Many-Body Interactions in Rare Gases: Krypton and Xenon

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The hypothesis that the properties of rare gases are well described by pair interactions together with long-ranged three-body interactions, in particular the Axilrod-Teller triple-dipole interaction, is tested for dense fluid krypton and xenon by Monte Carlo calculations. The agreement with experimental fluid properties found with use of the best available pair potentials with the Axilrod-Teller interaction is excellent. The net contribution of other many-body interactions to the properties of solid and dense fluid argon, krypton, and xenon must be very small.

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It has been known for many years that use of an accurate pair potential together with the Axilrod-Teller (AT) three-body interaction leads to accurate predictions of the properties of argon in gaseous, liquid, and solid states.[1-3] Similar conclusions have been drawn for neon, krypton, and xenon in the solid state; for reviews with references see Barker[4] and Klein and Koehler.[5] However, there has been relatively little study of the dense-fluid states of krypton and xenon.

Recent quantum-theoretical calculations[6-11] have indicated that there are exchange three-body interactions which are comparable in magnitude with the AT interaction and of opposite sign. It has been suggested[9-11] that the agreement with experiment found by using the AT interaction as the only many-body interaction must be regarded as fortuitous. In view of this it appeared desirable to make a study of the properties of dense-fluid krypton and xenon using the best available pair potentials. Monte Carlo calculations for dense-fluid krypton and xenon were performed by use of a perturbative method for evaluating three-body effects which has been described previously.[2]

Figure 1 shows values of pV/NkT for krypton at 297 K calculated using the pair potentials $K2$ of Barker, Klein, and Bobetic[12] and that of Aziz[13] and Fig. 2 shows the corresponding values of U/NkT where U is the internal energy. In each case calculated results are given both with and without the AT interaction. The curves represent the experimental data of Trappeniers, Wassenaar, and Wolkers.[14] Whichever pair potential is used the results calculated without the AT interaction are in very poor agreement with experiment, while for either pair potential, the results which include that interaction agree well with experiment. The potential of Barker, Klein, and Bobetic was determined partly from solid-state data while that of Aziz is completely independent of such data. Neither potential used any dense-fluid data in its determination.

Figure 3 shows values of pV/NkT for xenon calculated with the pair potential $X3$ of Barker, Klein, and Bobetic,[12] both with and without the AT interaction, while Fig. 4 shows the corresponding results for U/NkT. The values calculated without the AT interaction are in poor agreement with the experimental data of Michels and co-workers[15] shown as curves in Figs. 3 and 4, while the values including that interaction are in excellent agreement. There is no other potential of comparable accuracy for xenon.

It is clear that the best pair potentials give good agreement with experiment for dense-fluid and solid argon, krypton, and xenon if they are used with the AT three-body interaction, and not otherwise. It is a

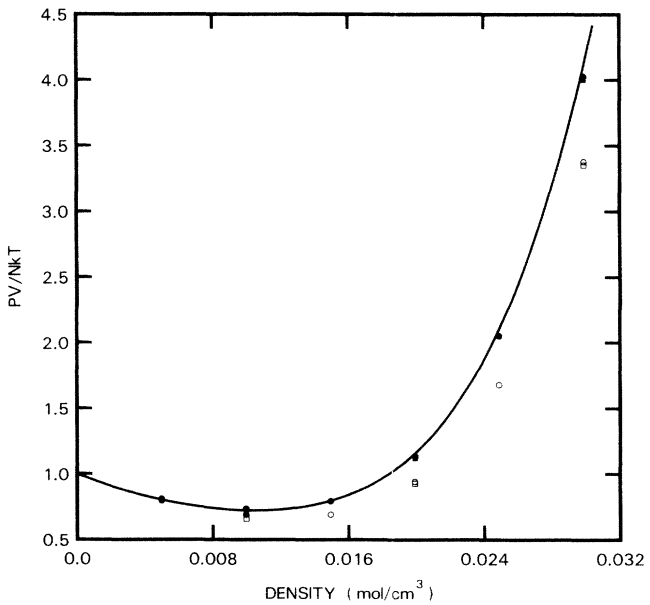

FIG. 1. Pressure as function of density for krypton at 297 K. The filled (open) circles are calculated for the potential of Barker, Klein, and Bobetic (Ref. 12) with (without) the AT interaction. The filled (open) squares are calculated for the potential of Aziz (Ref. 13) with (without) the AT interaction. The solid curve represents experimental data of Trappeniers, Wassenaar, and Wolkers (Ref. 14). The statistical uncertainty of the Monte Carlo results is indicated by the size of the symbols and the nonsystematic error in the experimental data is less than the width of the line.

