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LETTER TO THE EDITOR

Some remarks on the equation of state for hard repulsive potentials

Approximate evaluations of the classical configurational integral, Q, remain interesting because of the established difficulty in applying the Ursell-Mayer procedure exactly. Recently Byckling[1]) discussed an interesting method for reducing the configurational integral to a one-dimensional equivalent, and in part tested the validity of the scheme by comparison of the derived virial series with the known, exact results for hard spheres and parallel hard cubes. The first four virial coefficients for hard spheres are known exactly and the fifth approximately as a machine result. For hard cubes the situation is even more favorable; for, the first five were calculated exactly bij Zwanzig[2]), following earlier results of Geilikman[3]) and of Riddell and Uhlenbeck[4]), and more recently an exact calculation of the sixth and seventh has been accomplished[5]) [6]).

For cubes it is clear that a Mayer function $f_{ij}(x_{ij}, y_{ij}, z_{ij})$ can be factored as $f_{ij}(x_{ij})$ $f_{ij}(y_{ij})$ $f_{ij}(z_{ij})$, hence reduction to a one-dimensional problem is exact in this case. A comparison of the results of Byckling with those for cubes appears, therefore, to be an appropriate and sensitive test of the reduction scheme developed for the approximate evaluation of Q. The details of the reduction scheme remain unclear to us in spite of some efforts in this direction.

A gas of parallel hard cubes of length σ and specific volume $v = V/N$ has, according to Byckling, the equation of state

$$\frac{pv}{kT} = \sum_{l=1}^{\infty} \frac{l^2}{4^{l-1}} \left(\frac{b_0}{v}\right)^{l-1}, \qquad (1)$$

where the second virial coefficient, B_2, is given as $b_0 = 4\sigma^3$. An immediate consequence of eq. (1) is the fact that all the virial coefficients are positive. The first seven terms of eq. (1) are

$$\frac{pv}{kT} = 1 + \left(\frac{b_0}{v}\right) + 0.5625\left(\frac{b_0}{v}\right)^2 + 0.2500\left(\frac{b_0}{v}\right)^3 + 0.0977\left(\frac{b_0}{v}\right)^4 + 0.0352\left(\frac{b_0}{v}\right)^5 + 0.0120\left(\frac{b_0}{v}\right)^6, \qquad (2)$$

whereas the exact expansion yields[6]).

$$\frac{pv}{kT} = 1 + \left(\frac{b_0}{v}\right) + 0.5625\left(\frac{b_0}{v}\right)^2 + 0.1771\left(\frac{b_0}{v}\right)^3 + 0.0123\left(\frac{b_0}{v}\right)^4 - 0.0184\left(\frac{b_0}{v}\right)^5 - 0.0106\left(\frac{b_0}{v}\right)^6, \qquad (3)$$

from which it is seen that not only are the magnitudes of B_4 and B_5, as deduced by Byckling, in error, but in particular the signs of B_6 and B_7 are in error as well. The results of Byckling for two dimensions (hard squares) yield the so-called "Temperley Approximation" in which the successive virial coefficients are the sequance of positive integers, i.e., $B_l = l$. This result is also in conflict with the exact results for hard squares[6]) where in both cases the side length of the square is assigned unity.

For spheres, Alder and Wainwright[7]) have suggested that B_6 and B_7 are positive but no reliable estimates have been made relative to their magnitudes. Although Byckling necessarily obtains positive values for B_6 and B_7, the results must be considered tenuous in view of the clear failure of the scheme to give a reliable sign or magnitude for any known $B_l (l \geq 4)$ in the case of cubes. In addition it seems improbable, in view of the exact results for cubes, that all the virial coefficients for spheres are positive, especially since negative virial coefficients are needed to produce isotherms with van der Waals loops or flat regions. In particular, eq. (1) does not show a first-order phase transition in contrast with the suggestive machine results of Alder and Wainwright[7]).

The relationship of a given B_l for spheres and cubes has previously been discussed[5]), but it seems appropriate to mention that especially simple dependences of $B_l^{\bigcirc}/B_l^{\square}$ on $v^{\bigcirc}/v^{\square}$ (refer reference 1) are unlikely considering the extensive cancellations that occur among the star integrals contributing to the exact expansion[6]).

Finally, it should be mentioned that the correct seven term compressibility factor (pV/NkT) has already shown a maximum for cubes at $v_0/v \simeq 0.56$ and for v_0/v greater than this is in a descending portion of the curve, in contrast to the results depicted in figure 1 (Ref. 1), where the five-term result of Zwanzig[2]) is quoted for reference.

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