High pressure equation of state for solid argon from interatomic potentials

J. A. Barker

Citation: The Journal of Chemical Physics **86**, 1509 (1987); doi: 10.1063/1.452187
View online: http://dx.doi.org/10.1063/1.452187
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/86/3?ver=pdfcov
Published by the AIP Publishing

High pressure equation of state for solid argon from interatomic potentials

J. A. Barker
IBM Almaden Research Center, San Jose, California 95120-6099

(Received 25 September 1986; accepted 17 October 1986)

The pressure–volume isotherm for solid argon at 298 K is calculated by the Monte Carlo method using the pair potential of Barker, Fisher, and Watts (BFW) together with the Axilrod–Teller (AT) three-body interaction. Comparison is made with recent experimental data of Ross and co-workers extending up to 800 kbar. Agreement with experiment is good though not perfect. Comparison is made with the pair potentials of Aziz and Chen and Koide, Meath, and Allnatt and with the exp-6 "effective" pair potential of Ross.

I. INTRODUCTION

Recent work with diamond anvils and the ruby fluorescence pressure calibration has extended the range of pressures for which the compression behavior of solid argon has been measured from 20 up to 800 kbar (see Ross *et al.*[1]). It is of considerable interest to examine the extent to which these new data are consistent with existing information on interatomic potentials, both pair and many-body.

The pair potential of Barker, Fisher, and Watts[2] (BFW), shown to fit experimental data involving pairs of argon atoms, has also been shown to be consistent with a wide range of data on solid and dense fluid argon when used together with the Axilrod–Teller (AT) interaction[2–5]; these data cover a range of pressures up to 20 kbar in both solid and fluid phases. The more recent potential (HFD-C) of Aziz and Chen[6] (AC) is overall very similar to the BFW potential (see Fig. 1) except in the range of distances from 4.5 to 6 Å (where the AC potential is to be preferred), and for distances less than 3.5 Å, in the repulsive region (see Fig. 2). In this latter region the BFW potential was fitted to high-energy atomic beam scattering data of Amdur and Jordan[7,8] and proved to be close to later data of the same kind due to Foreman *et al.*[9] The AC potential on the other hand was fitted to Hartree–Fock calculations and lies appreciably higher (see Fig. 2). These differences are relatively unimportant for the properties of condensed phases at pressures below 20 kbar, and it has been shown[10] that the BFW and AC potentials give essentially the same results for solid argon in this pressure range, while the potential of Koide, Meath, and Allnatt[11] (KMA) also gives very similar results (see Fig. 3). The AC and KMA potentials also give rather similar results to the BFW potential in the fluid phase, as is illustrated in Table I. However the AC and KMA pressures are in slightly worse agreement with experiment than the BFW values in the direction of being too low, whereas in the solid phase at high pressures we shall find that they are too high.

At high pressures the differences of these potentials in the repulsive region (but not in the attractive region) become very important. The purpose of this paper is to compare with experimental data the predictions of these potentials and of the "effective" exp-6 pair potential of Ross which was fitted to high-pressure shock wave data.[12]

II. SOLID STATE RESULTS

We have calculated pressure as function of volume for solid argon at 298 K using the Monte Carlo method described elsewhere[2] and the BFW potential together with the AT interaction. We calculated corresponding results for the AC and KMA potentials with the AT interaction using the assumption that the thermal pressure is the same as for the BFW potential at the same density. The results are shown in Figs. 4 and 5 together with experimental data of Ross *et al.*[1] and results for the exp-6 potential of Ross[12] given by Ross *et al.*[1] The BFW + AT model is fairly close to the experimental data, possibly within the uncertainty of the ruby fluorescence pressure calibration,[13,14] which may be as high as 10%.[1,14] The exp-6 potential of Ross,[12] which was originally fitted to high-pressure shock data, is a little closer to the experimental data above 300 kbar, while the two models converge near 800 kbar. Also shown in Fig. 4 are results calculated with the BFW pair potential, AT interaction, and the nearest-neighbor first-order three-body exchange inter-

