Pramāna, Vol. 20, No. 4 April 1983, pp. 327-337. © Printed in India.

Perturbation theory for equilibrium properties of a binary mixture of hard discs

U N SINGH* and S K SINHA
Department of Physics, L S College, Bihar University, Muzaffarpur 842 001, India
*Department of Physics, R N College, Hajipur, Vaishali, India

MS received 14 October 1982; revised 23 February 1983

Abstract. The radial distribution function (RDF) and thermodynamic properties of a two-dimensional hard-disc mixture are calculated by using the perturbation theory. Numerical results are given for the RDF, pressure and excess-free energy of the binary mixture of both additive and non-additive hard discs. It is found that the thermodynamic properties of the binary mixture of non-additive hard discs increase with Δ, the non-additive parameter.

Keywords. Radial distribution function; excess free energy; binary mixture.

1. Introduction

The calculation of the radial distribution function (RDF) and the thermodynamic properties of two dimensional systems have been a subject of considerble interest in recent years (Dash 1975; Steele 1973, 1974, 1976; Lado 1968; Henderson 1975, 1977; Glandt and Fitts 1978; Toxvaerd 1980; Abraham 1980; Barker *et al* 1981). This is partly because of the fact that the two-dimensional fluid is often used as a model substance in the investigation of surface phenomena (Dash 1975; Steele 1973, 1974). Another reason for this interest is to know the extent to which dimensionality of the system affects the nature of the phase transition (melting and vaporization) (Toxaverd 1980; Abraham 1980; Barker *et al* 1981; Nelson and Halperin 1979).

Considerable progress has been made in recent years in understanding the structural and thermodynamic properties of the two-dimensional one-component fluid. However a two-dimensional fluid mixture has not yet been investigated systematically.

The hard sphere mixture holds a central position in the theory of fluid mixtures. In recent years, many theoretical attempts such as van der Waals one and two-fluid theories (Leland *et al* 1968; Henderson and Leonard 1971b); and perturbation theory (Henderson and Barker 1968; Smith 1971; Henderson and Leonard 1971a; Smith and Henderson 1972) have been made to understand the structural and thermodynamic properties of a three-dimensional binary mixture of hard spheres. The basis of the perturbation theory is to expand the properties of a hard-sphere mixture about that of a one-component fluid of hard spheres of diameter d_0 in power of $(d^n_{\alpha\beta} - d^n_0)$. It is observed that the first order theory becomes identical to the van der Waals one fluid VDW 1 theory, when $n=3$ (Smith and Henderson 1972; Adam and McDonald 1975). Although the perturbation expansion for the distribution function is successful only when the hard spheres are nearly equal in size, it is useful because it is the only practical scheme available for obtaining the distribution functions for multi-component mixture of hard spheres. This method can be extended to the two-dimensional hard-disc mixture. For the hard sphere mixture, $n=3$, which gives the correct second virial coefficient in the lowest order, gives good results for the thermodynamic properties (Smith 1971; Henderson and Leonard 1971a) as well as the distribution functions (Smith and Henderson 1972). For the hard-disc mixture, however, $n=2$ gives the correct second virial coefficient. As for the three-dimensional hard-sphere mixture, the perturbation theory with $n=2$ is expected to provide good results for the two-dimensional hard-disc mixture. We adopt $n=2$ to calculate the properties.

In this paper, we examine the perturbation theory for a two-dimensional binary mixture of hard-discs and study the RDF and thermodynamic properties of the system. In §2 we discuss the theory to calculate the RDF and thermodynamic properties for a binary mixture of hard-discs. The results are discussed in §3. Section 4 gives the summary of the paper.

2. Perturbation theory

We consider a two-dimensional fluid mixture of N_1 hard-disc molecules of species 1 and N_2 hard-disc molecules of species 2, such that the total number of molecules is $N=N_1+N_2$. Further we assume that the constituent molecules differ in size. The potential energy of the system is assumed to be pair-wise additive. Thus

$$U(1,2,\ldots,N)=\sum_{\alpha,\beta=1}^{2}\sum_{i<j}u_{\alpha\beta}(i,j), \tag{1}$$

where $u_{\alpha\beta}(i,j)$ is the pair potential between particle i of species α and particles j of species β and is given by

$$\begin{aligned} u_{\alpha\beta}(i,j) &= \infty, \quad r_{ij}<d_{\alpha\beta} \\ &= 0, \quad r_{ij}>d_{\alpha\beta}, \end{aligned} \tag{2}$$

$d_{\alpha\beta}$ being the diameter between hard discs of species α and β. In general, the effective diameter between hard discs of unlike species is given by (Henderson and Leonard 1971 b)

$$d_{12}=\tfrac{1}{2}(d_{11}+d_{22})(1+\Delta), \tag{3}$$

where $d_{\alpha\alpha}$ is the diameter of species α and Δ is the non-additive parameter. $\Delta=0$ for additive mixtures and $|\Delta|>0$ for non-additive mixtures.

