additional parameters were introduced to give the potential, in ev (Å):

$$v(r)=A\exp(-\alpha r-\beta r^6)-\frac{0\cdot869}{(r^2+a^2)^3}\left(1+\frac{2\cdot709+3a^2}{r^2+a^2}\right), \tag{2}$$

with $a=0\cdot675$ Å, $\alpha=4\cdot390$ Å^{-1}, $\beta=3\cdot746\times10^{-4}$ Å^{-6} and $A=398\cdot7$ ev for $r=0\cdot5$ Å to infinity. This potential has the correct long-range behaviour—in the limit as $r\to\infty$ the coefficients of equation (1) are $C_6=0\cdot869$ ev Å^6 and $C_8=2\cdot354$ ev Å^8 as calculated by Dalgarno and Kingston [6], and Davison [7], respectively—and the parameters a, α, β and A were adjusted to reproduce the calculated repulsion of Phillipson and the experimental data [1, 14–16]. In table 1 the short-range repulsion is compared with Phillipson's [2] calculation and the experimental results of Amdur [1].

The second virial coefficient for helium calculated with this potential taking quantum corrections up to second order into account [18] is compared with the experimental results [14–16] in figures 1 and 2. Keesom [16] has collected the

r (Å)	$v(r)$ (ev)				
	Phillipson†	Amdur and Jordan‡ (1967)	Amdur, Jordan and Colgate‡ (1961)	Amdur and Harkness‡ (1954)	Present work
0·500	27·76				27·76
0·625	17·33	14·17			17·38
0·750	10·78	8·28			10·74
0·875		4·85			6·51
1·000	4·059	2·84	3·471		3·886
1·125		1·66	1·919		2·289
1·250			1·130	1·252	1·333
1·375			0·700	0·711	0·770
1·500			0·452	0·424	0·440
1·625				0·264	0·249
1·750					0·139
1·875					0·0767
2·000					0·0413

† Reference [2], theoretical.
‡ Reference [1], experimental.

Table 1. Comparison of short-range repulsive part of the modified potential with the directly determined experimental and theoretical potential.

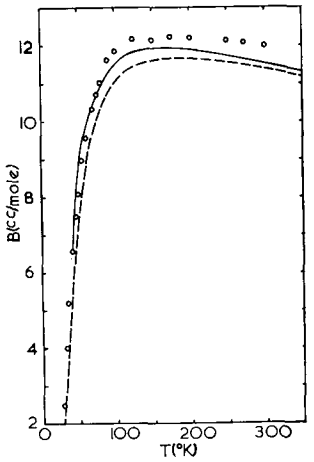

Figure 1. Comparison of the theoretical and experimental results for the second virial coefficient of helium for intermediate temperatures. The theoretical results (solid curve) were calculated with the modified potential, equation (2). The experimental results are those of White *et al.* (○) and the adopted coefficient of Keesom (dashed curve) which summarizes the earlier experiments.

early experimental data and adopted a smooth virial coefficient to summarize it; his smooth coefficient is shown in the figures. White *et al.* [15] estimate the error in their determination of $B(T)$ to be less than $\pm 0{\cdot}3$ cm^3/mole for high temperature and less than $\pm 0{\cdot}5$ cm^3/mole for low temperature, and Yntema and Schneider [14] estimate an error of less than $\pm 0{\cdot}3$ cm^3/mole for their coefficient. The coefficient for the modified potential falls within these bounds.

The higher-order quantum corrections become important for temperatures below 40°K, and for these temperatures $B(T)$ needs to be calculated quantum mechanically. The second virial coefficient has been calculated quantum mechanically [19, 20] for the Lennard-Jones 6–12 potential [21] (minimum $\epsilon = 8{\cdot}807 \times 10^{-4}$ ev at a radius of $r = 2{\cdot}886$ Å and a zero at $\sigma = 2{\cdot}556$ Å) for temperatures up to 60°K and found to be in agreement with the experimentally

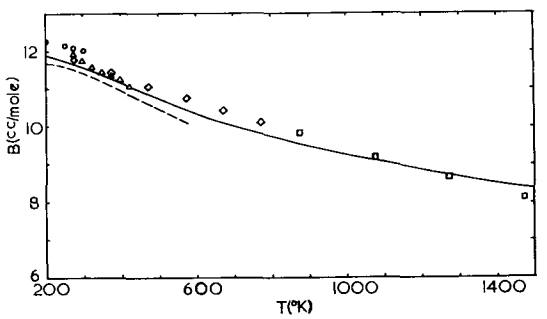

Figure 2. Comparison of the theoretical and experimental results for the second virial coefficient of helium for high temperatures. The theoretical results (solid curve) were calculated with the modified potential, equation (2). The experimental results are those of White *et al.* (○), Michels and Wouter (△), Schneider and Duffie (◇), Yntema and Schneider (□) and the adopted coefficient of Keesom (dashed curve) which summarizes the earlier experiments.

k^*	$(2l+1)\eta_l$						
	0	2	4	6	8	10	Sum
0·020	0·758	0					0·76
0·200	1·175	0·002	0				1·18
0·400	0·940	0·023	0·002	0	0		0·97
0·600	0·687	0·106	0·007	0·003	0·001	0	0·80
0·800	0·437	0·309	0·018	0·006	0·004	0·001	0·78
1·000	0·193	0·681	0·042	0·012	0·008	0·006	0·94
1·200	−0·045	1·215	0·086	0·022	0·013	0·009	1·30
1·400	−0·277	1·804	0·159	0·038	0·019	0·013	1·76
1·600	−0·503	2·278	0·272	0·061	0·029	0·021	2·15
1·800	−0·725	2·524	0·440	0·094	0·042	0·028	2·40
2·000	−0·943	2·525	0·675	0·140	0·059	0·038	2·49

Table 2. Phase shifts for modified potential ($k^* = \sigma k$ with $\sigma = 2{\cdot}56$ Å).

determined values of $B(T)$. The quantum mechanical calculation involves a weighted integration over the sum [19, 20] of the partial wave phase shifts which appears in the last column of table 2. The low momentum phase shift computed for helium using the modified potential are similar to those computed using the 6–12 potential (compare table 2 with table 1 of [19] and figures 1 and 3 of [20]) and one expects $B(T)$ computed quantum mechanically for this potential to agree with the low temperature experimental coefficient [22].

The modified interatomic potential for helium proposed in this paper has the correct short and long-range behaviour and only the depth and shape of the attractive well which have been fixed by fitting to the second virial coefficient are spectulative. The second virial coefficient data does not determine the well parameters uniquely, since potentials with very different well shapes yield coefficients which are consistent with the experimental data (see [22]). Demanding that the potential has the long-range behaviour given by equation (1) reduces the allowed range of these parameters but not to a unique set. To facilitate a comparison with other proposed potentials [11, 23] the well parameters of this potential are: a minimum, $\epsilon = 8{\cdot}936 \times 10^{-4}$ ev at a radius of $r_m = 2{\cdot}969$ Å, a zero at a radius of $\sigma = 2{\cdot}637$ Å and a reduced curvature:

$$\gamma = \frac{r_m^2}{\epsilon} \left.\frac{\partial^2 v(r)}{\partial r^2}\right|_{r=r_m} = 74{\cdot}31.$$

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