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# Five- and six-body effects on equation of state of solid $^4\text{He}$

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## Abstract

The interaction energies of hcp and fcc helium are calculated by using a many-body expansion and cluster approach. The two- to six-body contributions are evaluated based on numerical solution of the Schrödinger equation for  $N$ -atomic clusters in the frame of the Born–Oppenheimer approximation. The convergence of the many-body expansion and its truncation position are discussed for the molar volume from 8.4 to 1.744 cm<sup>3</sup> mol<sup>-1</sup>. It indicates that the five-body interactions become manifest at volume smaller than 3.0 cm<sup>3</sup> mol<sup>-1</sup>, providing negative correction to the potential energy; while the six-body interactions emerge at volume smaller than 2.3 cm<sup>3</sup> mol<sup>-1</sup>, with positive correction. With the use of the Einstein approximation for the zero-point contribution, the calculated 0 K equation of state is given up to 180 GPa and compared with measurements.

## 1. Introduction

Although the helium atom is one of the simplest atoms in the periodic table of elements, its solid phase equation of state (EOS) has not been well understood up to now [1, 2]. Obtaining a satisfactory theoretical description for its compression behaviour at high pressures is both a long-standing problem and a worthwhile objective, because of its quantum nature and the astrophysical relevance [3, 4]. Currently, the interaction between two isolated He atoms is accurately known from precise *ab initio* calculations, the experimental virial coefficients, and the viscosity of a dilute helium gas, etc, among which a famous form is the Aziz (HFDHE2) [5] potential, that selects Hartree–Fock calculation for short-range repulsion and semi-empirical dispersion coefficients for the long-range attraction. But the Aziz or some other two-body potentials such as the recently proposed SAPT one [6, 7] are too stiff to match the observations for solid helium [4, 8, 9]. The softening of the potential was attributed to the screening effects

of neighbour atoms [10, 11]. An attempt has been made to use an effective pair potential, i.e. the exponential-6 potential [12] obtained from fitting to shock-wave data, for explaining the compressibility of solid helium. It is still too repulsive to give a good prediction at pressure higher about 20 GPa [4]. In addition, the density function theory was applied to solid helium [1, 13], which determines the electronic structure of the system and reflects the symmetry of the crystal, thus including many-body interaction effects. Unfortunately, the obtained results are not reliable at pressure lower than about 10 GPa [1, 13]. Moreover, the band-structure calculation is a total-energy technique; it cannot directly illustrate the various many-body contributions.

On the other hand, the use of many-body expansion of interaction energy is of great value to describe the interatomic forces for crystalline properties. There are many reports on helium trimers ( $\text{He}_3$ ) and two analytic fits for three-body interactions were proposed respectively by Bruch and McGee (BM) [14, 15], and Cohen and Murell (CM) [16]. In the many-body expansion, the two- and three-body contributions for solid helium could be evaluated using their available analytic formulae [8, 17, 18]. However, a path integral Monte Carlo (PIMC) simulation gave a much softer EOS than that obtained from the experimental data [8], implying the higher-order terms in the many-body expansion to be included. At high densities of experiments the short-range many-body interactions play a dominant role [10, 17, 18]. In consideration that the helium atom has a simple electronic structure and its electrons are still closely located at the nucleus even at very high compression, an atomic cluster method was put forward in our previous works [19, 20]. It assumed that a many-body interaction of  $N$  atoms in the crystal can be approximated by that of an isolated  $\text{He}_N$  cluster with the same lattice geometry. By using the Hartree–Fock self-consistent-field (SCF) method, the short-range interaction energies of various  $\text{He}_4$  clusters in helium lattices can be directly computed. The five-body contribution was approximated by the difference between the total atomic potential and its many-body expansion that is only extended to the four-body term [20]. In this work, we show that this approximation is not applicable at very high densities, and a rule to evaluate the truncation error of the many-body expansion is thus self-consistently proposed. According to the quantum theoretical definition the five-body term is strictly computed. Moreover, the convergence of the many-body expansion is investigated to the extent of molar volume of  $1.744 \text{ cm}^3 \text{ mol}^{-1}$ , where the six-body contribution becomes manifest. Based on the many-body expansion, an EOS at 0 K is suggested and compared with experiments.

