



# Thermodynamic properties of polydisperse hard spheres

PAUL BARTLETT\*

Department of Chemistry, University of Bath, Bath, BA2 7AY, UK

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The virial expansion of a polydisperse system of hard spheres has been studied. The virial coefficients are shown to be a function of the total number density and the first three moments of the diameter distribution. The small number of moment variables identified is used to construct a simple but physically reasonable model of a polydisperse hard sphere crystal. Analytical expressions for the pressure and the moment chemical potentials are obtained.

## 1. Introduction

Understanding the stability of colloidal suspensions is important to a wide range of industrial applications including paint, detergent manufacture and the processing of many foodstuffs. Surprisingly, given the enormous economic importance of colloids, the phase behaviour of even the simplest realistic model for a colloidal system, a polydisperse mixture of hard spheres, remains poorly understood [1]. For instance, while the phase behaviour of uniform hard spheres has been known for in excess of thirty years [2] the equivalent polydisperse phase diagram is still not established and is a subject of active debate [3–6].

The reason for this difference is twofold. First, the statistical properties of polydisperse mixtures have been relatively little studied. To our knowledge for instance there is only one computer simulation study of a crystal of polydisperse hard spheres [3]. The liquid state has scarcely fared much better, with just two investigations [3, 7]. With the scarcity of simulation data theoretical treatments of polydisperse systems have either relied on uncontrolled approximations or idealized models [8]. A second difficulty has been that solving phase equilibria in a polydisperse system is considerably more complicated than for a monodisperse system. The standard thermodynamic procedure treats each particle as a separate conserved component so that the equations of equilibrium between coexisting phases become highly nonlinear functional equations [8]. Recently a systematic scheme [9, 10] has been developed to solve the problem in the case where the excess free energy depends on a limited number of moments of the diameter distribution. The powerful ‘annealed moments’ method of Sollich, Cates and Warren reduces the problem to a few algebraic equations.

In the present paper we develop simple analytical expressions for the thermodynamic properties of polydisperse solid and fluid mixtures of hard spheres valid for slightly polydisperse systems (that is ‘close’ to the monodisperse limit). The main purpose of this paper is to extend our earlier work [11] and to present analytical results which we hope will form a useful source for further work on polydisperse colloids. In a subsequent paper it is planned to use these expressions and the ‘annealed moment’ method to explore the effect of polydispersity on the freezing transition in hard spheres.

In section 2 we consider the virial expansion of the equation of state of a polydisperse hard sphere fluid. For low densities where the virial expansion is valid, the statistical properties of a polydisperse mixture depend on a small number of moment variables. The same simplification is evident also in the approximate scaled particle and Percus–Yevick theories which are more appropriate for high densities. Utilizing this symmetry the excess statistical properties of a polydisperse system may be identified formally with those of a suitably chosen binary hard sphere mixture. In section 3 we describe this mapping procedure in detail and in section 4 we apply it to a polydisperse crystal. Utilizing previous simulation data for hard sphere mixtures we construct a simple model of a polydisperse crystal. Predictions for the pressure and the chemical potential are fitted to symmetry-adapted analytical functions.

## 2. The Virial Expansion

A polydisperse hard sphere mixture is completely specified by the number density of spheres of every size. If the size of each particle is drawn from a distribution  $f(R)$  (with  $\int dR f(R) = 1$ ) then the number density of particles with diameter  $R$  is  $\rho f(R) dR$ , where  $\rho$  is the total number density. In this section we demonstrate

\* e-mail: P.Bartlett@bath.ac.uk

that many of the key properties of a polydisperse system may be expressed succinctly in terms of the *moments* of the diameter distribution,

$$m_i = \int dR f(R) R^i \quad \text{with } i = 1, 2, \dots, \quad (1)$$

rather than the complete distribution  $f(R)$ .

The properties of a polydisperse system are obtained most readily by generalizing the properties of an  $n$ -component finite mixture [12]. Therefore we consider first an  $n$ -component mixture of  $N_i$  hard spheres of diameter  $R_i$  enclosed in a volume  $V$  at the equilibrium temperature  $T$ . The composition of this mixture may be described in terms of the partial number densities,  $\rho_i = N_i/V$ , or else in terms of the total number density  $\rho = \sum_i \rho_i$  and the partial mole fractions  $x_i = N_i/N$  where  $N = \sum_i N_i$  is the total number of spheres.