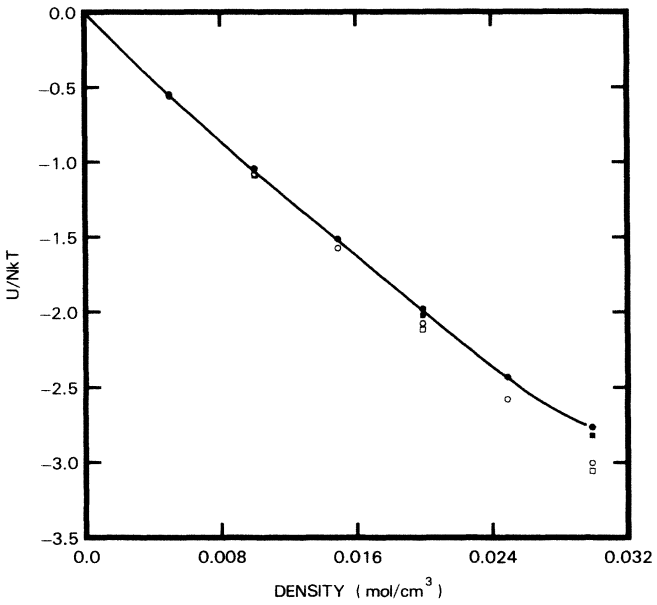

FIG. 2. Internal energy as function of density for krypton at 297 K. The filled (open) circles are calculated for the potential of Barker, Klein, and Bobetic (Ref. 12) with (without) the AT interaction. The filled (open) squares are calculated for the potential of Aziz (Ref. 13) with (without) the AT interaction. The solid curve represents experimental data of Trappeniers, Wassenaar, and Wolkers (Ref. 14). The statistical uncertainty of the Monte Carlo results is one fifth of the size of the symbols and the nonsystematic error in the experimental data is comparable with the width of the line.

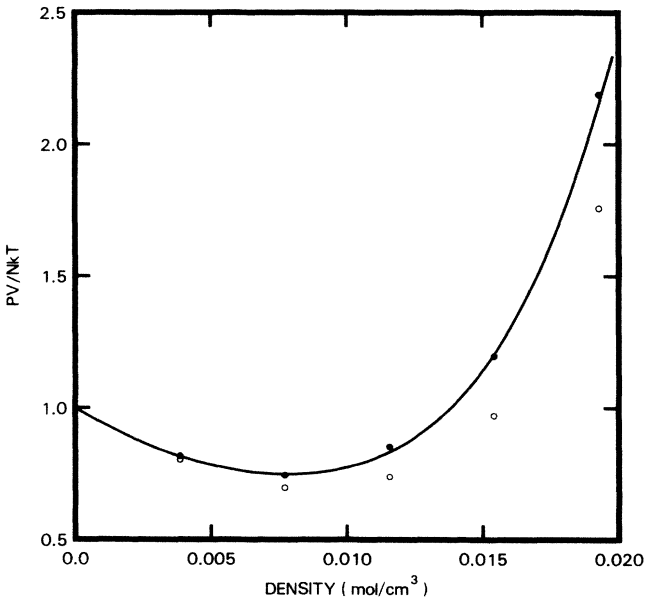

FIG. 3. Pressure as function of density for xenon at 423.16 K. The solid curve represents experimental data of Michels and co-workers (Ref. 15). The filled (open) circles are calculated for the potential of Barker, Klein, and Bobetic (Ref. 12) with (without) the AT interaction. The statistical uncertainty in the Monte Carlo results is indicated by the size of the symbols and the nonsystematic error in the experimental data is less than the width of the line.

