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Intermolecular forces and equation of state for solid molecular H_2, D_2, ^3He, ^4He, and ^{20}Ne

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Intermolecular potentials appropriate for solid H_2, D_2, ^3He, ^4He, and ^{20}Ne are deduced from analysis of the equation-of-state measurements of Stewart. Buckingham 6-exp potentials seem to be most appropriate. Lennard-Jones potentials fail to satisfactorily represent the data and full Buckingham potentials degenerate to 6-exp forms. The deduced intermolecular potentials are used to compute solid-phase thermodynamic functions over an extended pressure range.

I. INTRODUCTION

Pollock *et al.*[1] have shown that the harmonic approximation (HA) is valid for a class of Lennard-Jones and Buckingham 6-exp quantum solids by direct comparison of results with those from exact Monte Carlo calculations.[2] They also demonstrated that for the same class of solids the Domb-Salter[3] approximation introduces negligible error for pressures between a few kilobars and several megabars.

Using published values[4,5] of parameters appropriate to H_2, D_2, ^3He, ^4He, and ^{20}Ne Pollock *et al.*[1] computed equation-of-state curves at zero temperature and high densities in the HA. Good agreement with the experimental results of Stewart[6,7] was obtained for ^3He, ^4He, and ^{20}Ne. Poor agreement with the experimental results[6,7] for H_2 and D_2 led Pollock *et al.*[1] to suggest that something was amiss in the experiment or with the intermolecular potential used in their calculation. The latter possibility seemed the most likely to us.

We thought it useful to accept the HA, and within that limited context to adjust parameters in Lennard-Jones and Buckingham intermolecular potentials in such a way as to optimize agreement between Stewart's[6,7] PV values and those computed for the model solid. It should be noted that potentials thus obtained may implicitly account, in some matter specific to the solid, for physical effects (i.e., deviations from pairwise additivity, hindered rotation, etc.), which would not appear in the gas or liquid phases.

The optimal potentials we obtain are compared with others given in the literature and are used to compute solid-phase thermodynamic functions over an extended pressure range.

II. MODEL POTENTIALS AND THERMODYNAMIC FUNCTIONS

The model potentials chosen are the Lennard-Jones 6-12 potential

$$V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] ,$$

with ϵ and σ adjustable parameters and the (full) Buckingham potential

$$V(r) = \begin{cases} Be^{-Ar} - c/r^6 - c'/r^8, & r > r_{\mathrm{max}} , \\ \infty , & r < r_{\mathrm{max}} , \end{cases}$$

$$V(r) = \begin{cases} \dfrac{\epsilon}{1-6/\alpha}\left[\dfrac{6}{\alpha}\exp\left(\alpha - \dfrac{\alpha r}{r_{\mathrm{m}}}\right) - \left(\dfrac{r_{\mathrm{m}}}{r}\right)^6 - Z\left(\dfrac{r_{\mathrm{m}}}{r}\right)^8\right] , & r > r_{\mathrm{max}} , \\ \infty, & r < r_{\mathrm{max}} , \end{cases}$$

with ϵ, α, r_{m}, and Z adjustable parameters and r_{max} assumed small. The parameters A, B, C, and C' are defined in terms of ϵ, α, r_{m}, and Z by the second equality. We will also use $\epsilon_0 \equiv \epsilon/(1-6/\alpha)$. The second form has been included so as to easily relate our results to the Buckingham 6-exp potential.

We use the following notation and definitions in the remainder of this paper: Sums over spacings l on a lattice L having unit lattice constant and excluding the origin will be denoted $\sum(l; L)$ and we define $S(I, X) = C(I) X^{-I}$, with $C(I) = \sum(l; L) l^{-I}$ and $R(I, X) = \sum(l; L)(lX)^{I-2} e^{-lx}$. When $S(I)$ appears in an expression without an explicit X argument, take $X \equiv a/\sigma$ or a/r_m, where a is the lattice constant. When $R(I)$ appears without an explicit X argument

TABLE I. Summary of optimal parameters for the Buckingham potential.

