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High-Pressure Equation of State for Solid Krypton from Interatomic Potentials

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The pressure–volume isotherm for krypton at 300 K is evaluated by the Monte Carlo method using pair and three-body potentials. The pair potentials used are that of Aziz and Slaman and a slightly modified version of their potential which gives better agreement with high-energy scattering data. The three-body potentials considered are the Axilrod–Teller interaction and the first-order three-body exchange interaction as parametrized by Loubeyre. The results are compared with recent measurements at pressures up to 300 kbar and the implications of the comparison are discussed. The best agreement with experiment is found using the Axilrod–Teller interaction as the only many-body interaction, indicating that the three-body exchange interaction is to a large extent canceled by higher many-body interactions, at least in the highly symmetrical environment of the crystal.

KEY WORDS: High pressure; equation of state; krypton; interatomic potential; solid krypton; many-body interactions; Monte Carlo method.

1. INTRODUCTION

The use of diamond anvil cells has recently permitted pressure/volume measurements on rare gas crystals at pressures of several hundreds of kilobars, and this in turn has rekindled interest in the use of pair and many-body potentials to analyze the results of such measurements.[1–5]

Aziz and co-workers[6–8] have developed pair potentials for the rare gases which are accurate in the region of the attractive well and in the moderately repulsive region up to at most about 3000 K or 0.3 eV. The accuracy at the upper end of this range depends primarily on measurements of gas viscosities at temperatures above 1000 K, where there

This paper is dedicted to Howard Reiss on the occasion of his 66th birthday.

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are differences of about 2 % between the measurements of different authors (see, for example, ref. 2). Measurements on crystals at pressures of hundreds of kilobars probe the pair potentials at the upper end of this range and a little beyond. There are high-energy scattering measurements due to Rol and co-workers[9] which nominally probe the region from about 4000 K (0.4 eV) to 10,000 K (10 eV). The potentials of Aziz and co-workers do not all agree closely with these results, and I shall find occasion to modify their most recent krypton–krypton potential to produce better agreement with the data of Rol and co-workers.[9]

It is well known that the use of accurate pair potentials together with the Axilrod–Teller (AT) interaction leads to accurate predictions of the thermodynamic properties of neon, argon, krypton, and xenon in solid and fluid states at pressures up to 20 kbar.[10–14] Recently there have been reliable calculations of the first-order three-body exchange interaction by Bulski and co-workers[15–17] and it was pointed out by Meath and Aziz[14] that this term was comparable in magnitude with the AT term and of opposite sign, and that inclusion of this term would destroy the agreement with experiment found for the heavier rare gases.

It was suggested by McLean *et al.*[3] on the basis of earlier work by LeSar,[18] that the three-body exchange interaction was probably largely canceled by four- and higher-body interactions in crystals because extensive redistribution of charge, which is presumably the origin of the many-body exchange interactions, is impossible in the highly symmetrical environment of the crystal. In any event it was found[1–3] that pair potentials with only the AT many-body interaction gave fair agreement with experiment for xenon at pressures up to 500 kbar and for argon at pressures up to 800 kbar. In the case of argon,[3] inclusion of the relatively small many-body exchange interaction calculated by LeSar[18] using his "crystal perturbation" method gave excellent agreement with experiment, providing strong evidence for this cancellation, which is incorporated in the calculation of LeSar.

In this paper I examine this question in the case of krypton, for which measurements at 300 K and pressures up to 300 kbar have recently been made by Polian *et al.*[19]

2. RESULTS

I have made Monte Carlo calculations for fcc krypton at 300 K using methods which have been described previously.[20,21] The pair potentials used were that of Aziz and Slaman[7] and a modified version of that potential. The potential of Aziz and Slaman is given by

$$V(R) = \varepsilon V^*(x) \tag{1}$$

where ε/k is 201.2 K, x is R/R_m with R_m equal to 4.008 Å, and the form of the function $V^*(x)$ is specified by Eqs. (1)–(3) and Table 1 of ref. 7. The modified potential is given by

$$V(R) = \varepsilon V_1^*(x) \tag{2}$$

with

$$V_1^*(x) = V^*(x), \qquad x > 0.873$$

$$V_1^*(x) = V^*(x) - 4300(x - 0.873)^4/[1 + 45(x - 0.873)^4], \qquad x \leqslant 0.873 \tag{3}$$

The modification in Eq. (3) was introduced to give better agreement with the high-energy scattering data of Rol,[9] as shown in the comparison of Fig. 1. This modification has very little effect on the other properties used by Aziz and Slaman to determine the potential. The property most sensitive to the repulsive region of the potential is the gas viscosity. Gas viscosities calculated with the modified potential differ from those found with the unmodified potential by about 0.1 % at temperatures near 300 K, by less than 0.2 % at temperatures below 1200 K, and by less than 0.5 % at 2000 K. In view of the differences between different sets of measurements, which amount to 0.5 % near 300 K and about 2 % above 1200 K (see