2.1 *Thermodynamic properties*

The thermodynamic properties of the two-dimensional hard-disc mixture can be obtained by adopting the extended conformal solution theory (Henderson and Barker 1968; Smith 1971; Henderson and Leonard 1971), in which the configurational partition function is expanded about that of a reference pure hard-disc fluid with diameter d_0 in powers of $(d^n_{\alpha\beta} - d^n_0)$. The first order term is then annulled by choosing

$$d^n_0 = \sum_{\alpha,\beta} X_\alpha X_\beta d^n_{\alpha\beta}, \tag{4}$$

where $X_\alpha = N_\alpha/N$ is the concentration of the species α. As in the case of the hard-sphere mixture, the choice of n is free. However, if we choose to adopt the value $n = 2$, the first order approximation becomes identical to the van der Waals one fluid (VDW 1) theory (Leland *et al* 1968) of mixture.

In the VDW 1 theory of mixture the free energy and pressure of the mixture are written as

$$A = A_0 + NkT \sum_\alpha X_\alpha \ln X_\alpha + \text{second order term}, \tag{5}$$

$$P = P_0 + \text{second order terms}, \tag{6}$$

where A_0 and P_0 are respectively the free energy and pressure for the pure fluid containing N molecules in volume V at temperature T. For a hard-disc model having diameter d_0 given by (4) with $n=2$, P_0 and A_0 are given by (Henderson 1975)

$$\beta P_0/\rho = (1 + 0{\cdot}125\eta_0^2)/(1 - \eta_0)^2 \tag{7}$$

and
$$\frac{\beta A_0}{N} = \frac{9}{8}\frac{\eta_0}{(1-\eta_0)} - \frac{7}{8}\ln(1-\eta_0), \tag{8}$$

where
$$\eta_0 = \tfrac{1}{4}\pi\rho d_0^2. \tag{9}$$

These equations can be used to calculate the pressure and free energy of a binary mixture of both additive and non-additive hard-discs.

For the additive hard-discs, (7) and (8) are simplified to

$$\frac{\beta P_0}{\rho} = \frac{1 + 0{\cdot}125\eta^2}{(1-\eta)^2} - \frac{1}{4}\pi X_1 X_2 \left[\frac{1 + 0{\cdot}125\eta}{(1-\eta)^3}\right] \times \rho (d_{11} - d_{22})^2 + 0(X_1 X_2)^2 \tag{10}$$

and
$$\frac{\beta A_0}{N} = \frac{9}{8}\frac{\eta}{1-\eta} - \frac{7}{8}\ln(1-\eta) - \frac{1}{4}\pi X_1 X_2 \left[\frac{(1 - \frac{7}{16}\eta)}{(1-\eta)^2}\right]\rho(d_{11} - d_{22})^2 + 0(X_1 X_2)^2 \tag{11}$$

where $$\eta = \tfrac{1}{4}\,\pi\,\rho^* = \tfrac{1}{4}\,\pi\,\rho\,(X_1\,d_{11}^2 + X_2\,d_{22}^2). \tag{12}$$

For non-additive hard-discs, (7) and (8) can be written as

$$\frac{\beta\,(P_0 - P_0^a)}{\rho} = \tfrac{1}{4}\,\pi\,X_1\,X_2\,\rho\,(d_{11} + d_{22})^2 \left[\frac{1 + 0{\cdot}125\,\eta}{(1-\eta)^3}\right] \Delta\,(2+\Delta) + 0\,(X_1^2\,X_2^2), \tag{13}$$

$$\frac{\beta\,(A_0 - A_0^a)}{N} = \tfrac{1}{4}\,\pi\,X_1\,X_2\,\rho\,(d_{11} + d_{22})^2 \left[\frac{(1 - \frac{7}{16}\,\eta)}{(1-\eta)^3}\right] \Delta\,(2+\Delta) + 0\,(X_1^2\,X_2^2), \tag{14}$$

where P_0^a and A_0^a are respectively the pressure and free energy of a binary mixture of additive hard-discs and given by (10) and (11). However we prefer to use (7) and (8) for calculating the pressure and free energy of the binary mixture.