Substance	ϵ (K)	r_m (Å)	α	Z	A (Å^{-1})	$10^{-6}B$ (K)	$10^{60}C$ (erg cm^6)	Pressure range for data included in fit
H_2	37.26	3.479	10.67	0	3.066	2.056	20.82	$P \geq 0$ kbar
H_2	35.96	3.474	10.77	0	3.100	2.152	19.67	$P \geq 0.4$ kbar
H_2	36.28	3.468	10.79	0	3.111	2.205	19.60	$P \geq 3$ kbar
H_2	37.3	3.337	14.0	...	(4.19)	(33.6)	(10.0)	Ref. 11
D_2	18.99	3.790	11.84	0.4068	3.124	2.707	15.78	$P \geq 0$ kbar
D_2	14.25	3.904	12.41	0.6200	3.178	3.274	13.49	$P \geq 0.4$ kbar
D_2	35.62	3.482	10.40	Set = 0	2.986	1.595	20.70	$P \geq 0.4$ kbar
^{3}He	7.038	3.485	12.65	0.692	3.630	1.982	3.313	$P \geq 1$ kbar
^{3}He	22.25	3.112	10.07	0	3.235	0.7743	6.914	$P \geq 3$ kbar
^{4}He	15.39	3.095	10.76	0	3.476	0.9133	4.219	$P \geq 1$ kbar
^{4}He	15.33	3.100	10.73	0	3.461	0.8909	4.258	$P \geq 3$ kbar
He	9.16	3.135	12.4	...	(3.95)	(2.08)	(2.32)	Ref. 11
^{20}Ne	45.98	3.168	13.82	0	4.362	35.51	11.33	$P \geq 0$ kbar
Ne	38.0	3.147	14.5	...	(4.60)	(53.1)	(8.68)	Ref. 11

take $X = \alpha a/r$. Also define the deBoer parameter

$$\Lambda \equiv \hbar/(M\varepsilon\sigma^2)^{1/2} \quad \text{or} \quad \hbar/(M\varepsilon_0 r_m{}^2)^{1/2}.$$

Thus, in Domb-Salter[3] approximation we have (i) zero-point energy:

$$E_{ZP}^{LJ} = 2K\epsilon\Lambda[22S(14) - 5S(8)]^{1/2} \equiv 2K\epsilon\Lambda D^{LJ},$$

$$E_{ZP}^{B} = K\epsilon_0\Lambda\{\alpha e^{\alpha}[R(2) - 2R(1)] - 5S(8) - \tfrac{28}{3}ZS(10)\}^{1/2} \equiv K\epsilon_0\Lambda D^{B},$$

where $K = (\frac{9}{8})(\frac{10}{3})^{1/2}$;

(ii) static energy

$$E_S^{LJ} = 2\epsilon[S(12) - S(6)],$$

$$E_S^{B} = 0.5\epsilon_0[(6/\alpha)e^{\alpha}R(2) - S(6) - ZS(8)];$$

TABLE II. Summary of results for optimal potential for H_2 ($\epsilon = 37.26$ K, $r_m = 3.479$ Å, $\alpha = 10.67$). Experimental data from Ref. 6.

Molar volume (ml)	Zero-point energy (K)	Static potential energy (K)	Total energy (K)	Computed pressure (bar)	Measured pressure (bar)
22.65	8.694×10	-2.638×10^2	-1.768×10^2	7.462×10	1.000
21.00	1.120×10^2	-2.861×10^2	-1.741×10^2	2.239×10^2	2.000×10^2
20.00	1.291×10^2	-2.997×10^2	-1.706×10^2	3.845×10^2	4.000×10^2
19.20	1.442×10^2	-3.103×10^2	-1.662×10^2	5.646×10^2	6.000×10^2
18.00	1.694×10^2	-3.250×10^2	-1.556×10^2	9.527×10^2	1.000×10^3
16.10	2.177×10^2	-3.412×10^2	-1.235×10^2	2.020×10^3	2.043×10^3
15.10	2.484×10^2	-3.429×10^2	-9.443×10	2.943×10^3	3.000×10^3
14.30	2.763×10^2	-3.382×10^2	-6.190×10	3.963×10^3	4.000×10^3
13.20	3.206×10^2	-3.185×10^2	2.073	5.963×10^3	6.000×10^3
12.40	3.580×10^2	-2.897×10^2	6.829×10	8.049×10^3	8.000×10^3
11.80	3.894×10^2	-2.564×10^2	1.330×10^2	1.011×10^4	1.000×10^4
11.30	4.181×10^2	-2.186×10^2	1.995×10^2	1.226×10^4	1.200×10^4
10.60	4.629×10^2	-1.452×10^2	3.176×10^2	1.615×10^4	1.600×10^4
10.10	4.985×10^2	-7.380×10	4.247×10^2	1.975×10^4	2.000×10^4
9.00	5.900×10^2	1.650×10^2	7.551×10^2	3.128×10^4	
8.50	6.387×10^2	3.264×10^2	9.652×10^2	3.890×10^4	
8.00	6.927×10^2	5.351×10^2	1.228×10^3	4.872×10^4	
7.50	7.528×10^2	8.057×10^2	1.558×10^3	6.150×10^4	
7.00	8.197×10^2	1.159×10^3	1.978×10^3	7.833×10^4	
6.50	8.945×10^2	1.622×10^3	2.517×10^3	1.008×10^5	
6.00	9.781×10^2	2.237×10^3	3.215×10^3	1.311×10^5	
5.50	1.071×10^3	3.059×10^3	4.130×10^3	1.729×10^5	
5.00	1.175×10^3	4.173×10^3	5.348×10^3	2.315×10^5	
4.50	1.289×10^3	5.707×10^3	6.995×10^3	3.152×10^5	
4.00	1.409×10^3	7.854×10^3	9.262×10^3	4.376×10^5	
3.50	1.525×10^3	1.092×10^4	1.245×10^4	6.207×10^5	
3.00	1.605×10^3	1.541×10^4	1.701×10^4	8.998×10^5	
2.50	1.542×10^3	2.213×10^4	2.368×10^4	1.320×10^6	