possible criticism of the earlier studies for argon that some solid and liquid data were used in the determination of the pair potential, with the assumption that the AT was the only many-body interaction. It should be noted, however, that this assumption was already partly justified by the fact that it led to agreement with experimental third virial coefficients.[16] Furthermore, the condensed-phase data were used by BFW only to choose between different potentials, all of which fitted the low-density gas data, so that it is quite incorrect to regard the BFW as an "effective" potential which mimics the effect of many-body interactions (as the familiar Lennard-Jones potential appears to do). In any event, the assumption is thoroughly justified *a posteriori* by the fact that the BFW potential is very close to the potential of Aziz and Chen[17] which was determined totally independently of condensed-phase data, and above all by the fact that the latter potential also gives good agreement with the condensed-phase data when used with the AT interaction as the only many-body interaction.[18]

Similar remarks apply to the case of krypton, for which both the potential of Barker, Klein, and Bobetic,[12] based partly on solid-state data, and that of

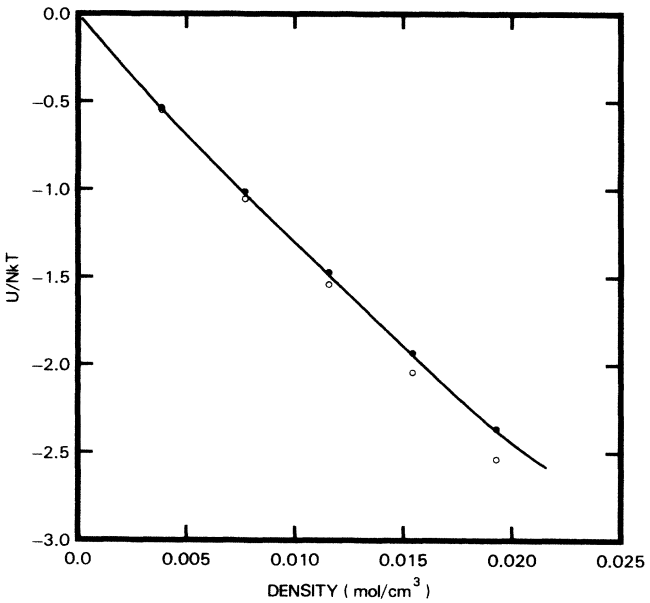

FIG. 4. Internal energy as function of density for xenon at 423.16 K. The solid curve represents experimental data of Michels and co-workers (Ref. 15). The filled (open) circles are calculated for the potential of Barker, Klein, and Bobetic (Ref. 12) with (without) the AT interaction. The statistical uncertainty of the Monte Carlo results is one fifth of the size of the symbols and the nonsystematic error in the experimental data is comparable with the width of the line.

Aziz,[13] based solely on the pair data, give good agreement with experiment for both dense-fluid and solid states.

The case of xenon is slightly different. Barker *et al.*[19] found it impossible to reconcile other experimental data with the then current value of the cohesive energy of solid xenon, and in their determination of the xenon-xenon potential they were forced to accept a discrepancy of about 2% with that experimental datum. Later, a reanalysis of the experimental cohesive energy by Crawford[20] with new specific-heat data led to a value in much better agreement with that found by Barker *et al.*[19] and in excellent agreement with that predicted by the later potential $X3$ of Barker, Klein, and Bobetic[12] which was used in the present calculations. Thus the xenon potential was determined to some extent in spite of the solid-state data. The point being made here is that the determination of the pair potential was not dependent on an assumption concerning the AT interaction.

It is clear that one must expect deviations from this correlation at temperatures and pressures which are sufficiently high that electronic overlap becomes large and electron delocalization may be significant. This requires higher pressures than those considered here, substantially above 20 kbar for solid Xe at low temperatures[12] and presumably higher pressures for the other rare gases.

