

Barker J A, Fisher R A & Watts R O. Liquid argon: Monte Carlo and molecular dynamics calculations. *Mol. Phys.* 21:657-73, 1971.

[IBM Research Laboratory, San Jose, CA and Diffusion Research Unit, Australian National University, Canberra, ACT, Australia]

Thermodynamic properties of liquid argon are calculated by Monte Carlo and molecular dynamics techniques, using accurate pair-potential functions determined from the properties of solid and gaseous argon, together with the Axilrod-Teller three-body interaction. Satisfactory techniques for evaluating three-body contributions to thermodynamic properties without excessive requirements of computer time are described. [The SC⁷® indicates that this paper has been cited in over 355 publications.]

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

and

R.O. Watts
Department of Chemistry
University of Washington
Seattle, WA 98195

April 12, 1988

We addressed the question of exactly how the microscopic forces between atoms and molecules determine the bulk properties of matter in solid, liquid, and gaseous states. The principles of statistical mechanics were applied to a simple example for which the microscopic forces could be determined quantitatively and in detail. This question had been pending since J.W. Gibbs and A. Einstein crystallized statistical mechanics at the turn of the century, and it happened that 1971 was the year in which a convincing answer could be written. Among the reasons for this were the availability of computers and the development of the Monte Carlo and molecular dynamics methods by N. Metropolis et al.,¹ B.J. Alder and T.E. Wainwright,² and A. Rahman.³ By 1971 these methods had been applied to a number of model systems (hard spheres, square well potentials) and the moderately realistic Lennard-Jones potential.³⁻⁵ We felt that it was time to make a precise study of a simple example,

namely, argon in its gaseous, liquid, and solid states. To this end we had to come to grips with the question of pair and many-body interactions. We found a pair potential from limited information on gas, solid, and liquid properties together with a hypothesis about many-body interactions (that only the long-range Axilrod-Teller triple-dipole interaction was important) that is still of wide interest.⁶

Our pair potential was soon confirmed in its essentials by important additional information, drawn from the relatively new molecular beam technique⁷ and the use of more traditional spectroscopic information.⁸ These developments made the period 1970-1972 a watershed for this kind of study and added to the timeliness of our paper. We were able to use the new results thanks to the courtesy of Y.T. Lee and E.B. Smith.

We showed how to include three-body interactions and quantum corrections in simulations. Our conclusion was that "the new potential gives excellent agreement with thermodynamic properties of solid, liquid and gaseous argon, and with transport properties of gaseous argon...[and] with molecular beam differential scattering cross sections and spectroscopic data on the Ar₂ molecule." This confirmation of our pair potential by the new information was strong evidence, after the fact, for our hypothesis concerning many-body interactions, and more recent detailed studies have not changed this situation.⁹

Our work was a transpacific collaboration with J.A. Barker at the IBM Research Laboratory in San Jose, California, and R.O. Watts and R.A. Fisher at the Australian National University in Canberra; it began earlier at the University of Waterloo in Canada.

We ascribe the continued interest in our paper partly to the great expansion in the use of computer simulation methods and partly to the ubiquity of phenomena depending on intermolecular potentials, but also to the fact that our hypothesis concerning many-body forces has proved to give a remarkably useful correlation of a wide range of data.⁶

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