TABLE III. Summary of results for optimal potential for D_2 ($\epsilon = 35.62$ K, $r_m = 3.482$ Å, $\alpha = 10.40$). Experimental data from Ref. 6.

Molar volume (ml)	Zero-point energy (K)	Static potential energy (K)	Total energy (K)	Computed pressure (bar)	Measured pressure (bar)
19.56	9.378×10	-2.957×10^2	-2.019×10^2	-1.106×10	1.000
18.50	1.077×10^2	-3.087×10^2	-2.009×10^2	1.992×10^2	2.000×10^2
17.80	1.179×10^2	-3.166×10^2	-1.986×10^2	3.936×10^2	4.000×10^2
17.20	1.273×10^2	-3.225×10^2	-1.952×10^2	6.063×10^2	6.000×10^2
16.40	1.410×10^2	-3.290×10^2	-1.879×10^2	9.749×10^2	1.000×10^3
14.90	1.709×10^2	-3.330×10^2	-1.622×10^2	2.044×10^3	2.043×10^3
14.00	1.919×10^2	-3.274×10^2	-1.354×10^2	3.042×10^3	3.000×10^3
13.30	2.103×10^2	-3.163×10^2	-1.060×10^2	4.094×10^3	4.000×10^3
12.40	2.371×10^2	-2.899×10^2	-5.282×10	5.950×10^3	6.000×10^3
11.70	2.607×10^2	-2.559×10^2	4.774	7.939×10^3	8.000×10^3
11.20	2.792×10^2	-2.218×10^2	5.746×10	9.758×10^3	1.000×10^4
10.70	2.994×10^2	-1.771×10^2	1.224×10^2	1.201×10^4	1.200×10^4
10.00	3.308×10^2	-9.131×10	2.395×10^2	1.611×10^4	1.600×10^4
9.50	3.558×10^2	-8.362	3.474×10^2	1.995×10^4	2.000×10^4
9.00	3.832×10^2	9.837×10	4.815×10^2	2.480×10^4	
8.50	4.132×10^2	2.357×10^2	6.489×10^2	3.098×10^4	
8.00	4.463×10^2	4.126×10^2	8.589×10^2	3.891×10^4	
7.50	4.827×10^2	6.412×10^2	1.124×10^3	4.920×10^4	
7.00	5.228×10^2	9.380×10^2	1.461×10^3	6.268×10^4	
6.50	5.670×10^2	1.326×10^3	1.893×10^3	8.055×10^4	
6.00	6.154×10^2	1.836×10^3	2.451×10^3	1.045×10^5	
5.50	6.681×10^2	2.513×10^3	3.181×10^3	1.372×10^5	
5.00	7.244×10^2	3.423×10^3	4.147×10^3	1.824×10^5	
4.50	7.821×10^2	4.659×10^3	5.441×10^3	2.460×10^5	
4.00	8.358×10^2	6.366×10^3	7.201×10^3	3.366×10^5	
3.50	8.711×10^2	8.758×10^3	9.629×10^3	4.673×10^5	
3.00	8.468×10^2	1.217×10^4	1.301×10^4	6.529×10^5	
2.50	5.917×10^2	1.706×10^4	1.765×10^4	8.667×10^5	

TABLE IV. Summary of results for optimal potential for ^{3}He ($\epsilon = 22.25$ K, $r_m = 3.112$ Å, $\alpha = 10.07$). Experimental data from Ref. 7.

