Rowlinson's Concept of an Effective Hard Sphere Diameter[†]

Douglas Henderson*

Department of Chemistry and Biochemistry, Brigham Young University, Provo, Utah 84602

Attention is drawn to John Rowlinson's idea that the repulsive portion of the intermolecular interaction may be replaced by a temperature-dependent hard sphere diameter. It is this approximation that made the development of perturbation theory possible for realistic fluids whose intermolecular interactions have a steep, but finite, repulsion at short separations.

Perturbation theory[1−4] is one of the important developments in the theory of the properties of simple liquids. In fact, perturbation theory was the first successful method for what previously had been an intractable theoretical problem. In perturbation theory, the fluid is considered to be similar to a reference fluid with known correlation functions and thermodynamic properties, and the functions and properties of the fluid of interest may be calculated by means of a rapidly convergent expansion.

Three steps contributed to the development and utility of perturbation theory. First, a convenient and accurate theory became available for the radial distribution function and thermodynamics of a useful unperturbed or reference fluid, the hard sphere fluid, whose intermolecular or pair potential is zero until the spheres come into contact at a distance, d, the hard sphere diameter, which then is positive and infinite. Secondly, convenient expressions have been formulated for the second- and higher-order perturbation terms in a perturbation expansion. However, without the third step, perturbation theory would have been restricted to fluids whose molecules had an infinitely hard repulsive core and, thus, would be limited in usefulness. The third contribution was the idea that the steep, but not infinitely steep, repulsive force between realistic molecules at short separations can be approximated by an effective temperature-dependent hard sphere potential. It is this third step that is the subject of this paper.

The pair potential is the potential energy of a pair of molecules in the fluid and is important because this function, when added together with the pair potentials of all of the pairs of molecules in the fluid, gives the dominant contribution to the potential energy of the system that is being considered (the entire contribution if the potential energy is pairwise additive). The thermodynamic properties are obtained from an integral, the partition function, of the Boltzmann term, the exponential of the negative of the potential energy, divided by kT, where k is the Boltzmann constant and T is the temperature.

Prior to the perturbation theories cited above, Frisch et al.[5] formulated a first-order perturbation theory for a Lennard−Jones 12-6 (LJ) fluid whose intermolecular potential is given by

$$u(R) = 4\epsilon\left\{\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right\} \tag{1}$$

where R is the separation of the molecules, ϵ is the maximum strength of the attractive interaction, and σ is the value of R at which $u(R)$ changes from negative to positive values. The LJ potential mimicks a realistic fluid, such as argon. However, their theory was limited in usefulness by the fact that the unperturbed fluid was a hard sphere fluid and, to a lesser extent, by the lack of higher order terms in the expansion. The repulsion between LJ molecules is not infinitely hard. Later, Barker and Henderson[1] (BH) developed a simple approximation for the second-order term, which they called the compressibility approximation, and successfully applied their approach to a fluid whose molecules interact by means of a square well potential (which does have a hard repulsion), and so separated the question of whether the repulsive core can be approximated as hard from the utility of perturbation theory. They obtained excellent results; this was a valuable step but, in the absence of a method of dealing with the finite slope of a repulsive potential, was not directly applicable to, say, the LJ fluid.

The key to the final step was the earlier work of Rowlinson.[6,7] He considered a repulsive, R^{-n}, intermolecular potential,

$$u(R) = \epsilon'\left(\frac{\sigma'}{R}\right)^{n} \tag{2}$$

$\epsilon' > 0$, σ', and $n > 0$ are parameters specifying the strength and steepness of this potential. Rowlinson suggested that if n was large, this inverse n fluid could be replaced by an equivalent hard sphere fluid with an effective diameter. He found that $n = 12$ was large enough for his method to be applicable. Consider the f-function for a given pair interaction, $u(R)$,

$$f(R) = \exp\{-\beta u(R)\} - 1 \tag{3}$$

where $\beta = 1/kT$. The f-function is the excess of the Boltzmann term of a molecular pair over that of a pair of ideal gas molecules.

We can obtain Rowlinson's result by defining the f-function of the equivalent, effective hard sphere potential by setting the integral of the equivalent hard sphere f-function equal to that of the R^{-n} fluid. Thus,

$$\int_0^\infty f_{\mathrm{HS}}(R)\, dR = \int_0^\infty f(R)\, dR \tag{4}$$

where $f_{\mathrm{HS}}(R)$ is the f-function of a hard sphere fluid of diameter d and $f(R)$ is the f-function of the fluid of interest, defined by eqs 2 and 3. Since $f_{\mathrm{HS}}(R)$ is -1 for $R < d$ and zero otherwise, the first integral is just $-d$. Evaluating the second integral and expanding to order n^{-1} gives Rowlinson's result for the temperature-dependent effective hard sphere diameter that represents the n^{-1} fluid,

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* Corresponding author. E-mail: doug@chem.byu.edu.