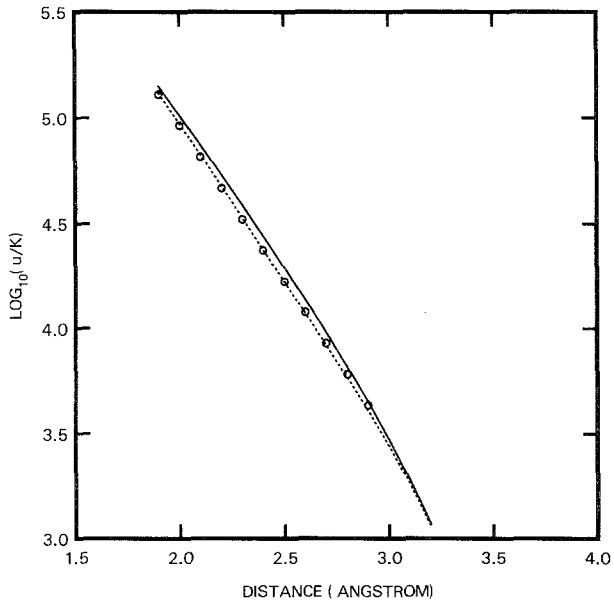

Fig. 1. Repulsive interaction for krypton. (—) Potential of Aziz and Slaman[7]; modified potential, Eq. (2)–(3); (○) high-energy scattering data of Rol and co-workers.[9]

Fig. 7 of ref. 7), these differences are barely significant. The form of Eq. (3) was chosen to make the resulting potential sufficiently smooth (in fact, it has continuous first, second, and third derivatives), and to ensure that it fits the scattering potential to within about 2 %, whereas the unmodified potential was higher than the scattering potential by up to 17 %. Since these scattering data are the only data which control the behavior of the potential in the highly repulsive region relevant for high-pressure studies, this accurate fitting is important.

The Axilrod–Teller three-body interaction has the form

$$V(123) = v(1 + 3\cos\theta_1 \cos\theta_2 \cos\theta_3)/(R_1 R_2 R_3)^3 \tag{4}$$

where R_i and θ_i are the sides and internal angles of the triangle formed by the three interacting atoms. For the coefficient v I used the value given by Leonard and Barker,[22] which is within 1 % of the value given by Kumar and Meath.[23]

There are no accurate calculations of the first-order three-body exchange interaction in krypton. Loubeyre[4] has given an estimate, based on an assumption that the three-body exchange interaction scales in the same way as the two-body exchange interaction on passing from argon to krypton and on the results of Bulski *et al.*[15–17] for argon, which has the form

$$V(123) = -A \exp[-\alpha(R_1 + R_2 + R_3)](1 + 3\cos\theta_1 \cos\theta_2 \cos\theta_3) \tag{5}$$

with $A/\varepsilon = 2695079$ and $\alpha = 1.546$ Å^{-1}. The details of this scaling argument are given in Eq. (8a) and (8b) of ref. 4. In the absence of more precise information, I have used this result, which must surely be correct at least as to order of magnitude. I have calculated this term as a static lattice sum, thus neglecting its effects on the thermal motion.

The Monte Carlo calculations were performed using the unmodified potential of Aziz and Slaman. Results for the modified potential were derived using the assumption that the thermal pressure was the same for both potentials. The thermal pressure and the difference between the two potentials are both small, so that the errors due to this assumption are probably negligible.

The results of the calculations are shown in Figs. 2 and 3, with the experimental data of Polian *et al.*[19] for comparison. For the unmodified potential the results show excellent agreement with the self-consistent phonon calculations of Loubeyre.

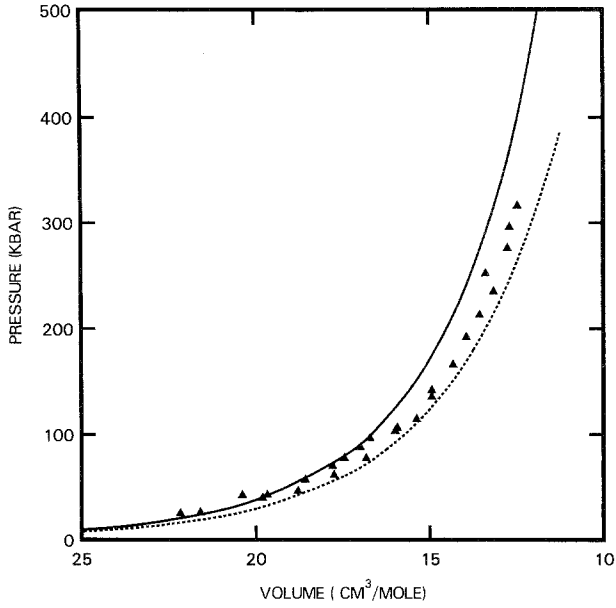

Fig. 2. Pressure–volume relation of krypton at 300 K. (—) Potential of Aziz and Slaman[7] with AT interaction; (···) result including also the three-body exchange interaction as parametrized by Loubeyre[4]; (▲) experimental data of Polian *et al.*[19]