Molar volume (ml)	Zero-point energy (K)	Static potential energy (K)	Total energy (K)	Computed pressure (bar)	Measured pressure (bar)
12.86	1.134×10^2	-1.991×10^2	-8.566×10	8.197×10^2	1.000×10^3
11.07	1.543×10^2	-2.123×10^2	-5.796×10	1.967×10^3	2.000×10^3
10.16	1.806×10^2	-2.120×10^2	-3.136×10	3.046×10^3	3.000×10^3
9.60	1.992×10^2	-2.073×10^2	-8.082	3.992×10^3	4.000×10^3
9.15	2.157×10^2	-1.999×10^2	1.585×10	4.971×10^3	5.000×10^3
8.79	2.300×10^2	-1.908×10^2	3.923×10	5.936×10^3	6.000×10^3
8.21	2.555×10^2	-1.685×10^2	8.702×10	7.938×10^3	8.000×10^3
7.76	2.776×10^2	-1.424×10^2	1.352×10^2	9.994×10^3	1.000×10^4
7.41	2.964×10^2	-1.151×10^2	1.813×10^2	1.200×10^4	1.200×10^4
7.12	3.131×10^2	-8.650×10	2.266×10^2	1.400×10^4	1.400×10^4
6.86	3.290×10^2	-5.535×10	2.737×10^2	1.611×10^4	1.600×10^4
6.66	3.420×10^2	-2.718×10	3.148×10^2	1.798×10^4	1.800×10^4
6.48	3.541×10^2	1.778	3.559×10^2	1.987×10^4	2.000×10^4
6.00	3.891×10^2	9.941×10	4.885×10^2	2.612×10^4	
5.50	4.298×10^2	2.428×10^2	6.726×10^2	3.512×10^4	
5.00	4.751×10^2	4.474×10^2	9.225×10^2	4.786×10^4	
4.50	5.248×10^2	7.416×10^2	1.266×10^3	6.619×10^4	
4.00	5.772×10^2	1.170×10^3	1.747×10^3	9.304×10^4	
3.50	6.273×10^2	1.802×10^3	2.430×10^3	1.329×10^5	
3.00	6.590×10^2	2.754×10^3	3.412×10^3	1.918×10^5	

TABLE V. Summary of results for optimal potential for ^{4}He ($\epsilon = 15.33$ K, $r_m = 3.100$ Å, $\alpha = 10.73$). Experimental data from Ref. 7.

Molar volume (ml)	Zero-point energy (K)	Static potential energy (K)	Total energy (K)	Computed pressure (bar)	Measured pressure (bar)
12.25	9.494×10	-1.364×10^{2}	-4.141×10	1.037×10^{3}	1.000×10^{3}
10.72	1.265×10^{2}	-1.406×10^{2}	-1.409×10	2.099×10^{3}	2.000×10^{3}
9.93	1.470×10^{2}	-1.372×10^{2}	9.787	3.049×10^{3}	3.000×10^{3}
9.38	1.634×10^{2}	-1.307×10^{2}	3.263×10	3.977×10^{3}	4.000×10^{3}
8.96	1.773×10^{2}	-1.226×10^{2}	5.473×10	4.891×10^{3}	5.000×10^{3}
8.59	1.908×10^{2}	-1.124×10^{2}	7.843×10	5.889×10^{3}	6.000×10^{3}
8.01	2.145×10^{2}	-8.859×10	1.259×10^{2}	7.938×10^{3}	8.000×10^{3}
7.58	2.344×10^{2}	-6.269×10	1.717×10^{2}	9.973×10^{3}	1.000×10^{4}
7.21	2.534×10^{2}	-3.276×10	2.207×10^{2}	1.220×10^{4}	1.200×10^{4}
6.94	2.685×10^{2}	-5.259	2.633×10^{2}	1.419×10^{4}	1.400×10^{4}
6.72	2.817×10^{2}	2.146×10	3.031×10^{2}	1.608×10^{4}	1.600×10^{4}
6.53	2.937×10^{2}	4.819×10	3.419×10^{2}	1.795×10^{4}	1.800×10^{4}
6.37	3.043×10^{2}	7.371×10	3.780×10^{2}	1.972×10^{4}	2.000×10^{4}
6.00	3.309×10^{2}	1.453×10^{2}	4.762×10^{2}	2.464×10^{4}	
5.50	3.718×10^{2}	2.785×10^{2}	6.504×10^{2}	3.374×10^{4}	
5.00	4.196×10^{2}	4.719×10^{2}	8.915×10^{2}	4.703×10^{4}	
4.50	4.756×10^{2}	7.563×10^{2}	1.232×10^{3}	6.692×10^{4}	
4.00	5.414×10^{2}	1.182×10^{3}	1.724×10^{3}	9.765×10^{4}	
3.50	6.185×10^{2}	1.835×10^{3}	2.454×10^{3}	1.468×10^{5}	
3.00	7.069×10^{2}	2.867×10^{3}	3.574×10^{3}	2.288×10^{5}	