2.2 *Radial distribution function*

The RDF of a mixture is given by

$$g_{\alpha\beta}\,(r_{12}) = V^2 \frac{\int \exp\,[-\beta\,U]\,\prod_{i=3}^{N} d\bar{r}_i}{\int \exp\,[-\beta\,U]\,\prod_{i=1}^{N} d\bar{r}_i}. \tag{15}$$

To calculate the RDF $g_{\alpha\beta}\,(r_{12})$ for a mixture of hard-discs, we adopt the method of Smith and Henderson (1972) originally developed for a mixture of hard-spheres and expand $Y_{\alpha\beta}\,(r_{12})$, which is defined by

$$Y_{\alpha\beta}\,(r_{12}) = \exp\,[\beta u_{\alpha\beta}\,(r_{12})]\;g_{\alpha\beta}\,(r_{12}), \tag{16}$$

in the form

$$Y_{\alpha\beta}\,(r_{12}) = Y_0\,(r_{12}) + \sum_{\gamma,\delta=1}^{2} \left[\frac{\partial\,Y_{\alpha\beta}\,(r_{12})}{\partial d_{\gamma\delta}^n}\right]_{d\gamma\delta=d_0} (d_{\gamma\delta}^n - d_0^n), \tag{17}$$

where $Y_0\,(r_{12})$ is the distribution function of the pure hard-disc reference system of diameter d_0 defined by (4).

We extend the method of Smith and Henderson (1972) to the hard-disc mixture and obtain

$$Y_{\alpha\beta}\,(r_{12}^*) = Y_0\,(r_{12}^*) - \rho\,d^2\,\xi\,(r_{12}^*) \sum_{\gamma=1}^{2} X_\gamma\,(\Delta_{\alpha\gamma} + \Delta_{\beta\gamma}), \tag{18}$$

$$\xi\,(r_{12}^*) = \frac{2}{r_{12}^*}\, Y_0\,(r_{12}^*)\; Y_0\,(1) \int\limits_{|r_{12}^* - 1|}^{r_{12}^* + 1} [(g_0\,(r_{13}^*) - 1)]\,\frac{dr_{13}^*}{\sin\,\theta_{23}'}, \tag{19}$$

with $\cos\,\theta_{23}' = \dfrac{r_{12}^{*2} + r_{13}^{*2} - 1}{2\,r_{12}^*\,r_{13}^*}$,

$r_{ij}^* = r_{ij}/d_0$;

and
$$\Delta_{\alpha\beta} = \frac{1}{n}\left[\frac{d_{\alpha\beta}^n}{d_0^n} - 1\right]. \tag{20}$$

From (18) we obtain expressions for the distribution function for a binary mixture with $X_1 = X_2 = 0{\cdot}5$

$$Y_{11}\,(r^*) = Y_0\,(r^*) + \tfrac{1}{2}\,\rho\,d^2\,\xi\,(r^*)\,[\Delta_{22} - \Delta_{11}], \tag{21}$$

$$Y_{12}\,(r^*) = Y_0\,(r^*), \tag{22}$$

$$Y_{22}\,(r^*) = Y_0\,(r^*) - \tfrac{1}{2}\,\rho\,d^2\,\xi\,(r^*)\,[\Delta_{22} - \Delta_{11}]. \tag{23}$$

Thus, for a binary mixture of hard discs, with $X_1 = X_2 = 0{\cdot}5$, like that of hard spheres (Smith and Henderson 1972), we have

$$Y_{12}\,(r^*) = [\,Y_{11}\,(r^*) + Y_{22}\,(r^*)]/2. \tag{24}$$

The distribution function obtained in this way can be used to calculate the thermodynamic properties of the system. Thus the pressure equation for a hard-disc mixture is given by

$$\frac{\beta P}{\rho} = 1 + \frac{1}{2}\pi\,\rho \sum_{\alpha,\,\beta} X_\alpha\, X_\beta\, d_{\alpha\beta}^2\; Y_{\alpha\beta}\,(d_{\alpha\beta}). \tag{25}$$

Equations (18) and (19) can be applied to additive as well as nonadditive hard-disc mixture. We discuss the results for the additive and non-additive mixture in the following section.

