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TRIPLET CORRELATIONS IN HARD SPHERES

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The central issue in what has become known as the many-body problem is how to express higher order correlations in terms of lower order ones, specifically pair correlations, so as to get an accurate pair distribution function, $g^{(2)}(r_{12})$, or averaging function with which to determine the thermodynamic properties; r_{ij} is the pair separation. Evaluation of the triplet distribution function, $g^{(3)}(r_{12}, r_{13}, r_{23})$, for hard spheres over the entire density range leads to the following conclusions:

(1) $g^{(3)}(1, 1, 1)$ in the dense fluid and solid region for spheres in contact, $r_{ij} = 1$, can be expressed by a triple product of the pair distribution functions (superposition approximation, abbreviated as SA) to within a few percent accuracy.

(2) $g^{(2)}(r_{12})$ derived by means of the SA directly from $g^{(3)}(r_{12}, r_{13}, r_{23})$ is more accurate than the best theoretical $g^{(2)}(r_{12})$ so far obtained.

(3) At low densities the SA is less adequate, indicating that it is not appropriate to judge the validity of an approximation in the liquid region by the accuracy with which the fourth virial coefficient is calculated.

(4) The poor results previously obtained from the SA in the liquid region are due to an extreme magnification of the error by the integral equations in which it was introduced.

(5) The introduction of the SA first in pair space and then in triplet space indicates that its introduction in successively higher dimensions might lead to a rapidly convergent series.

The low-density behavior of $g^{(3)}$ is obtained by an analytic evaluation of the first term in the den-

sity expansion¹ from which it can be concluded that the SA overestimates the triplet correlation at all particle separations. The largest error occurs at the point of contact, which for spheres is the only value required for determining the thermodynamic properties. It is well known that this lowest density term leads to a fourth virial coefficient which the SA calculates incorrectly by more than 20%.² Away from contact the ratio, $R^{(3)}(r_{12}, r_{13}, r_{23})$, of $g^{(3)}$ to its approximate superposition value,³ $g^{(2)}(r_{12})g^{(2)}(r_{13})g^{(2)}(r_{23})$, rapidly and uniformly approaches unity as the particle separations increase. The SA overestimates the net attractive forces between a pair of particles because it fails to take into account the specific shielding effects of a third particle which protects the pair from collisions of other particles whose over-all effect is to force the pair of particles together.

As an approximation to the high-density situation, due to the large number of equivalent triplet configurations, a third particle in contact with a pair can be considered as spherically distributed about the pair so that all collisions are equally screened and no specific three-body correlations occur. The validity of this argument is indicated by the exact value of $R^{(3)}$ obtained by counting triplets and pairs in a close-packed crystal of spheres, $R^{(3)}(1, 1, 1) = 2\sqrt{2}\pi/9 = 0.988$. At other triplet configurations shown in Table I, the SA is not as quantitative but still surprisingly good. In a close-packed lattice, $R^{(3)}$ is the ratio of delta functions at the values of the distances indicated

Table I. Values of $R^{(3)}$ for a close-packed face-centered lattice of hard spheres.

r_{12}^2	r_{13}^2	r_{23}^2	$R^{(3)}/\pi$	$R^{(3)}$
1	1	1	$2\sqrt{2}/9$	0.99
1	1	2	4/9	1.40
1	1	3	$(2/27)^{1/2}$	0.86
1	1	4	$\sqrt{2}/9$	0.49
1	2	3	$2/\sqrt{27}$	1.21
1	3	3	$1/\sqrt{18}$	0.74
1	3	4	$(8/27)^{1/2}$	1.71
2	2	4	$16\sqrt{2}/9$	7.91
2	3	3	2/3	2.10
3	3	3	$1/\sqrt{24}$	0.64
3	3	4	$1/\sqrt{18}$	0.74
4	4	4	$16\sqrt{2}/9$	7.91

in Table I and zero for some configurations where the triplet of squared distances, such as 222, does not exist in the face-centered lattice.

In the fluid region $g^{(2)}$ and $g^{(3)}$ have been numerically evaluated from the configurations generated on a computer by the molecular dynamics method⁴ and the ratio tabulated. The values of $R^{(3)}$ are accurate to a few percent and represent the average over fairly large intervals in r_{ij} , so that $R^{(3)}$ at contact had to be obtained by a considerable extrapolation. These latter values are given in Table II at various volumes, v , relative to the close-packed volume, v_0 . Also given are the actually determined values of $R^{(3)}$ at the mean value of r_{ij} for the smallest triad of equal distances. From these numbers it is apparent that at higher densities the SA becomes increasingly more accurate for $R^{(3)}(1, 1, 1)$. Not only is the SA accurate at contact but at other particle separations as well, as Table III shows. In Table III the correct $g^{(2)}$, obtained from the numerical method, is given in the first column and is to be compared to the one obtained from the direct application of the SA to

Table II. Values of $R^{(3)}$ when all distances are equal at various densities.

v/v_0^a	$R^{(3)}$ at r		$R^{(3)}(1, 1, 1)^b$
3.0(F)	0.91	1.129	0.87
2.0(F)	0.86	1.076	0.81
1.7(F)	0.88	1.048	0.84
1.6(F)	1.00	1.088	0.94
1.5(S)	0.97	1.085	0.97
1.0(S)			0.99

^aF and S stand, respectively, for fluid and solid.

^bExtrapolated except at $v/v_0 = 1$.