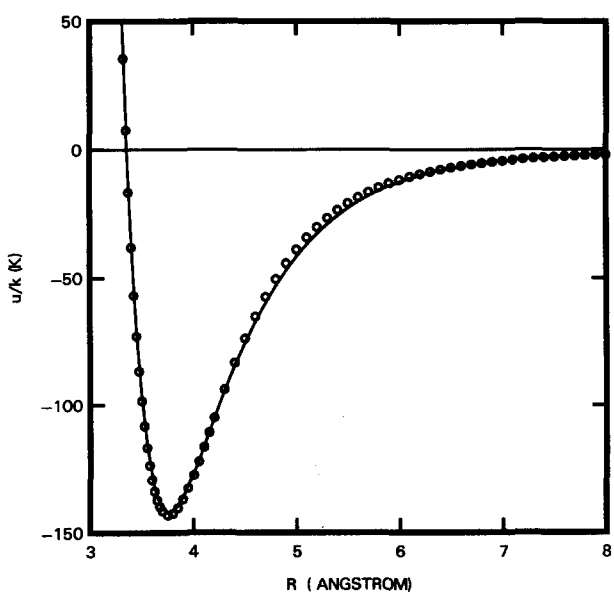

FIG. 1. Pair potentials for argon in the well region. Solid curve, BFW potential (Ref. 2); circles, AC potential (Ref. 6).

 0021-9606/87/031509-03$02.10

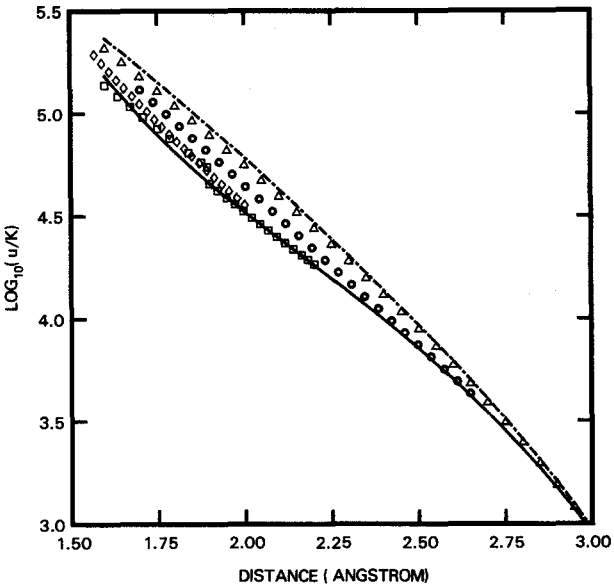

FIG. 2. Pair potentials for argon in the repulsive region. Open squares, beam scattering data of Ref. 7; open diamonds, beam scattering data of curve, Ref. 8; open circles, beam scattering data of Ref. 9; solid line, BFW potential; dash–dotted line, AC potential; open triangles, KMA potential.

action.[15] The inclusion of the latter interaction leads to disagreement with experiment. The AC and KMA potentials with AT interaction give results which are substantially too high.

In Fig. 3 we show calculated results for pressures up to 20 kbar at 0 K, with the experimental data of Anderson and Swenson for comparison.[16] In this range the BFW, AC and KMA potentials with the AT interaction give very similar

TABLE I. Values of pV/NkT and U/NkT for liquid argon at 100 K and 27.04 cm^3/mol calculated for BFW, AC, and KMA pair potentials; all values include quantum corrections.

	pV/NkT	U/NkT
Experiment	2.15	−7.21
BFW without AT	0.90	−7.64
BFW with AT	2.09	−7.21
AC without AT	0.77	−7.64
AC with AT	1.95	−7.21
KMA without AT	0.71	−7.62
KMA with AT	1.89	−7.20

results in good agreement with experiment if the AT interaction is included, while the exp-6 potential is somewhat less satisfactory. If the nearest-neighbor first-order three-body interaction[15] is included the agreement with experiment is destroyed.

III. DISCUSSION

Considering both low pressure and high pressure data, the BFW potential with the AT interaction fits the experimental data reasonably well, possibly within a realistic estimate of overall experimental uncertainty (which is largely determined by the uncertainty of the pressure calibration). The exp-6 potential of Ross gives results closer to the high-pressure data but is less satisfactory at low pressures. The exp-6 potential was described[1] as "an effective pair-potential because it includes in a phenomenological fashion the effects of the many-body interactions," and viewed in this light it is