TABLE VI. Summary of results for optimal potential for ^{20}Ne ($\epsilon = 45.98$ K, $r_m = 3.168$ Å, $\alpha = 13.82$). Experimental data from Ref. 6.

Molar volume (ml)	Zero-point energy (K)	Static potential energy (K)	Total energy (K)	Computed pressure (bar)	Measured pressure (bar)
14.00	7.221×10	-3.676×10^{2}	-2.954×10^{2}	-1.251×10^{2}	1.000
13.70	7.731×10	-3.727×10^{2}	-2.954×10^{2}	1.332×10^{2}	2.000×10^{2}
13.50	8.088×10	-3.757×10^{2}	-2.948×10^{2}	3.349×10^{2}	4.000×10^{2}
13.30	8.460×10	-3.783×10^{2}	-2.937×10^{2}	5.633×10^{2}	6.000×10^{2}
13.00	9.048×10	-3.814×10^{2}	-2.909×10^{2}	9.634×10^{2}	1.000×10^{3}
12.30	1.057×10^{2}	-3.835×10^{2}	-2.777×10^{2}	2.236×10^{3}	2.043×10^{3}
12.00	1.130×10^{2}	-3.814×10^{2}	-2.683×10^{2}	2.968×10^{3}	3.000×10^{3}
11.60	1.236×10^{2}	-3.748×10^{2}	-2.512×10^{2}	4.174×10^{3}	4.000×10^{3}
11.10	1.383×10^{2}	-3.586×10^{2}	-2.203×10^{2}	6.153×10^{3}	6.000×10^{3}
10.80	1.480×10^{2}	-3.434×10^{2}	-1.954×10^{2}	7.662×10^{3}	8.000×10^{3}
10.40	1.621×10^{2}	-3.148×10^{2}	-1.527×10^{2}	1.016×10^{4}	1.000×10^{4}
10.20	1.697×10^{2}	-2.962×10^{2}	-1.264×10^{2}	1.165×10^{4}	1.200×10^{4}
9.70	1.907×10^{2}	-2.336×10^{2}	-4.290×10	1.633×10^{4}	1.600×10^{4}
9.40	2.047×10^{2}	-1.824×10^{2}	2.237×10	1.993×10^{4}	2.000×10^{4}
9.00	2.254×10^{2}	-9.314×10	1.322×10^{2}	2.596×10^{4}	
8.50	2.548×10^{2}	6.250×10	3.173×10^{2}	3.613×10^{4}	
8.00	2.890×10^{2}	2.860×10^{2}	5.750×10^{2}	5.042×10^{4}	
7.50	3.291×10^{2}	6.062×10^{2}	9.354×10^{2}	7.076×10^{4}	
7.00	3.766×10^{2}	1.066×10^{3}	1.443×10^{3}	1.001×10^{5}	
6.50	4.331×10^{2}	1.731×10^{3}	2.164×10^{3}	1.431×10^{5}	
6.00	5.011×10^{2}	2.701×10^{3}	3.203×10^{3}	2.075×10^{5}	
5.50	5.839×10^{2}	4.136×10^{3}	4.720×10^{3}	3.061×10^{5}	
5.00	6.860×10^{2}	6.296×10^{3}	6.982×10^{3}	4.611×10^{5}	
4.50	8.140×10^{2}	9.622×10^{3}	1.044×10^{4}	7.130×10^{5}	
4.00	9.775×10^{2}	1.489×10^{4}	1.587×10^{4}	1.139×10^{6}	
3.50	1.191×10^{3}	2.356×10^{4}	2.475×10^{4}	1.896×10^{6}	

(iii) pressure:

$$P^{LJ}=(\epsilon/V)\{8S(12)-4S(8)+(\tfrac{4}{3}K\Lambda)[77S(14)-10S(8)]/D^{LJ}\},$$

$$P^{B}=(\epsilon_0/V)\{(e^{\alpha}/\alpha)R(3)-S(6)-ZS(8)+(\tfrac{1}{6}K\Lambda)[\alpha e^{\alpha}R-40S(8)-\tfrac{280}{3}ZS(10)]/D^{B}\},$$

where $R=R(3)-2R(1)-2R(2)$ and D^{LJ} and D^{B} are defined above.