$g^{(3)}$, namely, by taking the cube root of $g^{(3)}$ when all particle separations are the same. The close agreement found there is to be contrasted with the poor $g^{(2)}$ obtained by introducing the SA into the Born and Green integral equation⁵ (BG column). The $g^{(2)}$ derived from $g^{(3)}$ is also more accurate than the best presently available $g^{(2)}$ from a solution of an integral equation as shown in the last column⁶ (Percus-Yevick, PY column).

The large error in $g^{(2)}$ from the Born-Green integral equation can also not be explained by large deviations from the SA at asymmetric triplet configurations. The asymmetric configuration leading to the largest value of $|R^{(3)} - 1|$ is given in Table IV, which shows that the maximum error in $g^{(2)}$, obtained directly from $g^{(3)}$ by the SA would be about 12% (cube root of 1.37). The maximum error of about 80% found in the Born-Green $g^{(2)}$ indicates that the integral equation greatly magnifies the error. A crude error analysis given earlier⁷ shows that an error in $g^{(2)}(r)$ on the right-hand side of the integral equation results in a magnification of that error on the left-hand side of $(4\sqrt{2}v_0/3v)g^{(2)}(1)g^{(2)}(r)$. For the contact value at $v/v_0 = 1.6$, this means a 90-fold amplification, while at $v/v_0 = 3$ it is about eightfold.

Table III. Pair distribution functions at $v/v_0 = 1.60$.

r_{12}	$g^{(2)}(r_{12})$	$[g^{(3)}(r, r, r)]^{1/3}$	BG	PY
1.000	4.95	4.85 ^a	2.78	4.27
1.088	2.72	2.72	2.35	2.79
1.253	1.12	1.18	1.59	1.18
1.399	0.73	0.74	1.11	0.66
1.531	0.64	0.61	0.81	0.60
1.652	0.71	0.69	0.69	0.73
1.764	0.88	0.94	0.67	0.89
1.870	1.08	1.15	0.73	1.06
1.970	1.24	1.24	0.88	1.24

^aExtrapolated.

Table IV. Values of $R^{(3)}$ for an asymmetric triplet configuration at $v/v_0 = 1.60$.

r_{23}	$R^{(3)}(1.088, 1.088, r_{23})$
1.088	1.00
1.253	1.13
1.399	1.24
1.531	1.34
1.652	1.37
1.764	1.33
1.870	1.13
1.970	0.88

These facts encourage the use of the SA in other integral equations which do not amplify the error so much. Furthermore, it appears worthwhile in such integral equations to apply the SA in higher dimensional configuration spaces, since, judging by the values of $R^{(2)}$ and $R^{(3)}$, the maximum value of $R^{(n)}$ seems to approach unity rapidly as n increases. The maximum value of $R^{(2)}$ is equal to the maximum value of $g^{(2)}$, since the singlet distribution function is unity, and at v/v_0 of 1.60 is about 5, while the corresponding value of $R^{(3)}$ is 1.4. Finally, it is unlikely that the conclusions reached here will be altered if an attractive potential of interaction is present as well since, as a first approximation, the attractive potential can be considered as only providing a uniform nega-

tive potential over the entire system. It is planned, however, to check this point for square-well molecules with molecular dynamics.

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DETECTION OF PLASMA RADIATION FROM ELECTRON-BOMBARDED Al AND Mg FOILS

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A suggestion by Ferrell¹ in 1958 has led to an intensive search for monochromatic photons from the decay of plasma oscillations in electron-bombarded metal foils.^{2,3} A peak in the Ag spectrum at 3300 Å has been observed previously but the interpretation is complicated by interband effects.⁴ The band structure of Al has been shown to be nearly free electronlike and should provide a better test for the plasma oscillation theory. Electron energy loss experiments show sharp discrete losses in Al at multiples of 15.3 eV.⁵ The decay of this plasmon should be accompanied by the emission of photons at approximately 800 Å.

The details of the present experiment have been described previously.³ Self-supported Al foils 600 Å to 800 Å in thickness were bombarded with 60- to 100-keV electrons. The light emitted at 30° from the foil normal was analyzed with a 50-cm Seya-Namioka vacuum ultraviolet spectrometer. The detector was an EMI-6256B photomultiplier whose quartz window was coated with sodium salicylate. A sharp peak at 815 Å ± 15 Å was found in the Al spectrum (Fig. 1) in good agreement with the characteristic energy loss experiments and with theoretical predictions. The theoretical spectrum was calculated by inserting the optical constants of Al determined by Hunter⁶ into the transition radiation equation given by Ritchie and Eldridge.⁷

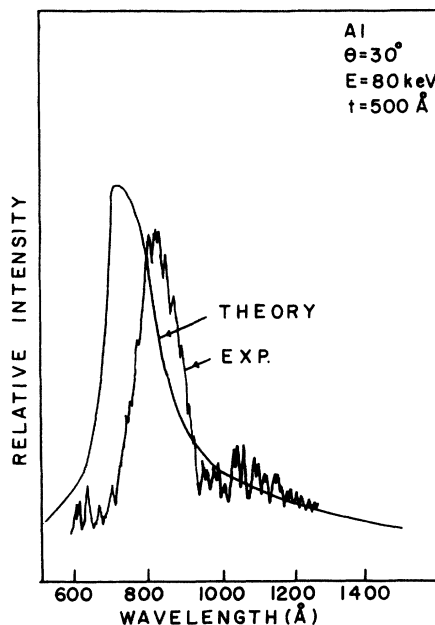


FIG. 1. Photon emission from electron-bombarded Al foil 800 Å in thickness (spectrum uncorrected for spectrometer response).

In order to verify the fact that the peak in the Al spectrum was 815 Å radiation and not due to scattered photons, a LiF filter which only transmits radiation of wavelengths longer than 1100 Å