## 2. *Ab initio* calculation of many-body contributions for solid helium

### 2.1. The method

As solid helium is compressed, the average interatomic distance is reduced. Each He atom simultaneously interacts with a number of its surrounding neighbours. Here, we considered one atom (labelled O) and its  $(n - 1)$  surrounding neighbours in a lattice. These  $n$  interacting atoms form an  $\text{He}_n$  system. The interaction energy between the central atom O and its  $(n - 1)$  neighbours is equal to the system energy difference by removing the central atom O from the lattice position  $\mathbf{r}_0$  to infinity, so the potential energy (labelled  $U$ ) of the atom O in the crystal lattice can be expressed as [20]

$$U = E_n(\mathbf{r}_0, \mathbf{r}_1, \dots, \mathbf{r}_{n-1}) - [E_{n-1}(\mathbf{r}_1, \dots, \mathbf{r}_{n-1}) + E_1] \quad (1)$$

where  $1, 2, 3, \dots, n-1$  denote its nonidentical neighbours, and  $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{n-1}$  are their actual coordinations in a lattice, respectively.  $E_1$  is the ground-state energy of an isolated helium atom, and  $E_n$  represents the ground-state energy of the system of  $\text{He}_n$ . If a sufficient number

of neighbours are included the outside neighbour contributions can be neglected due to the many-body screening effects. Thus  $U$  would approach the exact potential energy of atom O in the crystal lattice. These  $n$  atoms can be looked on as a simple molecule with a closed-shell electronic structure and  $n$   $\text{He}^+$  nuclei. Based on the Born–Oppenheimer approximation we can write its Schrödinger equation, and the ground-state energy can be obtained by the SCF method. The calculations were performed by the Gamess program [23]. A 6311G basis set is selected for each He atom, and the energy converges to  $10^{-8}$  Hartree/molecule in the restricted Hartree–Fock calculation.

The interaction energy  $U$  of atom O with its neighbours can be developed in a many-body expansion:

$$\begin{aligned}
 U &= \sum_{n-1 \geq i \geq 1} u_2(\text{O}, i) + \sum_{n-1 \geq j > i \geq 1} u_3(\text{O}, i, j) + \sum_{n-1 \geq k > j > i \geq 1} u_4(\text{O}, i, j, k) \\
 &\quad + \sum_{n-1 \geq l > k > j > i \geq 1} u_5(\text{O}, i, j, k, l) \\
 &\quad + \sum_{n-1 \geq m > l > k > j > i \geq 1} u_6(\text{O}, i, j, k, l, m) \cdots \\
 &= U_2 + U_3 + U_4 + U_5 + U_6 + \cdots
 \end{aligned} \tag{2}$$

where  $i, j, k, l, m$  denote its different neighbours,  $(n - 1)$  is the total number of considered neighbours, and the summations extend over all considered neighbours in the system.  $U_2$  represents the total two-body interaction energy of atom O with its neighbours,  $U_3$  the total three-body contribution of atom O with its neighbour,  $U_4$  the total four-body contribution of atom O with its neighbour, and so on. A two-body interaction between central atom O and one of its neighbours  $i$  can be expressed as

$$u_2(\text{O}, i) = E_2(\mathbf{r}_0, \mathbf{r}_i) - 2E_1 \tag{4}$$

where  $E_2(\mathbf{r}_0, \mathbf{r}_i)$  is the ground-state energy of the composite system of atom O and its neighbour  $i$ . A three-body interaction  $u_3(\text{O}, i, j)$  between the atom O and its two arbitrary neighbours  $i, j$  is defined by

$$\begin{aligned}
 u_3(\text{O}, i, j) &= [E_3(\mathbf{r}_0, \mathbf{r}_i, \mathbf{r}_j) - 3E_1] - [u_2(\text{O}, i) + u_2(\text{O}, j) + u_2(i, j)] \\
 &= [E_3(\mathbf{r}_0, \mathbf{r}_i, \mathbf{r}_j) - 3E_1] - U(2, 3)
 \end{aligned} \tag{5}$$

where  $U(M, N)$  ( $M < N$ ) denotes the total  $M$ -body interactions in the composite system of cluster  $\text{He}_N$ . A four-body interaction  $u_4(\text{O}, i, j, k)$  between four atoms in cluster  $\text{He}_4$ , formed by the atom O and its three arbitrary neighbours (i.e.  $i, j$  and  $k$ ), is evaluated by subtracting all the three-body interactions  $U(3, 4)$  and all two-body interactions  $U(2, 4)$  from the interaction energy of the  $\text{He}_4$  cluster

$$u_4(\text{O}, i, j, k) = [E_4(\mathbf{r}_0, \mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) - 4E_1] - U(3, 4) - U(2, 4). \tag{6}$$

Analogously,  $u_5(\text{O}, i, j, k, l)$  and  $u_6(\text{O}, i, j, k, l, m)$  can be written respectively as