For small densities, the pressure  $\beta P$  where  $P$  is the pressure,  $\beta = 1/k_B T$  and  $k_B$  is Boltzmann's constant, can be expanded in a virial series [13]

$$\beta P = \sum_{m=1}^{\infty} B_m \rho^m, \quad (2)$$

where  $B_m$  is the  $m$ th virial coefficient of the mixture (with  $B_1 = 1$ ). For a multicomponent mixture  $B_m$  can be decomposed further into partial virial coefficients  $b_m(R_i, R_j, \dots)$  defined by analogy with the expression for the second virial coefficient

$$B_2 = \sum_{i=1}^n \sum_{j=1}^n x_i x_j b_2(R_i, R_j). \quad (3)$$

Here the partial coefficient  $b_2(R_i, R_j)$  depends only on the interactions between components  $i$  and  $j$ . Although the calculation of the polydisperse-averaged second virial coefficient  $B_2$  is well known [12], we briefly repeat the main steps here in order to illustrate the basis for our treatment of the higher coefficients. To transform to the polydisperse case, we let  $n \rightarrow \infty$  and recognize that in a polydisperse system where the distribution function  $f(R)$  is continuous, no two spheres can have the same diameter, so  $x_i = x_j = 1/n$ . The polydisperse generalization of the second virial coefficient is, from equation (3),

$$\bar{B}_2 = \lim_{n \rightarrow \infty} \frac{1}{n^2} \sum_{i=1}^n \sum_{j=1}^n b_2(R_i, R_j), \quad (4)$$

which may be written concisely as

$$\bar{B}_2 = \langle b_2(R_i, R_j) \rangle_{ij} \quad (5)$$

where  $\langle \dots \rangle_{ij} = \int \int dR_i dR_j f(R_i) f(R_j) (\dots)$ . In the polydisperse limit the variables  $R_i$  and  $R_j$  are statistically independent so, for instance,

$$\langle R_i^p R_j^q \rangle_{ij} = \langle R_i^p \rangle_i \langle R_j^q \rangle_j = m_p m_q. \quad (6)$$

The second virial coefficient of a binary mixture of spheres is well known,

$$\begin{aligned} b_2(R_i, R_j) &= \frac{\pi}{12} (R_i + R_j)^3 \\ &= \frac{\pi}{12} (R_i^3 + 3R_i^2 R_j + 3R_i R_j^2 + R_j^3), \end{aligned} \quad (7)$$

so that the polydisperse average is simply,

$$\bar{B}_2 = \left( \frac{\pi}{6} \right) (m_3 + 3m_1 m_2). \quad (8)$$

The polydisperse form of the third virial coefficient can be obtained similarly from the exact expression for  $b_3$  in a tertiary mixture [14], namely

$$\begin{aligned} b_3(R_i, R_j, R_k) &= \frac{16\pi^2}{27} [R_i^3 R_j^3 + R_j^3 R_k^3 + R_i^3 R_k^3 \\ &\quad + 3R_i R_j R_k (R_i + R_j + R_k) \\ &\quad \times (R_i R_j + R_j R_k + R_i R_k)]. \end{aligned} \quad (9)$$

Averaging yields

$$\begin{aligned} \bar{B}_3 &= \langle b_3(R_i, R_j, R_k) \rangle_{ijk} \\ &= \left( \frac{\pi}{6} \right)^2 [m_3^2 + 3m_2^3 + 6m_1 m_2 m_3]. \end{aligned} \quad (10)$$

Inspection of equations (8) and (10) reveals that the two lowest virial coefficients are functions only of a limited number of the set of possible moments. We demonstrate below that this simplification holds also for all the higher virial coefficients.