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$$d = \sigma(\beta\epsilon)^{-n}\left(1 + \frac{\gamma}{n}\right) \qquad (5)$$

where $\gamma = 0.5772157...$ is Euler's constant. Rowlinson found that an effective diameter given by eq 5 gave good results for a fluid described by eq 2 with $n = 12$.

McQuarrie and Katz[8] then applied the theory of Frisch et al. with the R^{-6} part of the LJ potential being the perturbation energy and with the R^{-12} term being the potential that defines the unperturbed fluid. They treated the unperturbed system by Rowlinson's method. The results were not encouraging. This is partly due to the fact that the perturbation expansion was taken only to first order but, as pointed out by Barker and Henderson,[2] is mainly due to the fact that the magnitude of the maximum value of the perturbation energy in their treatment is 4ϵ. As a result, because the perturbation parameter enters as $\beta u(R)$, the expansion parameter can become as large as 4 (or even larger near the triple point). Thus, the McQuarrie−Katz treatment is really a theory of the LJ fluid at high temperatures, much above the critical temperature.

Barker and Henderson[2] proposed another separation of the LJ potential into the unperturbed energy and the perturbation energy. They suggested that the unperturbed part of $u(R)$ be the part for which $R < \sigma$ and the perturbation energy be the part for which $R > \sigma$. They developed a parametrization of $u(R)$ for $R < \sigma$ in terms of an inverse steepness parameter, α, such that, for $\alpha = 0$, the perturbation energy was the hard sphere energy and, for $\alpha = 1$, the $R < \sigma$ part of the LJ energy was recovered. Although the approach is seemingly different from that of Rowlinson, it is interesting that the BH approach led to eq 4 but with the upper limit in the integral on the right-hand side (rhs) equal to σ rather that ∞. Thus, the hard sphere fluid with a temperature-dependent value of d could be used as a reference fluid. This is very convenient. Values for $d(T)$ can be computed at the beginning and parametrized. The BH theory, when taken to second order using the compressibility approximation, gave accurate results, even for temperatures as low as the triple-point temperature, where $\beta\epsilon$ is about 1.4.

Subsequently, Weeks, Chandler, and Andersen developed an alternative perturbation theory that is based on a different separation of $u(R)$ into unperturbed and perturbed energies. It is interesting that their theory also represents the reference fluid by a hard sphere fluid with a state-dependent diameter. In their theory, the effective diameter is given by an equation that is similar to eq 4 but with a hard sphere correlation function inside the integral on the rhs. This leads to values of d that are temperature- and density-dependent, which is slightly less convenient but manageable.

Personal Note

John Rowlinson has made many contributions to the development and history of science and to the growth of science in the U.K. For these contributions he deservedly has been knighted. A few years ago, I teased John about the fact that a colleague of mine addressed John in an email as Sir Rowlinson, rather the more correct Sir John. I trust that John realizes that I was amused by my colleague's error and not John's knighthood, which I endorse wholeheartedly.

Literature Cited

(1) Barker, J. A.; Henderson, D. Perturbation theory and equation of state for fluids: the square-well potential. *J. Chem. Phys.* **1967**, *47*, 2856–2861.
(2) Barker, J. A.; Henderson, D. Perturbation theory and equation of state for fluids. II. A successful theory of liquids. *J. Chem. Phys.* **1967**, *47*, 4714–4721.
(3) Barker, J. A.; Henderson, D. What is 'liquid'? Understanding the states of matter. *Rev. Mod. Phys.* **1976**, *48*, 587–671.
(4) Weeks, J. D.; Chandler, D.; Andersen, H. C. Role of repulsive forces in determining the equilibrium structure of simple liquids. *J. Chem. Phys.* **1971**, *54*, 5237–5247.
(5) Frisch, H. L.; Katz, J. L.; Praestgaard, E.; Lebowitz, J. L. High-temperature equation of state-argon. *J. Phys. Chem.* **1966**, *70*, 2016–2020.
(6) Rowlinson, J. S. An equation of state of gases at high temperatures and densities. *Mol. Phys.* **1964**, *7*, 349–361.
(7) Rowlinson, J. S. The statistical mechanics of systems with steep intermolecular potentials. *Mol. Phys.* **1964**, *8*, 107–115.
(8) McQuarrie, D. A.; Katz, J. L. High temperature equation of state. *J. Chem. Phys.* **1966**, *44*, 2393–2397.

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