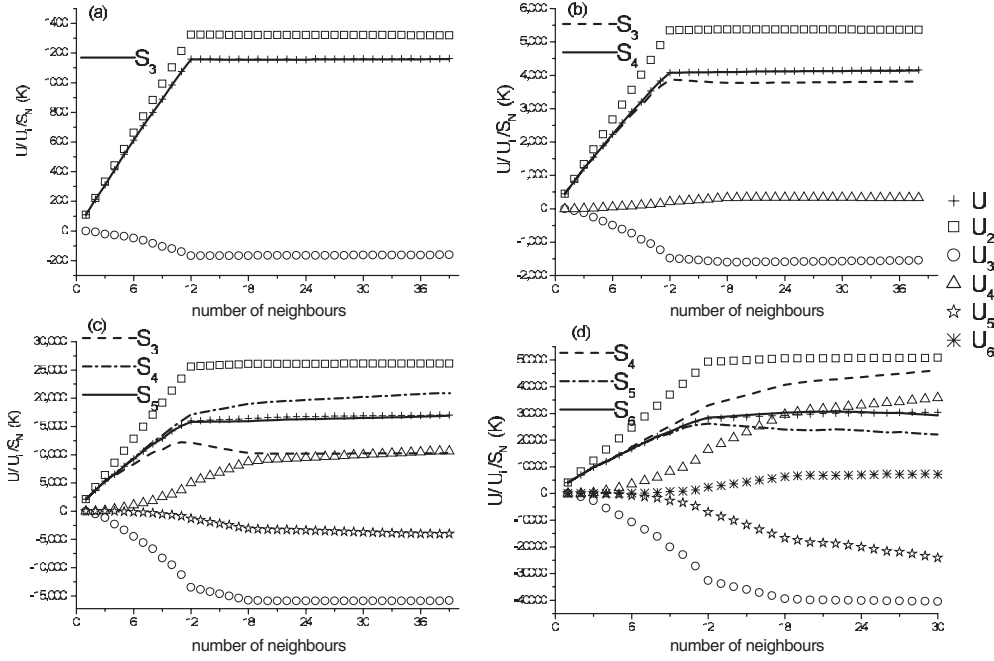
$$u_5(\text{O}, i, j, k, l) = [E_5(\mathbf{r}_0, \mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k, \mathbf{r}_l) - 5E_1] - U(4, 5) - U(3, 5) - U(2, 5) \tag{7}$$

and

$$\begin{aligned}
 u_6(\text{O}, i, j, k, l, m) &= [E_6(\mathbf{r}_0, \mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k, \mathbf{r}_l, \mathbf{r}_m) - 6E_1] \\
 &\quad - U(5, 6) - U(4, 6) - U(3, 6) - U(2, 6).
 \end{aligned} \tag{8}$$

In all cases, the atoms in the cluster are located at their positions the same as those in the lattice. Consequently the cohesive energy per atom  $E_s$  due to the SCF contribution is

$$E_s = \frac{1}{2}U_2 + \frac{1}{3}U_3 + \frac{1}{4}U_4 + \frac{1}{5}U_5 + \frac{1}{6}U_6 + \cdots \tag{9}$$



**Figure 1.** Atomic potential in hcp phase and its many-body expansion approximations. (a)  $R = 2.4 \text{ \AA}$ , (b)  $R = 2.1 \text{ \AA}$ , (c)  $R = 1.75 \text{ \AA}$ , (d)  $R = 1.6 \text{ \AA}$ .

Here  $\frac{1}{N}U_N$  denotes the  $N$ -body interaction contributions to the cohesive energy per atom. It is noted that the applicability of equations (3) and (9) is based on the assumption that the many-body expansion is convergent. We will check whether this assumption is rational in the next section.

## 2.2. The convergence and truncating position of the many-body expansion at different densities

Below  $\sim 12 \text{ GPa}$  and  $\sim 15 \text{ K}$ , solid He crystallized in hcp structure [2, 4, 9, 24]. With increasing temperature an fcc phase is stabilized from  $\sim 15 \text{ K}$  and  $\sim 0.1 \text{ GPa}$  to  $\sim 285 \text{ K}$  and  $\sim 12 \text{ GPa}$ . Apart from this small stability region, the hcp phase remains stable up to  $58 \text{ GPa}$  [4]. The recent density function theoretical results also predicted that the hcp structure is the most stable low-temperature phase of He at pressures up to  $100\text{--}200 \text{ GPa}$  [1]. In this study, our calculations are performed on hcp structure in the whole interesting compression range, while on fcc structure only in the relevant low pressure region. From equation (1), we can evaluate the interaction energy,  $U$ , for an atom in the lattice. According to equation (2), the atomic potential  $U$  can be expanded in a many-body interaction series. We let the sum of the many-body contribution terms on the right-hand side of equation (3) be written as