The $S(I,X)$ and $R(I,X)$ are related to the two types of S^I functions of Pollack *et al.*,[1] viz., $S(I,X)=S^I$ and $R(I,X)=X^{I-2}S^I$.

III. NUMERICAL DETAILS

The $C(I)$ lattice sums were computed on a $40\times40\times40$-cell fcc lattice and agreed with those given in Ref. 1, where such values where given. The required $R(I,X)$, $I=1, 2, 3$ were computed for integer X from 1 to 100 on lattices including $12\times12\times12$ cells at the larger X values and ranging up to $40\times40\times40$ cells for $X\leq 3$. The logarithm of the functions were fit with cubic splines to allow interpolation to noninteger X values.

The data were usually fit by minimizing the squared deviations of the computed from the measured product of pressure and volume. The Rosenbrock[8] algorithm was employed to determine the optimal set of parameters. Even in the four parameter fits with a "bad-guess" start, less than 500 iterations of the algorithm sufficed for convergence.

IV. RESULTS AND DISCUSSION

A satisfactory representation of Stewart's[6,7] experimental data in the quantum solids H_2, D_2, ^{3}He, and ^{4}He with a Lennard-Jones potential is not possible even after adjustment of the parameter values to fit the experimental data. The optimal set of parameters is found to depend strongly on the subset of data fit; e.g., the ϵ parameter for H_2 is found to be about twice as large for a fit to all of Stewart's data as for a fit to the data above 2 kbar.

On the other hand the ^{20}Ne data could be well described with a Lennard-Jones potential. The optimal set of parameters being practically independent of the choice of data subset, e.g., the ϵ parameter is found to be 37.6 K for a fit to all the data and 36.4 K for a fit to the data above 2 kbar. (σ is 2.83 Å in both cases.) These optimal parameters with respect to Stewart's ^{20}Ne data compare reasonably with the values of Brown as reported in Ref. 1, viz., $\epsilon=36.8$ K and $\sigma=2.79$ Å.

The experimental data in the quantum solids (with the exception of D_2) and ^{20}Ne are satisfactorily represented with a Buckingham potential. However, the optimal parameters in H_2, ^{3}He (excluding the 1- and 2-kbar points from the fit), ^{4}He, and ^{20}Ne exhibit a remarkable effect: The Z (or C') parameter, which gives the strength of the induced-dipole induced-quadrupole interaction, is essentially zero. This result implies that the intermolecular potential in H_2, ^{3}He, ^{4}He, and ^{20}Ne can be satisfactorily represented by a Buckingham 6-exp potential.

The ^{3}He molar volumes for 1 and 2 kbar which appear in Table II of Ref. 7 were deduced by combining the Grilly-Mills[9] molar volume measurements along the melting curves of ^{3}He and ^{4}He with the Dugdale-Simon[10] ^{4}He isochores. When these values are included the optimal parameters in a Buckingham potential for ^{3}He change markedly from those deduced when they are excluded; in particular, a nonzero Z is obtained.

The D_2 data are not well represented by the Buckingham potential in the sense that different optimal parameter sets, including nonzero Z, are obtained for different data subsets. However, when Z is fixed at zero, the Buckingham 6-exp parameters obtained are consistent with those determined for H_2 and a satisfactory fit to the experimental data is obtained.

The Buckingham potential results are summarized in Table I. Thermodynamic results are summarized for the optimal 6-exp potentials in Tables II–VI.

The deduced parameters do not agree well with those derived from virial coefficient and viscosity measurements[11] (except for the ^{20}Ne Lennard-Jones parameters). However, the repulsive potential deduced for H_2 and D_2 is consistent with the estimates of Hoover *et al.*[12] based upon the calculations of Tapia *et al.*,[13] and also with the calculations of Magnasco and Musso.[14] (See also the review article of McMahon *et al.*[15])

We have performed our high-pressure extrapolations using the intermolecular potentials deduced separately from the H_2 and D_2 data and from the ^{3}He and ^{4}He data. We do not mean to imply that we believe the intermolecular potential for the hydrogen or helium isotopes to be different but rather to indicate the uncertainty in the determination of these potentials and thus in the extrapolated thermodynamic functions.

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