3. Results and discussion

3.1 *Binary mixture of additive hard-discs*

We have evaluated the distribution function $Y_{\alpha\beta}\,(r)$ for the additive hard-disc mixture for the densities in the range $0{\cdot}461880 \leqslant \rho\, d_0^2 \leqslant 0{\cdot}790794$ using (18) and (19). In our calculation we need to know $Y_0\,(r^*)$. We have used machine simulation (Woods 1968, 1970; Chae *et al* 1969) values of $g_0\,(r^*)$ for $r^* \geqslant 1$. However, there are no machine simulation values of $Y_0(r^*)$ for $r^* < 1$. Chae *et al* (1969) have found the following expression from the solution of modified Born-Green-Yuon (BGYM) integral equation.

$$Y_0(r^*) = g_0(1) \exp \{2 \rho g_0(1) [\cos^{-1}(r^*/2) - \tfrac{1}{4} r^* (4 - r^{*2})^{1/2} - \tfrac{1}{3}\pi + \tfrac{1}{4}\sqrt{3}]\}, r^* \leq 1. \quad (26)$$

The values found from this relation are used to calculate $Y_{\alpha\beta}(r)$.

One can calculate $Y_{\alpha\beta}(r)$ for the cases $n = 1$ and 2. The $n = 2$ is only expected to provide good results for the hard disc mixture and we calculate the results for the case $n = 2$.

The values for $Y_{\alpha\beta}(r)$ for an equimolar binary mixture ($X_1 = X_2 = 0{\cdot}5$) with $R = d_{22}/d_{11} = 1{\cdot}1$ and 3 are obtained from (21) to (23) for $n = 2$. For $r \geq d_{\alpha\beta}$, the RDF's $g_{\alpha\beta}(r)$ are identical to the $Y_{\alpha\beta}(r)$. The values of $g_{\alpha\beta}(r)$ for a binary hard-disc mixture with $X_1 = X_2 = 0{\cdot}5$ and $R = 1{\cdot}1$ are shown in figure 1 for $\rho^* = 0{\cdot}75$. We find that $g_{11}(d_{11}) < g_{22}(d_{22})$. In figure 2, we have reported the values of $g_{\alpha\beta}(r)$ for $\rho^* = 0{\cdot}51$ at $X_1 = X_2 = 0{\cdot}5$ and $R = 3$. In this case $g_{11}(d_{11})$ is large whereas