In 1974 Barker *et al.*[19] wrote, "*A priori* it is possible that one chooses incorrect pair potentials which mimic in condensed phases the behavior of unknown many-body interactions. Given the accurate molecular-beam and viscosity data now available the multiple coincidence required for this to happen for neon, argon (both solid and liquid), krypton, and xenon appears to have unacceptably low probability." We can now add dense-fluid krypton and xenon to the list of successful tests, we now have pair potentials determined independently of condensed-phase data and known to be consistent with precise spectroscopic information on rare-gas dimers, and we still find agreement with experiment when the AT interaction is used as the only many-body interaction. This is a remarkable empirical fact; the probability that it is an accidental consequence of incorrectly chosen pair potentials is surely now negligible.

There is one experiment which appears to disagree with the model under discussion and that is the neutron-scattering determination of the structure factor of dense-gaseous krypton.[21,22] In the analysis of these papers the results appear to require an additional repulsive three-body interaction over and above the AT interaction. The present results make it clear that if there is such an interaction it must somehow contribute nothing to the pressure and internal energy over the range of fluid densities which we have studied. Furthermore, such an additional interaction would be of opposite sign to the three-body exchange interaction suggested by the theoretical studies.[6–11] Unless and until one can think of a form for a many-body potential which would affect the structure while leaving the pressure and internal energy unaffected over a wide range of densities these neutron-scattering results must be treated with reserve.

A discussion of theoretical calculations of many-body interactions is given by Meath and Aziz[9] who confirm that the long-range multipole many-body interactions make up essentially the whole of the observed nonpair interaction in ground-state rare-gas crystals, but point out that there are grounds for concern since recent calculations[6–8] indicate that the first-order three-body exchange interaction is comparable to the AT interaction. They consider a number of terms which might have restored agreement with experiment without identifying a satisfactory candidate. Barker[23] showed that inclusion of the first-order-exchange three-body interaction for argon led to results in serious disagreement with experiment and emphasized the difficulty of the theoretical calculations. We have here an astonishingly accurate empirical correlation in search of a rigorous theoretical justification.

[1]M. V. Bobetic and J. A. Barker, Phys. Rev. B **2**, 4169 (1970).

[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 Ref. 4, Chap. 6.

[6]M. Bulski and G. Chalasinski, Theor. Chim. Acta **56**, 210 (1980).

[7]M. Bulski and G. Chalansinski, Chem. Phys. Lett. **89**, 450 (1982).

[8]M. Bulski, Chem. Phys. Lett. **78**, 361 (1981).

[9]W. J. Meath and R. A. Aziz, Mol. Phys. **52**, 225 (1984); this paper contains a survey with references to earlier work.

[10]B. H. Wells and S. Wilson, Mol. Phys. **55**, 199 (1985).

[11]B. H. Wells and S. Wilson, Mol. Phys. (to be published).

[12]J. A. Barker, M. L. Klein, and M. V. Bobetic, IBM J. Res. Dev. **20**, 222 (1976).

[13]R. A. Aziz, Mol. Phys. **38**, 177 (1979).

[14]N. J. Trappeniers, T. Wassenaar, and G. J. Wolkers, Physica (Utrecht) **32**, 1503 (1966).

[15]A. Michels, T. Wassenaar, and P. Louwerse, Physica (Utrecht) **20**, 99 (1954); A. Michels, T. Wassenaar, G. J. Wolkers, and J. Dawson, Physica **22**, 17 (1956).

[16]J. A. Barker and A. Pompe, Aust. J. Chem. **21**, 1683 (1968).

[17]R. A. Aziz and H. H. Chen, J. Chem. Phys. **67**, 5719 (1977).
[18]J. A. Barker and M. V. Bobetic, J. Chem. Phys. **79**, 6306 (1983).
[19]J. A. Barker, R. O. Watts, J. K. Lee, T. P. Schafer, and Y. T. Lee, J. Chem. Phys. **61**, 3081 (1974).
[20]R. K. Crawford, in *Rare Gas Solids,* edited by M. L. Klein and J. A. Venables (Academic, New York, 1977), Vol. 2, Chap. 11.
[21]A. Teitsma and P. A. Egelstaff, Phys. Rev. A **21**, 367 (1980).
[22]P. A. Egelstaff, A. Teitsma, and S. S. Wang, Phys. Rev. A **22**, 1702 (1980).
[23]J. A. Barker, Mol. Phys. **57**, 755 (1986).