Although expressions for the second and third virial coefficients are well known, no analytical results exist for the general form of the fourth (or higher) coefficients [14]. Solutions exist, for instance, for  $b_4$  only in the cases where either the particles are all of identical size [15] or where there is a large size asymmetry [16]. To express the  $m$ th virial coefficient in terms of moments, our starting point is the exact expression for  $b_m$  [17]

$$b_m(R_1 \dots R_m) = \frac{1-m}{m!} V^{-1} \int \dots \int V_m d\mathbf{r}_1 \dots d\mathbf{r}_m, \quad (11)$$

where the quantity  $V_m$  is the sum of all labelled stars [13] with  $m$  points. Each star consists of a product of Mayer  $f$  functions which for hard spheres have the simple form:

$$f_{ij} = \begin{cases} -1 & \text{if spheres } i \text{ and } j \text{ overlap,} \\ 0 & \text{otherwise.} \end{cases} \quad (12)$$

The number of star integrals that contribute to the  $m$ th virial coefficient increases rapidly with  $m$ , so to illustrate our arguments we shall look in detail only at the fourth virial coefficient. The integrals that contribute to  $b_4$  are conveniently represented pictorially:

$$\begin{aligned}
 -8b_4 = & \begin{array}{c} \begin{array}{ccc} (i-j) & & (i-l) \\ | & & | \\ (l-k) & & (k-j) \end{array} + \\ & \begin{array}{ccc} (i-j) & & (i-l) \\ | & & | \\ (l-k) & & (k-j) \end{array} + \\ & \begin{array}{ccc} (i-j) & & (i-l) \\ | & & | \\ (l-k) & & (k-j) \end{array} + \\ & \begin{array}{ccc} (j-i) & & (j-l) \\ | & & | \\ (k-l) & & (k-i) \end{array} + \\ & \begin{array}{ccc} (j-i) & & (j-l) \\ | & & | \\ (k-l) & & (k-i) \end{array} + \\ & \begin{array}{ccc} (k-i) & & (k-l) \\ | & & | \\ (j-l) & & (j-i) \end{array} + \\ & \begin{array}{ccc} (i-j) & & (i-l) \\ | & & | \\ (l-k) & & (k-j) \end{array} . \end{array} \quad (13)
 \end{aligned}$$

Integration is over all possible positions of the different particles, represented by the nodes of the diagram, with one particle fixed. Each solid line, linking pairs of particles, denotes the combination of  $f$  functions which appear in the integrand. From equation (12) the contribution to the cluster diagram is nonzero only if the two connected particles overlap.

Our first task is to establish how the value of each of these diagrams depends upon the diameter of one of the spheres, for instance the  $i$ th sphere. Consider first the final diagram in the third line of equation (13), in which all pairs of the four particles overlap. The contribution to this diagram from the integration over  $dr_i$  depends upon the locations of the spheres  $j$ ,  $k$  and  $l$ . It is nonzero only when all four spheres overlap, so for the configuration illustrated in figure 1 particle  $i$  must overlap the hashed region  $K$ . The volume  $v_p$  subsequently mapped out by the centre of particle  $i$  (the sum of the hashed and shaded regions in figure 1) may be estimated using the tools of integral geometry [18]. It is clear from figure 1 that  $v_p$  is the volume of the *parallel* body  $K_p$ , consisting of all points which lie within a distance  $\leq R_i/2$  of  $K$ . Since the intersection of two *convex* sets is itself convex, the region  $K$  must be convex. For a convex body, Steiner's formula [18] gives the parallel volume  $v_p$  as

$$v_p = v + \frac{A}{2}R_i + \frac{M}{4}R_i^2 + \frac{\pi}{6}R_i^3 \quad (14)$$

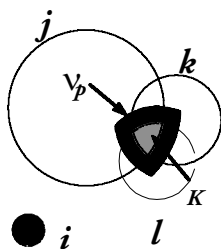


Figure 1. Specific configuration of three different size particles ( $j$ ,  $k$  and  $l$ ). A fourth sphere of diameter  $R_i$  will overlap the spheres  $j$ ,  $k$  and  $l$  when its centre is located inside the subvolume  $v_p$  (shown outlined in bold). The inner hashed region  $K$  represents the region of overlap of the three fixed spheres  $j$ ,  $k$  and  $l$ . The star integral is nonzero only when the centre of sphere  $i$  lies inside the region  $v_p$ .

where  $v$  is the volume of  $K$ . The quantities  $A$  and  $M$  in equation (14) denote the surface area and the integral mean curvature of the boundary  $\partial K$  of the region  $K$

$$\begin{aligned}
 A &= \int_{\partial K} df, \\
 M &= \frac{1}{2} \int_{\partial K} \left( \frac{1}{R_1} + \frac{1}{R_2} \right) df. \end{aligned} \quad (15)$$

Here  $df$  is the area element on  $K$  and  $R_1$  and  $R_2$  are the principal radii of curvature of the boundary  $\partial K$ .