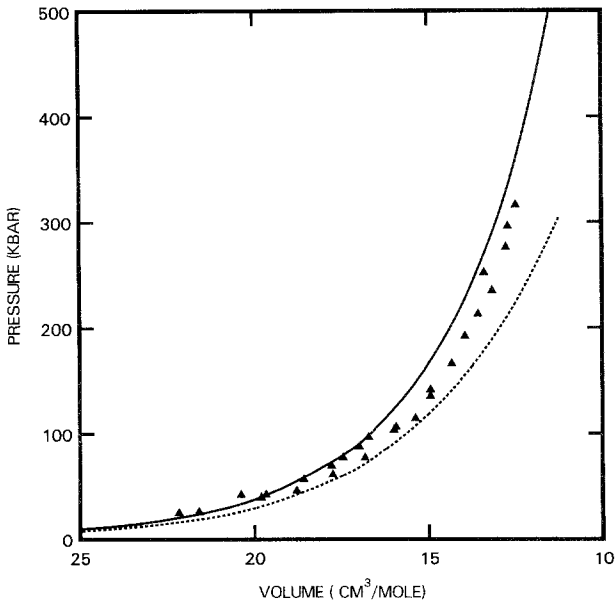

Fig. 3. Pressure–volume relation of krypton at 300 K. (—) Modified potential, Eq. (2)–(3) with AT interaction; (···) result including also the three-body exchange interaction as parametrized by Loubeyre[4]; (▲) experimental data of Polian *et al.*[19]

3. DISCUSSION

Loubeyre concluded that by inclusion of the three-body exchange interaction agreement with experiment is "much improved." This is a reasonable conclusion for the unmodified potential, as shown in Fig. 2. However, for the modified potential the results calculated without the three-body exchange interaction give substantially better agreement. These results are still a little higher than the experimental data, so that a smaller many-body exchange correction such as would be predicted by the crystal perturbation method of LeSar[18] would improve the agreement. However, inclusion of the three-body exchange term estimated by Loubeyre[4] on the basis of the data of Bulski *et al.*[15–17] leads to a substantial discrepancy between calculated and experimental results. Thus, the data for krypton appear be consistent with the same conclusion as was reached for argon,[2,3] that the three-body exchange interaction alone overestimates the total exchange many-body interaction, and that an estimate like that given by the crystal perturbation theory of LeSar[18] is to preferred. The results for xenon[1] also appear to be consistent with this.

Loubeyre[4] noted that use of the AT interaction as the only many-body interaction gives better agreement with experiment at low pressures.

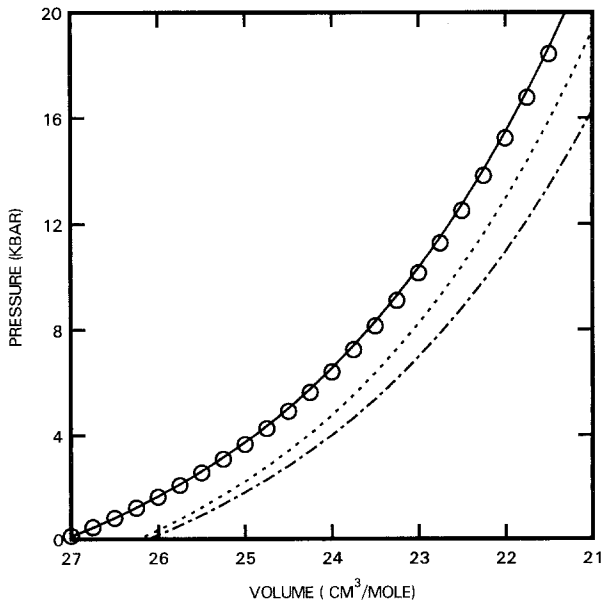

Fig. 4. Pressure–volume relation of krypton at 0 K. (—) Potential of Aziz and Slaman[7] with AT potential; (---) result including three-body exchange interaction as parametrized by Loubeyre[4]; (···) pair potential alone; (○) experimental data of Anderson and Swenson.[24]

In fact, both pressure measurements made with the well-established piston displacement method at pressures up to 20 kbar (see Fig. 4) and calorimetric measurements which give values of cohesive energy at 0 K agree very well[14] with calculations using pair potentials plus AT, but not with calculations including the first-order three-body exchange interaction. This is consistent with the present conclusions from the high-pressure data.

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