$$S_N = \sum_{i=2}^N U_i \quad (N = 2, 3, 4, 5, 6, \dots). \quad (10)$$

For a given  $N$  if  $S_N/U$  approaches unity then the terms behind  $U_N$  in equation (3) can be truncated. Figure 1 shows that the potential energy  $U$  of an atom in hcp structure converges rapidly, and its many-body expansion terms also approach a stable value when several neighbour shells are considered. Figure 1 also gives the comparison of  $U$  with its

approximation  $S_N$  at several nearest-neighbour distances,  $R$ , for hcp helium. Figure 1(a) demonstrates that at  $R = 2.4 \text{ \AA}$  ( $V = 5.887 \text{ cm}^3 \text{ mol}^{-1}$ ) the two-body term  $U_2$  overestimates the value of  $U$ , but it would be approximated by  $S_3$ , whereas at a smaller distance of  $R = 2.1 \text{ \AA}$  ( $V = 3.944 \text{ cm}^3 \text{ mol}^{-1}$ ) the sum of  $S_3$  is lower than  $U$ , but it would be approximated by  $S_4$  (see figure 1(b)). Also, figure 1(c) indicates that at  $R = 1.75 \text{ \AA}$  or  $V = 2.282 \text{ cm}^3 \text{ mol}^{-1}$  the sum of  $S_3$  and  $S_4$  is either lower or higher than  $U$ , but it is well approximated by  $S_5$ , whereas at  $R = 1.6 \text{ \AA}$  ( $V = 1.744 \text{ cm}^3 \text{ mol}^{-1}$ )  $S_6$  is in good agreement with  $U$  accompanied by a higher  $S_4$  and a lower  $S_5$ .

The calculated data are listed in table 1, in which the last columns give the ratio of  $S_N$  to  $U$  at different distances. It shows the absolute values of  $U_i$  obey the relation of  $|U_2| > |U_3| > |U_4| > |U_5| > |U_6|$ , with the sign of  $U_3$  and  $U_5$  being negative and the others being positive. It should be noted although the three-body interactions for some selected  $\text{He}_3$  clusters (the isosceles triangular geometries, the included angle  $\theta$  between the equal sides in the range  $30^\circ$ – $180^\circ$ ) were computed [14, 22], being negative for  $\theta < 120^\circ$  and positive for  $\theta = 150^\circ$  and  $180^\circ$ , the properties of solid helium are dependent on the total contribution of all three-body effects in a lattice rather than the individual one. Our calculations indicate that the total three-body contribution  $U_3$  from a large number of different geometries of  $\text{He}_3$  is negative for close-packed solid helium, and the total five-body contribution  $U_5$  has the same sign as that of the three-body term, whereas the total two-, four-, and six-body contributions are repulsive. It also shows for hcp helium at  $R = 2.7 \text{ \AA}$  ( $V = 8.4 \text{ cm}^3 \text{ mol}^{-1}$ ) that the two-body contribution is adequate to satisfactorily describe the atomic potential, i.e.  $S_2/U = 102.7\%$ ; however, the higher-term contributions become manifest with decreasing distance. For example, at  $R = 2.6$ – $2.3 \text{ \AA}$  or  $V = 7.5$ – $5.2 \text{ cm}^3 \text{ mol}^{-1}$ , truncating the many-body expansion after the three-body term would give a good approximation for  $U$ , with a truncation error less than 2%. In the range of  $2.2$ – $2.0 \text{ \AA}$  or  $4.5$ – $3.0 \text{ cm}^3 \text{ mol}^{-1}$ , the sum of  $S_4$  would well represent the atomic potential with a uncertainty less than 2%. At the volume below  $3.0 \text{ cm}^3 \text{ mol}^{-1}$  the four-body corrections lead to an excessive stiffening of the potential energy and the effect of five-body interactions is necessary to be included to offset the excessive repulsive effect arising from the four-body term. Truncating the expansion after the five-body term would work well from  $1.9$  to  $1.75 \text{ \AA}$  or from  $3.0$  to  $2.3 \text{ cm}^3 \text{ mol}^{-1}$ , but for even smaller volume this  $S_5$  approximation fails to give a good result. For example, it provides 88% ( $S_5/U$ ) atomic potential at  $R = 1.65 \text{ \AA}$  or  $V = 1.913 \text{ cm}^3 \text{ mol}^{-1}$ , whereas adding the six-body contribution could improve the agreement up to 98.7% ( $S_6/U$ ). The fcc structure calculation gives nearly the same results as those of the hcp case at the same studied distance.

In order to validate the results we obtained, the total short-range two-body interaction energy  $U_2$  and three-body one  $U_3$  are compared with those computed from the repulsion of Aziz and SAPT potentials, and the three-body exchange part of BM and CM potentials for hcp helium, given in figure 2. It can be seen that the present two-body term locates between Aziz and SAPT calculations at small distances, and approaches the latter at large distances. For the three-body term, the agreement between the present result and those of BM and CM are excellent over the entire studied region. It implies that the present many-body calculation would be reliable in the following studies.