Clearly the shape of the region  $K$  depends upon the positions of the three spheres ( $j$ ,  $k$  and  $l$ ) so that the total value of the diagram may be written as  $1/V \int \int \int v_p dr_j dr_k dr_l$ . To evaluate this integral we substitute in equation (14) and write the result in the form

$$\begin{array}{ccc} (i-j) & & (i-l) \\ | & & | \\ (l-k) & & (k-j) \end{array} = a_0 + a_1 R_i + a_2 R_i^2 + a_3 R_i^3, \quad (16)$$

where the coefficients are independent of  $R_i$  and are fixed by the diameters of the species  $j$ ,  $k$  and  $l$ . The diagram must be symmetric in the diameters of the different spheres. Incorporating this symmetry equation (16) may be generalized further to

$$\begin{array}{ccc} (i-j) & & (i-l) \\ | & & | \\ (l-k) & & (k-j) \end{array} = \sum_{n_1=0}^3 \sum_{n_2=0}^3 \dots \sum_{n_4=0}^3 c_{n_1, n_2, n_3, n_4} R_i^{n_1} R_j^{n_2} R_k^{n_3} R_l^{n_4}, \quad (17)$$

where the coefficients are now purely numerical. Dimensional considerations restrict the possible combinations of the exponents so that only terms with  $n_i + n_j + n_k + n_l = 9$  contribute to the sum. The polydisperse average of equation (17) is (with  $m_0 = 1$ )

$$\begin{aligned}
 \left\langle \begin{array}{ccc} (i-j) & & (i-l) \\ | & & | \\ (l-k) & & (k-j) \end{array} \right\rangle_{ijkl} &= \sum_{n_1=0}^3 \sum_{n_2=0}^3 \dots \\ &\times \sum_{n_4=0}^3 c_{n_1, n_2, n_3, n_4} m_{n_1} m_{n_2} m_{n_3} m_{n_4} \end{aligned} \quad (18)$$

which depends *only* on the moments,  $m_1$  through to  $m_3$ , of the diameter distribution. It is straightforward to show that the sum of the diagrams in the first two lines of equation (13) also can be expressed in an equivalent form (the complete analytical expression for this combination of diagrams is given in [16]). Consequently the polydisperse fourth virial coefficient is a function solely of the first three diameter moments. We conjecture that this conclusion holds for all the higher virial

coefficients so that in general we may write the  $m$ th polydisperse coefficient in the form

$$\bar{B}_m = \sum_{n_1=0}^3 \sum_{n_2=0}^3 \cdots \sum_{n_m=0}^3 a_{n_1, n_2, \dots, n_m} \prod_{i=1}^m m_{n_i}, \quad (19)$$

with  $m_0 = 1$  and  $\sum_{i=1}^m n_i = 3^{m-1}$ . In three dimensions the virial equation of state is a function solely of the variables  $\rho$  and  $m_1$  through to  $m_3$ .

The structure of the virial coefficients leads to two important conclusions. First, all of the excess thermodynamic properties of a polydisperse mixture depend, like the equation of state, solely on  $\rho$  and the moments  $m_1$  to  $m_3$ . To see this, consider, for instance, the excess free energy per unit volume,  $f^{\text{ex}} = F^{\text{ex}}/V$ , which may be expressed in terms of the pressure using the result

$$\beta f^{\text{ex}} = \rho \int_0^\rho \frac{d\rho'}{\rho'} \left( \frac{\beta P(\rho', \{x_i\})}{\rho'} - 1 \right). \quad (20)$$

