This Week's Citation Classic

Barker J A & Henderson D. Perturbation theory and equation of state for fluids II. A successful theory of liquids. *J. Chem. Phys.* **47**:4714-21, 1967.
[Div. Applied Chemistry, CSIRO Chem. Res. Labs., Melbourne, Australia]

This paper described the first theory of the liquid state which was firmly based in statistical mechanics and also permitted quantitatively accurate calculation on the thermodynamic properties of a liquid starting from information on the forces between the molecules. [The *SCI®* indicates that this paper has been cited over 300 times since 1967.]

J.A. Barker and D. Henderson
IBM Research Laboratory
5600 Cottle Road
San Jose, CA 95193

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"When our extended collaboration began in Melbourne in 1966 we shared a desire, no doubt somewhat obsessive, to find a theoretical description of the liquid state which would be both rigorously based in statistical mechanics and 'exact,' or at least capable of being systematically refined towards exactness. We wanted something with the power and certainty of, for example, the Taylor series for the exponential function. The use of thermodynamic perturbation theory, which makes it possible to express the properties of a complicated system in terms of a simpler reference system, seemed a promising approach to this ideal. The value of this technique had been shown by the work of H.C. Longuet-Higgins[1] on 'conformal solutions' and an elegant formal analysis was given by R.W. Zwanzig.[2] As early as 1950 one of us[3] applied perturbation theory to dipolar fluids using a non-polar fluid as a reference system. The 'new' element in our 1967 work was the use of a fluid composed of hard spheres as a reference system. This idea can actually be traced back to the work of J.D. van der Waals, and it had been given new life by the work of Longuet-Higgins, B. Widom, E. A. Guggenheim, H Reiss, J.S. Rowlinson, D.A. McQuarne, J.L. Katz, and others. The essence of our contribution was to imbed this idea in a formally rigorous yet practical perturbation theory which made it possible to take account of the 'softness' of the intermolecular repulsion as well as the longer ranged intermolecular attraction.

"In addition we demonstrated the validity of the approach by detailed comparison both with experimental data on liquids and with the results of computer simulations which were available as a result of the work of B.J. Alder, W.W. Wood, L. Verlet, and others. This latter test was important because comparisons with experiment were rendered somewhat uncertain by lack of detailed knowledge of intermolecular forces. Thus we put together a number of elements to provide a firm basis for a great deal of further work by ourselves and others, which is extensively reviewed in the article 'What is "Liquid"; Understanding the States of Matter.'[4]

"The title of this article highlights the fact that we were trying to answer a rather basic question: why does matter exist in distinct solid, liquid, and gaseous states? Looking back in 1980 we feel that in 1966-7 we made substantial progress towards answering that question. The difference between solid and dense fluid is a matter of statistical geometry—even the hard-sphere fluid shows a solid-fluid phase transition. The difference reflects two alternative ways of occupying space economically. On the other hand, the difference between liquid and highly compressed gas is much less fundamental. The structures are very similar and determined by short-range repulsion but in the gas the molecules are pushed together by an external pressure whereas in the liquid they are pulled together by attractive forces, which mimic rather closely the effect of external pressure. This is of course in perfect harmony with van der Waals' idea of the continuity of gaseous and liquid states."

1. **Longuet-Higgins H C.** *Proc. Roy. Soc. London A* **205**:247, 1951.
2. **Zwanzig R W.** *J. Chem. Phys.* **22**:1420, 1954.
3. **Barker J A.** *J. Chem. Phys.* **19**:1430-1, 1951.
4. **Barker I A & Henderson D.** *Rev. Mod. Phys.* **48**:587-671, 1976.