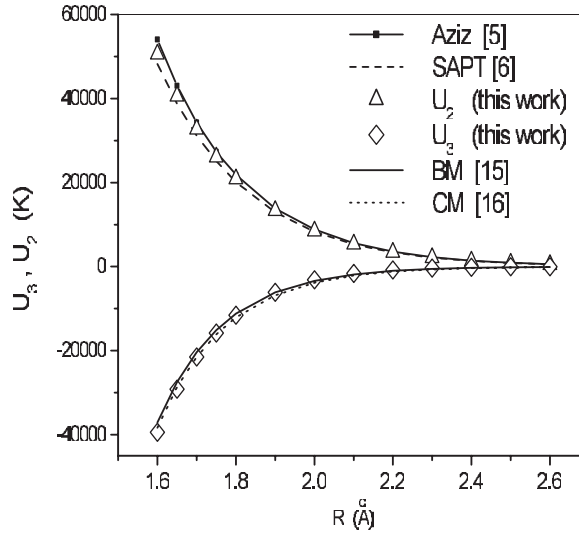
### 3. Equation of state

At zero temperature the pressure of solid helium consists of static and zero-point vibration contributions, written as [25]

$$P = P_{\text{ST}}(V) + P_{\text{ZP}}(V) \quad (11)$$

**Table 1.** Atomic potential energy and its many-body expansion in hcp/fcc He. The number  $L$  of neighbour shells used for calculation is given in the fourth column.

Phase	$R$ (Å)	$V$ (cm <sup>3</sup> mol <sup>-1</sup> )	$L$	$U$ (K)	$U_2$ (K)	$U_3$ (K)	$U_4$ (K)	$U_5$ (K)	$U_6$ (K)	$S_2/U$	$S_3/U$	$S_4/U$	$S_5/U$	$S_6/U$
hcp	1.6	1.744	3	29 723.4	50 634.6	-39 895.1	31 355.9	-18 335.6	6835.5	1.704	0.361	1.416	0.799	1.029
			2	29 300.4	50 558.3	-39 458.1	29 615.2	-16 747.7	6302.6					
			1	28 030.7	49 292.6	-32 646.2	16 470.8	-7 007.2	2 289.5					
	1.65	1.913	3	24 475.8	40 630.1	-29 458.7	20 954.6	-10 581.6	2613.7	1.660	0.456	1.313	0.880	0.987
			2	24 162.8	40 581.0	-29 184.8	19 857.4	-9 745.1	2532.0					
			1	23 280.5	39 672.2	-24 413.3	11 182.3	-4 115.5	989.5					
	1.7	2.092	3	20 145.3	32 569.3	-21 674.1	13 898.2	-5961.2	648.3	1.617	0.541	1.231	0.935	0.967
	1.75	2.282	3	16 571.3	26 082.1	-15 887.0	9 141.3	-3 253.0		1.574	0.615	1.167	0.971	
	1.8	2.483	3	13 621.9	20 867.5	-11 600.1	5 956.9	-1 698.6		1.532	0.680	1.118	0.993	
	1.85	2.696	3	11 188.3	16 680.5	-8 435.9	3 841.3	-828.7		1.491	0.737	1.080	1.006	
	1.9	2.921	3	9 180.6	13 322.1	-6 108.9	2 447.0	-358.0		1.451	0.786	1.052	1.013	
	2.0	3.047	3	6 159.8	8 475.1	-3 160.0	949.0			1.376	0.863	1.017		
			2	6 127.3	8 476.0	-3 158.5	913.9							
	2.1	3.944	1	6 080.3	8 409.3	-2 851.0	564.3							
			3	4 109.6	5 371.8	-1 599.7	335.5				1.307	0.918	1.000	
			2	4 094.5	5 372.9	-1 601.7	324.2							
	2.2	4.534	1	4 078.1	5 348.5	-1 480.1	208.1							
			2	2 715.0	3 390.1	-789.5	96.0				1.249	0.958	0.993	
	2.3	5.181	2	1 783.4	2 125.6	-373.7				1.192	0.982			
	2.4	5.887	2	1 155.9	1 321.0	-166.1				1.143	0.999			
2.5	6.653	2	738.5	810.1	-66.1				1.097	1.007				
2.6	7.484	2	459.9	487.1	-20.8				1.059	1.014				
2.7	8.381	2	276.9	284.3					1.027	1.019				
fcc	2.1	3.944	2	4 094.9	5 372.9	-1 600.5	324.9			1.312	0.921	1.001		
	2.2	4.543	2	2 715.1	3 390.1	-788.8	96.1			1.249	0.958	0.993		
	2.3	5.181	2	1 798.8	2 123.2	-359.3				1.180	0.981			
	2.4	5.887	2	1 157.1	1 321.0	-166.0				1.142	0.998			
	2.5	6.653	2	738.1	810.1	-66.1				1.098	1.008			
	2.6	7.484	2	459.9	487.1	-20.8				1.059	1.014			
	2.7	8.381	2	276.9	284.3					1.027				