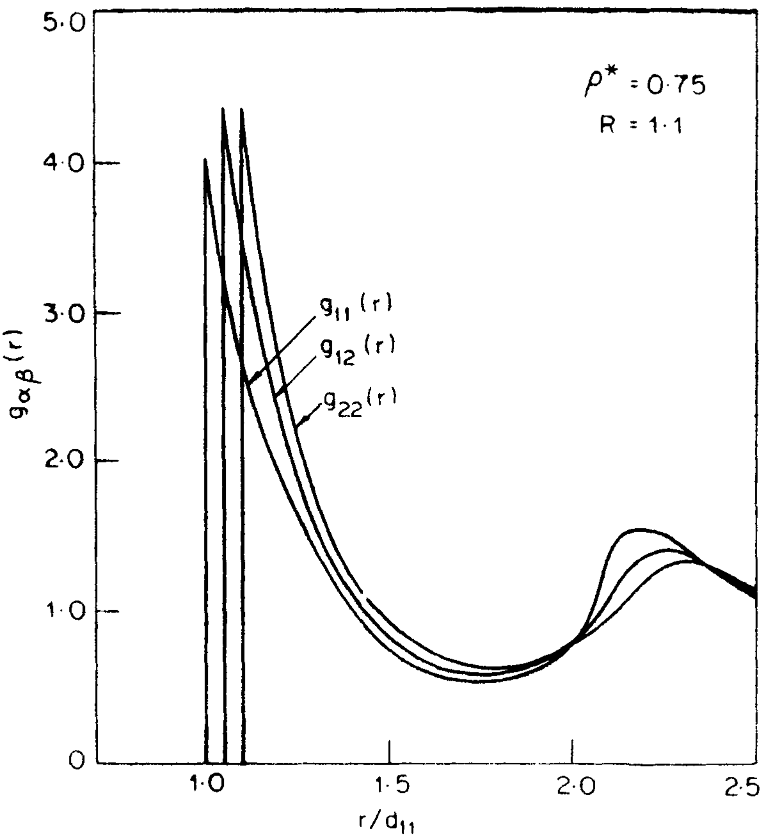

Figure 1. Pair distribution function $g_{\alpha\beta}(r)$ for a binary hard-disc mixture with $X_1 = X_2 = 0{\cdot}5$ and $R = 1{\cdot}1$ for $\rho^* = 0{\cdot}75$.

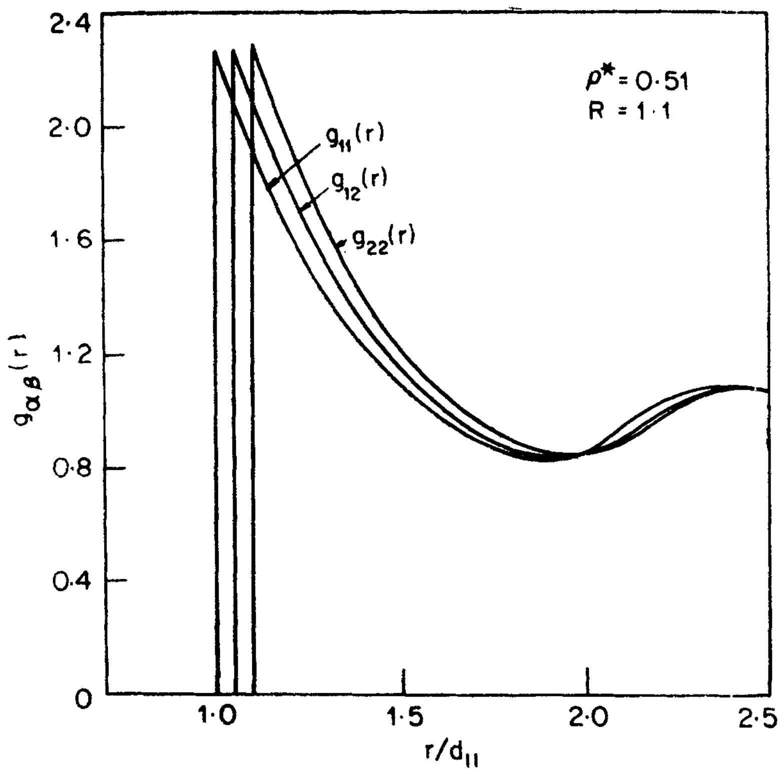

Figure 2. Pair distribution function $g_{\alpha\beta}(r)$ for a binary hard-disc mixture with $X_1 = X_2 = 0{\cdot}5$ and $R = 3$ for $\rho^* = 0{\cdot}51$.

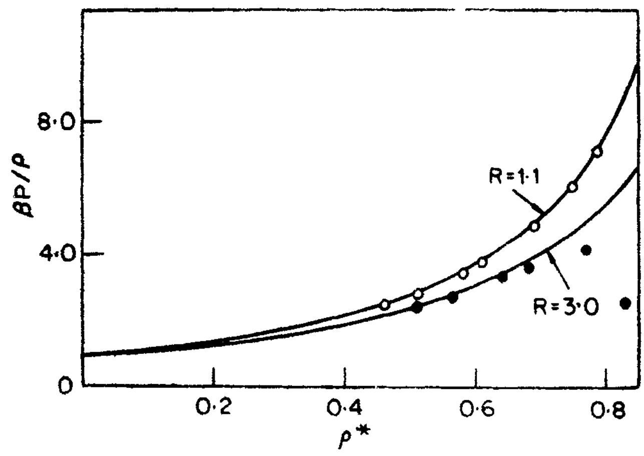

Figure 3. Equation of state $\beta P/\rho$ for a binary hard-disc mixture with $X_1 = X_2 = 0{\cdot}5$; and $R = 1{\cdot}1$ and 3. The white and black points give the results obtained from (25) for $R = 1{\cdot}1$ and 3 respectively.

$g_{22}(d_{22})$ is low, as in the case of the hard sphere mixture (Smith and Henderson 1972). This shows that even the qualitative feature $g_{22}(d_{22}) \geqslant g_{11}(d_{11})$ has been lost for $R = 3$.