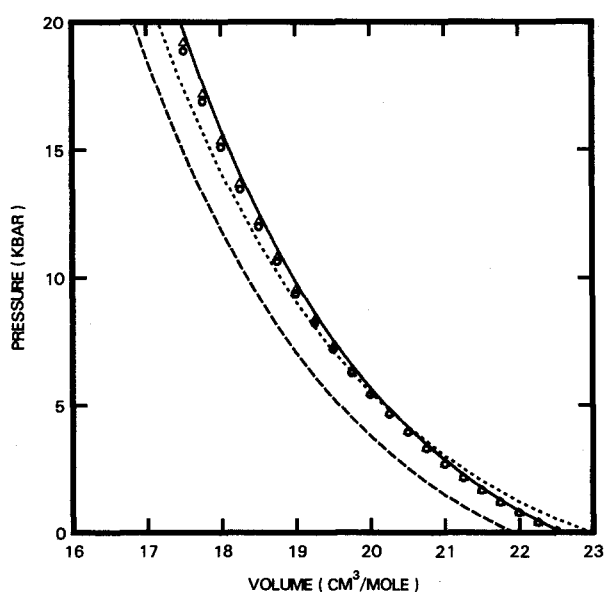

FIG. 3. Pressure as function of volume for argon at 0 K. Solid curve, BFW or AC potential with AT interaction; open triangles, KMA potential with AT interaction; dotted curve, exp-6 potential; dashed curve, BFW or AC potential with AT interaction and nearest-neighbor first-order three-body exchange interaction; open circles, experimental data of Anderson and Swenson (Ref. 15).

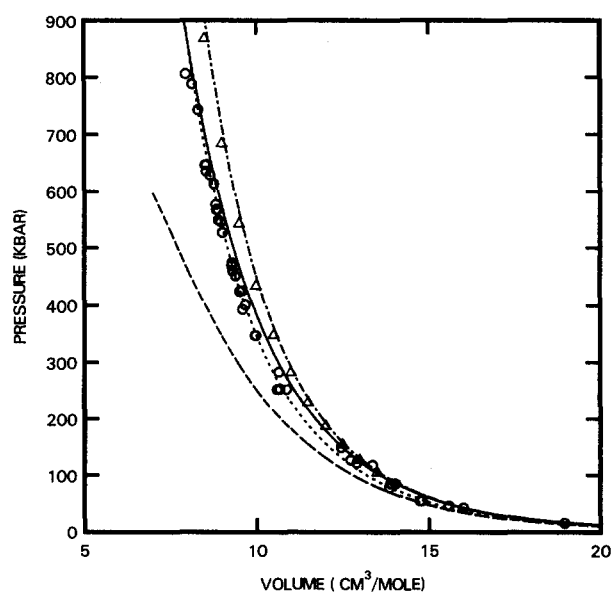

FIG. 4. Pressure as function of volume for argon at 298 K. Solid curve, BFW potential with AT interaction; dotted curve, exp-6 potential; dash–dotted curve, AC potential with AT interaction; dashed curve, BFW potential with AT interaction and first-order exchange three-body interaction; open triangles, KMA potential with AT interaction; open circles experimental data of Ross *et al.* (Ref. 1).

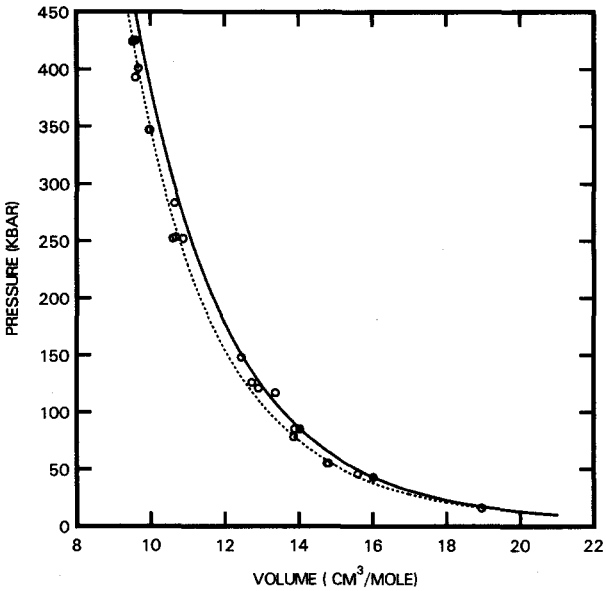

FIG. 5. Pressure as function of volume for argon at 298 K. Solid curve, BFW potential with AT interaction; dotted curve, exp-6 potential; open circles, experimental data of Ross *et al.* (Ref. 1).