**Figure 2.** Comparisons among the short-range two- and three-body interaction calculations for hcp helium.

where  $P_{\text{ST}}$  is the static pressure, and  $P_{\text{ZP}}$  the zero-point vibration pressure.  $P_{\text{ST}}$  can be deduced from the volume differentiation of the static energy

$$P_{\text{ST}} = -\frac{dE_{\text{ST}}}{dV} \quad (12)$$

where  $E_{\text{ST}}$  is the total cohesive energy per atom, which is usually expressed as a sum of the SCF and correlation energies [26], i.e.

$$E_{\text{ST}} = E_s + E_c. \quad (13)$$

In our approach only  $E_s$  has been given by a many-body expansion obtained from the SCF calculation. For the correlation contribution  $E_c$ , we use a pairwise standard van-der-Waals form [5]  $\phi(r_i)$  with semi-empirically determined dispersion coefficients  $c_6$ ,  $c_8$ , and  $c_{10}$  to describe

$$E_c = \frac{1}{2} \sum_i \phi(r_i) \quad (14)$$

where

$$\phi(r_i) = -\left(\frac{c_6}{x_i^6} + \frac{c_8}{x_i^8} + \frac{c_{10}}{x_i^{10}}\right) F(x_i) \quad (15)$$

and

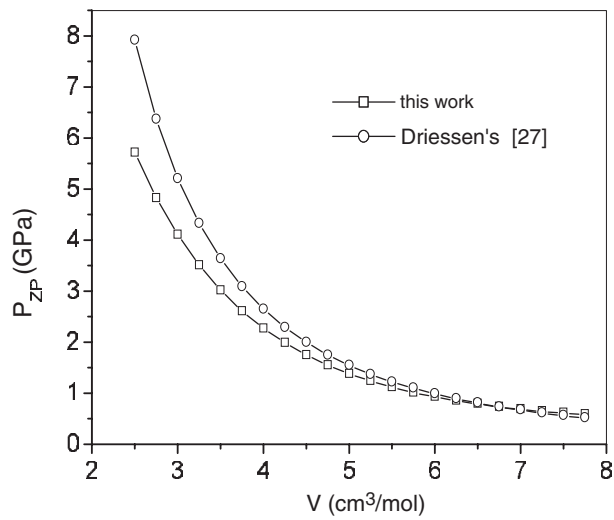
$$F(x_i) = \begin{cases} \exp\left[-\left(\frac{D}{x_i} - 1\right)^2\right] & (x < D) \\ 1 & (x \geq D) \end{cases} \quad (16)$$

where  $x_i = r_i/r_m$ , and  $r_i$  is the distance between the central atom and the  $i$ th neighbours.  $D$  and  $r_m$  are constants, having  $D = 1.28$  and  $r_m = 2.9673 \text{ \AA}$  from [5].

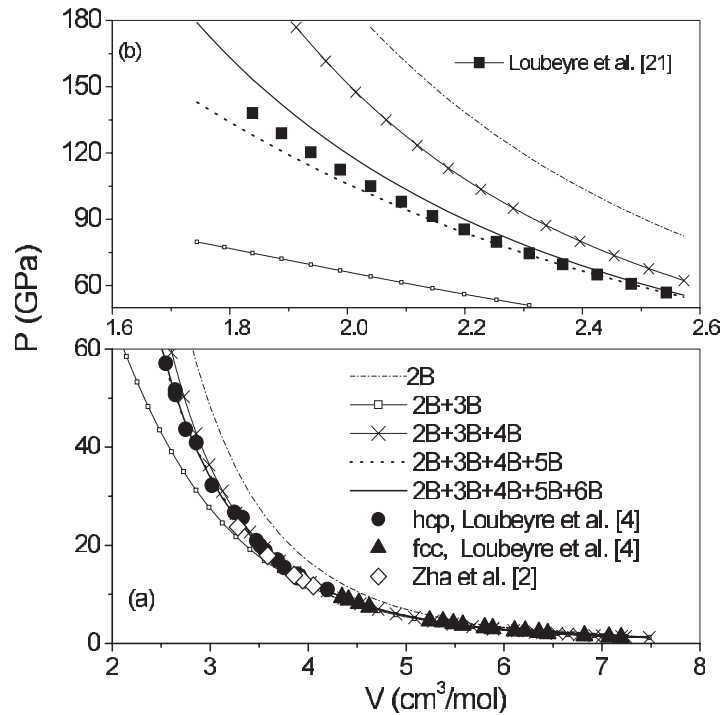
The zero-point pressure  $P_{\text{ZP}}$  could be calculated from the Einstein approximation and Mie-Grüneisen model [25]