The equation of state $\beta P/\rho$ for a binary hard-disc mixture with $X_1 = X_2 = 0{\cdot}5$ and $R = 1{\cdot}1$ and 3 has been calculated from (7) and (25) using $n = 2$. The results are demonstrated in figure 3. The results for $R = 3$ are less than that for $R = 1{\cdot}1$.

From the figure we find that the results obtained from (25) are in good agreement with that obtained from (7) for $R = 1{\cdot}1$. However, the agreement is poor for $R = 3$; specially at high densities, where the pressure equation of the state decrease with the increase of density, so that even the qualitative result has been lost at high density. Thus for $R = 3$, the values for the $Y_{\alpha\beta}(r)$ give poor results at high denisty whereas at low density the results are good.

3.2 *Binary mixture of non-additive hard-discs*

In this section we have evaluated the distribution functions and thermodynamic properties for a binary mixture of non-additive hard-discs.

The values of the distribution functions for an equimolar binary mixture ($X_1 = X_2 = 0{\cdot}5$) with $R = d_{22}/d_{11} = 1{\cdot}1$ are obtained from (21)—(23) for $n = 2$. The values of $g_{\alpha\beta}(r)$ for a binary mixture of non-additive hard discs with $X_1 = X_2 = 0{\cdot}5$ and $R = 1{\cdot}1$ are shown in figures 4 and 5 for $\rho^* = 0{\cdot}4185$ at $\Delta = 0{\cdot}1$ and for $\rho^* = 0{\cdot}5638$ at $\Delta = -0{\cdot}1$ respectively. We find that $g_{11}(d_{11}) < g_{22}(d_{22})$ even for a non-additive mixture for $R = 1{\cdot}1$. However, the values of $g_{12}(d_{12})$ depend on the value of Δ; $g_{12}(d_{12}) < g_{11}(d_{11})$ when $\Delta = 0{\cdot}1$ and $g_{12}(d_{12}) > g_{22}(d_{22})$ when $\Delta = -0{\cdot}1$.

In figure 6, the values of $\beta A/N$, obtained from (5) and (8) are reported as a function

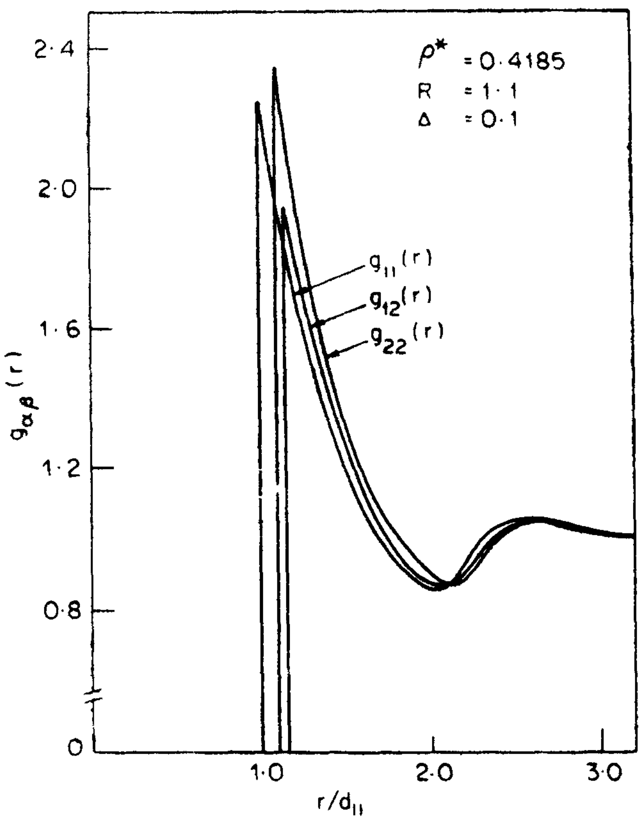

Figure 4. The RDF $g_{\alpha\beta}(r)$ for a binary mixture of non-additive hard-discs with $X_1 = X_2 = 0{\cdot}5$ and $R = 1{\cdot}1$ for $\rho^* = 0{\cdot}4185$ at $\Delta = 0{\cdot}1$.