good at high pressures. However it is "not sufficiently flexible to fit both the very high pressure and very low pressure data"[1] (see Fig. 3). The AC and KMA potentials give pressures which are too high in the high-pressure region. Both of these potentials are higher and steeper in the repulsive region than the BFW potential or the potentials from scattering data (see Fig. 2). Undoubtedly this is because they were fitted to Hartree–Fock calculated results which are too high if the experimental scattering results in Fig. 2 are correct. The BFW potential on the other hand was fitted to the scattering data of Amdur and Jordan[7] and it is very close in magnitude and, most importantly, in slope, to the later scattering potential of Foreman *et al.*[9] in the important region near 2.6 Å (this is the nearest-neighbor separation at the molar volume 7.5 cm^3/mol). The BFW potential becomes lower than the scattering potential of Foreman *et al.*[9] at smaller distances but this is irrelevant for the present solid state data; Ross[12] has constructed a potential which avoids this by joining the BFW to the scattering potential by a Lagrange interpolation function.

Ross *et al.*[1] state that "the difference observed between the exp-6 and the HFD-C (i.e., AC) must be attributed to an effective softening of the short-range repulsion by many-body interactions." That differs from our interpretation of the facts shown in Fig. 2, and from the earlier conclusions of Ross.[12] There are several sets of experimental scattering data which indicate that the true pair potential is lower than the AC potential. The AC potential lies above the experimental potential because of the way in which it was fitted to Hartree–Fock results and its treatment of correlation effects. The BFW potential reproduces the gas transport properties which depend on the potential in the repulsive region about as well as the AC potential, and also agrees with the beam results near 2.6 Å. It is at least equally plausible that there is a difference between the HFD-C and the true pair potential in the repulsive region due simply to the AC procedure. Of course there may still be important many-body interactions other than the AT interaction in the solid state, especially at the highest pressures, but there is no strong evidence for that in the results we have presented here.

If the AC potential were used with the AT potential and higher order multipole terms as well as the calculated first-order exchange three-body interaction, the resulting pressures would be reasonably close to experiment at high pressures. However, this would lead to serious disagreement with experiment below 20 kbar as shown in Fig. 3 and also to disagreement with the experimental cohesive energy at zero pressure and liquid state data.

[1] M. Ross, H. K. Mao, P. M. Bell, and J. A. Xu, J. Chem. Phys. **85**, 1028 (1986).
[2] J. A. Barker, R. A. Fisher, and R. O. Watts, Mol. Phys. **21**, 657 (1971).
[3] J. A. Barker and M. L. Klein, Phys. Rev. B **7**, 4707 (1973).
[4] J. A. Barker, in *Rare Gas Solids*, edited by M. L. Klein and J. A. Venables (Academic, New York, 1976), Vol. 1, Chap. 4.
[5] M. L. Klein and T. R. Koehler, in *Rare Gas Solids*, edited by M. L. Klein and J. A. Venables (Academic, New York, 1976), Vol. 1, Chap. 6.
[6] R. A. Aziz and H. H. Chen, J. Chem Phys. **67**, 5719 (1977).
[7] I. Amdur and J. E. Jordan, as cited in D. D. Konawolow and S. Carra, Phys. Fluids **8**, 1585 (1965).
[8] I. Amdur and J. E. Jordan, Adv. Chem. Phys. **X**, 29 (1966).
[9] P. B. Foreman, R. B. Lees, and P. K. Rol, as cited by M. Ross, J. Chem. Phys. **73**, 4445 (1980).
[10] J. A. Barker and M. V. Bobetic, J. Chem. Phys. **79**, 6306 (1983).
[11] A. Koide, W. J. Meath, and A. R. Allnatt, Mol. Phys. **39**, 895 (1980).
[12] M. Ross, J. Chem. Phys. **73**, 4445 (1980).
[13] H. K. Mao, P. M. Bell, J. W. Shaner, and D. J. Steinberg, J. Appl. Phys. **49**, 3276 (1978).
[14] H. K. Mao, P. M. Bell, K. J. Dunn, R. M. Chrenko, and R. C. DeVries, Rev. Sci. Instrum. **50**, 1002 (1979).
[15] M. Bulski and G. Chalasinski, Chem. Phys. Lett. **89**, 450 (1982).
[16] M. S. Anderson and C. A. Swenson, J. Phys. Chem. Solids **36**, 145 (1975).