$$P_{\text{ZP}} = \frac{\gamma}{V} \frac{3}{2} \hbar \omega(V) \quad (17)$$





**Figure 3.** Zero-point vibration pressure of solid helium.



**Figure 4.** Comparison between theoretical and experimental equations of state for solid He. (a) The circles, triangles and diamonds represent the 0 K isotherms deduced from measurements. (b) The filled squares represent the 300 K experimental isotherm which is given by the Vinet EOS in [21].

where  $\gamma$  is the Grüneisen parameter, defined as  $\gamma = -d \ln \omega / d \ln V$ ,  $\omega(V)$  is the average vibration frequency of an atom around its equilibrium position, which is a function of molar

**Table 2.** The 0 K isothermal EOS of solid  $^4\text{He}$ .

Volume ( $\text{cm}^3 \text{mol}^{-1}$ )	$P_{2B}$ (GPa)	$P_{2B+3B}$ (GPa)	$P_{2B+3B+4B}$ (GPa)	$P_{2B+\dots+5B}$ (GPa)	$P_{2B+\dots+6B}$ (GPa)
1.744	289.8	79.7	244.7	142.8	178.9
1.913	216.9	70.6	176.7	117.3	136.4
2.092	162.8	61.1	128.8	95.0	104.4
2.282	122.2	52.0	94.7	76.0	80.2
2.483	92.2	43.5	70.2	60.3	61.7
2.619	77.2	38.6	58.1	51.7	52.2
2.696	69.9	36.0	52.4	47.4	47.6
2.833	58.9	31.8	43.9	40.8	40.6
2.921	52.9	29.4	39.4	37.1	36.8
3.012	47.5	27.1	35.3	33.7	33.3
3.281	35.0	21.4	26.0	25.5	25.1
3.422	30.0	18.9	22.4	22.1	21.8
3.588	25.2	16.4	18.9	18.8	18.6
3.680	23.0	15.2	17.2	17.2	17.0
3.750	21.4	14.3	16.1	16.1	16.0
3.857	19.2	13.1	14.5	14.6	14.5
3.944	17.7	12.2	13.4	13.5	13.4
4.051	16.0	11.2	12.2	12.2	12.2
4.110	15.1	10.7	11.5	11.6	11.6
4.170	14.3	10.2	10.9	11.0	11.0
4.534	10.3	7.6	8.0	8.1	8.1
5.181	6.0	4.8	4.9	4.9	4.9
5.887	3.5	3.0	3.0	3.0	3.0
7.484	1.3	1.2	1.2	1.2	1.2

volume. For a given volume  $\omega$  can be approximately derived from the change of atomic potential when the atom moves away from its equilibrium position while its neighbours are frozen at their lattice site. For solid helium, its zero-point contribution is important. In figure 3, the present  $P_{ZP}$  estimation, from equation (17), is compared with that of Driessen *et al* [27], which was deduced from the Debye approximation and at  $V \geq 2.5 \text{ cm}^3 \text{ mol}^{-1}$ . The agreement between these two estimations is obvious at rather low densities. The maximum difference of  $\sim 2$  GPa happens at  $V = 2.5 \text{ cm}^3 \text{ mol}^{-1}$ , which is reasonable when compared to the corresponding total pressure of  $\sim 60$  GPa in this case; see figure 4(a).

Combining equations (11)–(17), several 0 K isothermal EOSs can be calculated from the many-body expansion using from two- to six-body terms respectively; see table 2. These calculations are compared with available experimental data shown in figure 4. It can be seen that the two-body term is only applicable for rather lower pressure, and more-body interaction terms are required to extend the applicable pressure range. Quantitatively, incorporation of three-body interactions can extend the applicable pressure up to  $\sim 8$  GPa, further adding four-body interactions up to  $\sim 30$  GPa. Moreover, use of the five-body term would reproduce the measurements up to  $\sim 80$  GPa. Figure 4(b) shows the effect of the six-body term would be important at higher pressures, considering that the isothermal curve becomes much stiffer than that of five-body interactions. Moreover, the compressibility measurements of solid helium up to 130 GPa [21] can be better interpreted when the six-body contribution is taken into account. A Vinet function can be used to represent the present isothermal EOS at 0 K within 5%, giving the results of  $V_0 = 23.72 \text{ cm}^3 \text{ mol}^{-1}$ , and  $K_0 = 0.0079$  GPa, and  $K'_0 = 9.83$  over the volume regime  $1.744\text{--}7.0 \text{ cm}^3 \text{ mol}^{-1}$ .