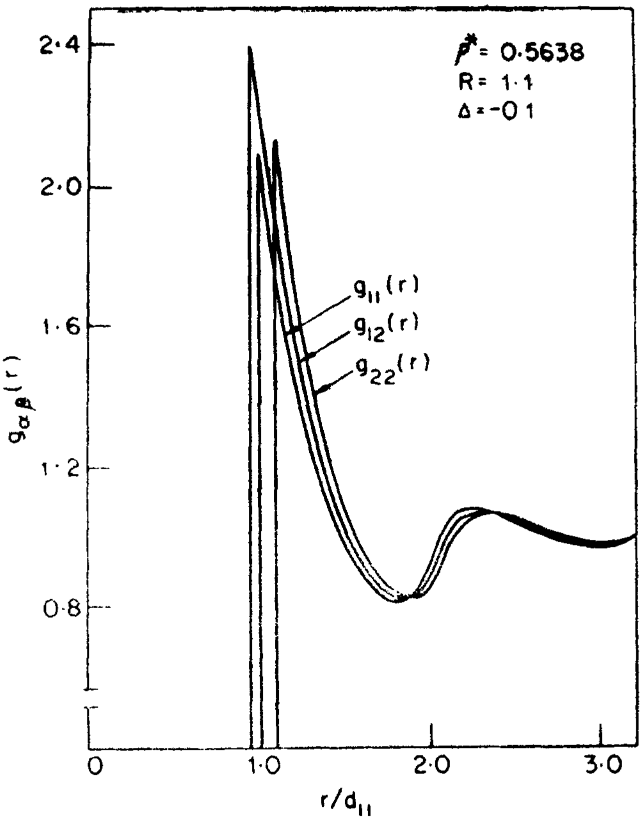

Figure 5. The RDF $g_{\alpha\beta}(r)$ for a binary mixture of non-additive hard-discs with $X_1 = X_2 = 0{\cdot}5$ and $R = 1{\cdot}1$ for $\rho^* = 0{\cdot}5638$ at $\Delta = -0{\cdot}1$.

of Δ, the non-additive parameter for $\rho^* = 0{\cdot}4$, $0{\cdot}6$ and $0{\cdot}8$ at $R = 1$. We find that the free energy increases with Δ. In figure 7, the values of $\beta P/\rho$ obtained from (7) are given as a function of Δ for $\rho^* = 0{\cdot}4$, $0{\cdot}6$ and $0{\cdot}8$ at $R = 1$. We see that the pressure also increases with Δ. Further we find that the thermodynamic properties increase with the density.

4. Conclusions

We have applied the perturbation theory to calculate the thermodynamic properties and RDF for the two-dimensional binary mixture of hard discs. We have calculated the results using $n = 2$, which gives the correct second virial coefficient in the lowest order. As for the hard sphere mixture (Smith 1971; Henderson and Leonard 1971a, b), the perturbation theory is expected to provide good results for the thermodynamic properties.

From the study we find that the thermodynamic properties of the binary hard

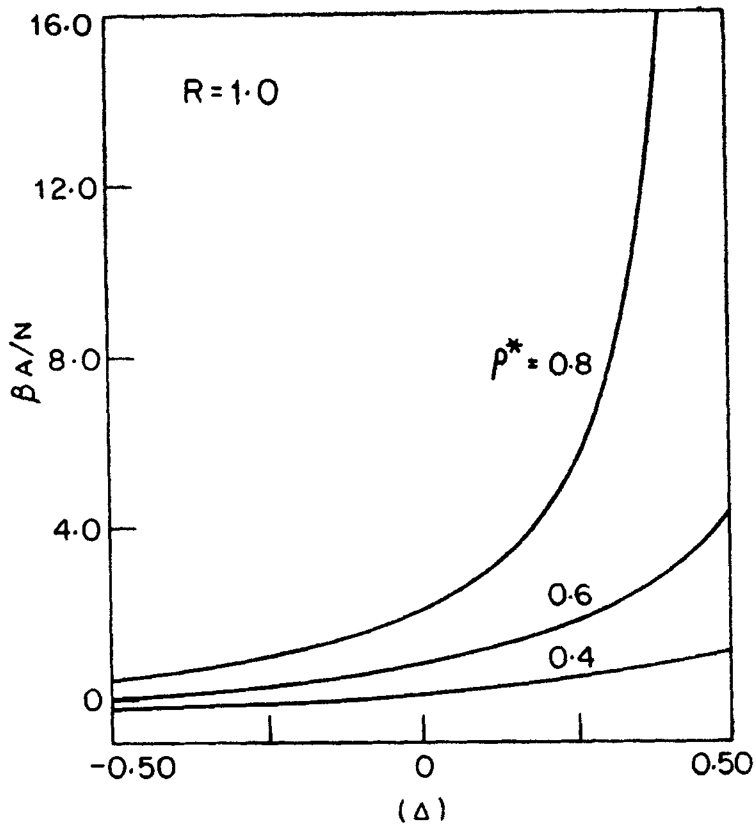

Figure 6. The free energy $\beta A/N$ of a binary mixture of non-additive hard-discs as a function of Δ for $\rho^* = 0{\cdot}4$, $0{\cdot}6$ and $0{\cdot}8$ at $X_1 = X_2 = 0{\cdot}5$ and $R = 1$.

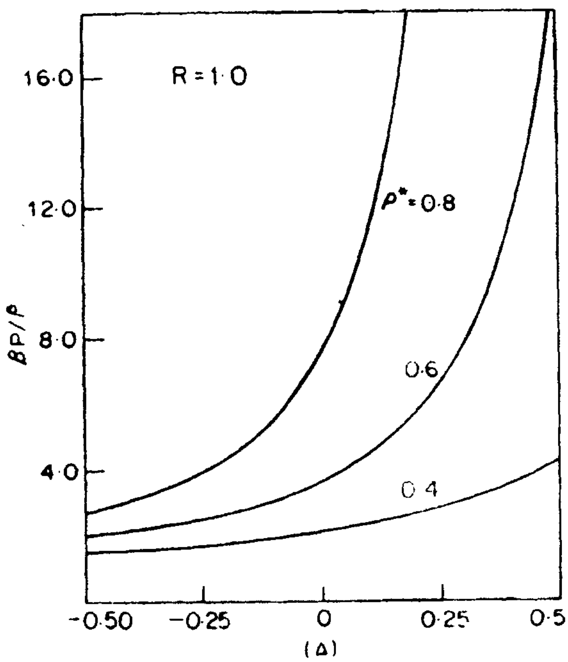

Figure 7. The equation of state $\beta P/\rho$ of a binary mixture of non-additive hard-discs as a function of Δ for $\rho^* = 0{\cdot}4$, $0{\cdot}6$ and $0{\cdot}8$ at $X_1 = X_2 = 0{\cdot}5$ and $R = 1$.

disc mixture, like that of the binary hard sphere mixture, are maximum at $R = 1$ and decrease as the value of R goes away from 1.

References

Abraham F F 1980 *Phys. Rev. Lett.* **44** 463
Adam D J and McDonald I R 1975 *J. Chem. Phys.* **63** 1900
Barker J A, Henderson D and Abraham F F 1981 *Physica* **A106** 226
Chae D G, Ree F H and Ree T 1969 *J. Chem. Phys.* **50** 1551
Dash J G 1975 *Film on solid surfaces* (New York: Academic Press)
Glandt E D and Fitts D D 1978 *Mol. Phys.* **35** 205
Henderson D 1975 *Mol. Phys.* **30** 971
Henderson D 1977 *Mol. Phys.* **34** 301
Henderson D and Barker J A 1968 *J. Chem. Phys.* **49** 3377
Henderson D and Leonard P J 1971a *Proc. Natl. Acad. Sci.* (USA) **68** 2354
Henderson D and Leonard P J 1971b Physical Chemistry—*An Advance treatise* (New York: Academic Press)
Lado F 1968 *J. Chem. Phys.* **49** 3092
Leland T W, Rowlinson J S and Sather G A 1968 *Faraday Soc.* **64** 1447
Nelson D R and Halparin 1979 *Phys. Rev.* **B19** 2457
Smith W R 1971 *Mol. Phys.* **21** 105
Smith W R and Henderson D 1972 *Mol. Phys.* **24** 773
Steele W A 1973 *Surf. Sci.* **39** 149
Steele W A 1974 *The interaction of gases with solid surfaces* (New York: Pergamon Press)
Steele W A 1976 *J. Chem. Phys.* **65** 5256
Toxvaerd S 1980 *Phys. Rev. Lett.* **44** 1002
Woods W W 1968 *J. Chem. Phys.* **48** 415
Woods W W 1970 *J. Chem. Phys.* **52** 729