#### 4. Summary

An investigation of five- and six-body effects in highly compressed solid  $^4\text{He}$  is conducted based on a many-body expansion of interaction energy. The two- to six-body terms in the expansion are calculated from 8.4 to  $1.744\text{ cm}^3\text{ mol}^{-1}$  by using the SCF method and atomic cluster technique, in which the configurations of atom clusters are chosen as the same as those in the actual lattice. Moreover, an independent theoretical rule to evaluate the truncation error of the many-body expansion is self-consistently set up. This work shows the many-body expansion of interaction energy is an useful tool to understand the high-pressure behaviours of solid helium over a wide compression range, i.e. from a low-density region where two-body interactions play a dominant role to a high-density region where higher-order many-body effects prevail. The calculations indicate that at volume below  $3.0\text{ cm}^3\text{ mol}^{-1}$  the five-body interactions become manifest and provide negative correction. However, at volume below  $2.3\text{ cm}^3\text{ mol}^{-1}$  the six-body interaction contribution appears and is necessary to be included to offset the excessive softening effect arising from five-body interactions. The compression behaviour of solid helium for the pressure from 1 to 180 GPa is described.

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#### References

- [1] Nabi Z, Vitos L, Johansson B and Ahuja R 2005 *Phys. Rev. B* **72** 172102
- [2] Zha C S, Mao H K and Hemley R J 2004 *Phys. Rev. B* **70** 174107
- [3] Moroni S, Pederiva F, Fantoni S and Boninsegni M 2000 *Phys. Rev. Lett.* **84** 2650
- [4] Loubeyre P, Le Toullec R and Pinceaux P 1993 *Phys. Rev. Lett.* **71** 2272
- [5] Aziz R A, Nain V P S, Carley J S, Taylor W L and McConville G T 1979 *J. Chem. Phys.* **70** 4330
- [6] Janzen A R and Aziz R A 1997 *J. Chem. Phys.* **107** 914
- [7] Korona T, Williams H L, Bukowskj R and Szalewicz K 1997 *J. Chem. Phys.* **106** 5109
- [8] Chang S Y and Boninsegni M 2001 *J. Chem. Phys.* **115** 2629
- [9] Mao H K, Hemley R J, Wu Y, Jephcoat A P, Finger L W, Zha C S and Basset W A 1988 *Phys. Rev. Lett.* **60** 2649
- [10] Lesar R 1988 *Phys. Rev. Lett.* **18** 2121
- [11] Younger S M, Harrison A K and Sugiyama G 1989 *Phys. Rev. A* **40** 5256
- [12] Ross M and Young D A 1986 *Phys. Lett. A* **118** 463
- [13] Young D A, McMahan A K and Ross M 1981 *Phys. Rev. B* **24** 5119
- [14] Novaro O A and Beltran-Lopez V 1972 *J. Chem. Phys.* **56** 815
- [15] Bruch L M and McGee I J 1973 *J. Chem. Phys.* **59** 409
- [16] Cohen M J and Murrel J N 1996 *Chem. Phys. Lett.* **260** 371
- [17] Loubeyre P 1987 *Phys. Rev. Lett.* **58** 21857
- [18] Loubeyre P 1988 *Phys. Rev. B* **37** 5432
- [19] Tian C L, Liu F S, Cai L C and Jing F Q 2003 *Acta Phys. Sin.* **52** 1218 (in Chinese)
- [20] Tian C L, Liu F S, Cai L C and Jing F Q 2003 *Chin. Phys. Lett.* **20** 706
- [21] Loubeyre P, LeToullec R, Hanfland M, Ulivi L and Datchi F 1998 *Phys. Rev. B* **57** 10403
- [22] Haskins P J and Cook M D 1992 *Phil. Trans. R. Soc. A* **339** 395
- [23] Schmidt M W, Baldrige K K, Boatz J A and Elbert S T 1993 *J. Comput. Chem.* **14** 1347
- [24] Frank J P and Daniels W B 1980 *Phys. Rev. Lett.* **44** 259
- [25] Jing F Q 1999 *Introduction to Experimental Equation of State* 2nd edn (Beijing: Science Press) p 31 (in Chinese)
- [26] Hobza P and Šponer J 1999 *Chem. Rev.* **99** 3249
- [27] Driessen A and van der Poll E 1986 *Phys. Rev. B* **33** 3269