Inserting equation (2) into equation (20) gives the following expansion for the finite-mixture case

$$\beta f^{\text{ex}} = \sum_{m=1}^{\infty} \frac{\rho^{m+1}}{m} B_{m+1}(\rho, \{x_i\}). \quad (21)$$

where the coefficients, when generalized to the polydisperse limit, become functions of  $(\rho, m_1, m_2, m_3)$ . Second, the (excess) chemical potential  $\mu^{\text{ex}}$  of a species with diameter  $R$  is a cubic polynomial of  $R$ . This is seen readily from the expression for the excess chemical potential of species  $i$ ,  $\mu_i^{\text{ex}} = \partial f^{\text{ex}} / \partial \rho_i$ , which for a finite mixture is, from equation (21),

$$\beta \mu_i^{\text{ex}} = \sum_{m=1}^{\infty} \frac{m+1}{m} \rho^m b_{m+1}. \quad (22)$$

The chemical potential in the polydisperse system is therefore

$$\beta \mu^{\text{ex}}(R) = \sum_{m=1}^{\infty} \frac{m+1}{m} \rho^m \langle b_{m+1}(R, R_1 \dots R_m) \rangle_{1\dots m}, \quad (23)$$

where the coefficients are obtained by integrating the partial coefficients  $b_{m+1}$  over the variables  $R_1 \dots R_m$ . It follows from equation (17) that the chemical potential is therefore a cubic function of the diameter  $R$ . For instance, to first order the excess chemical potential is, from equation (7),

$$\begin{aligned} \beta \mu^{\text{ex}}(R) &= 2\rho \langle b_2(R, R_i) \rangle_i \\ &= \frac{\pi \rho}{6} \{ R^3 + 3m_1 R^2 + 3m_2 R + m_3 \}. \end{aligned} \quad (24)$$

The virial expansion is, of course, rigorously convergent only for low densities. (The radius of convergence of the virial series is not known for polydisperse hard spheres but for uniform-sized spheres a truncated seven-

term virial series [2] for the pressure agrees within 10% with the data from computer simulation over the whole of the stable fluid phase. This suggests that the virial expansion may provide useful information over a wide range of densities up to freezing.) For high densities, approximate theories such as the scaled particle and Percus–Yevick predictions agree more closely with data from machine simulation [15]. These theories, although approximate, display the same symmetry as the more exact virial expansion described above. For instance, within scaled particle theory the pressure of a mixture of hard spheres may be shown readily to be an explicit function of just three diameter moments [19]. The same simplification is evident also in the approximate equation of state (EOS) obtained from the Percus–Yevick closure [20] for a system of polydisperse hard spheres. For instance, in the case of the ‘improved’ EOS obtained by Boublik [21] and Mansoori *et al.* [22] from an interpolation between the Percus–Yevick virial and compressibility equations, the pressure of a polydisperse fluid of volume fraction  $\phi$  is given explicitly as

$$\begin{aligned} \frac{\pi}{6} \beta P_{BM} &= \frac{1}{m_3} \left( \frac{\phi}{1-\phi} \right) + \frac{3m_1 m_2}{m_3^2} \left( \frac{\phi}{1-\phi} \right)^2 \\ &+ \left( \frac{m_2}{m_3} \right)^3 \left( \frac{\phi}{1-\phi} \right)^3 [3-\phi] \end{aligned} \quad (25)$$

in terms of the three diameter moments  $m_1$  through to  $m_3$ . Using this expression it is then straightforward to show that the excess chemical potential is a third-order polynomial in  $R$  of form

$$\begin{aligned} \beta \mu_{BM}^{\text{ex}}(R) &= R^3 \left\{ \frac{\pi}{6} \beta P_{BM} + \left( \frac{m_2}{m_3} \right)^3 \frac{\phi(\phi-2)}{1-\phi} \right. \\ &\quad \left. - 2 \left( \frac{m_2}{m_3} \right)^3 \ln(1-\phi) \right\} \\ &+ R^2 \left\{ 3 \left( \frac{m_1}{m_3} \right) \frac{\phi}{1-\phi} + 3 \left( \frac{m_2}{m_3} \right)^2 \frac{\phi}{(1-\phi)^2} \right. \\ &\quad \left. + 3 \left( \frac{m_2}{m_3} \right)^2 \ln(1-\phi) \right\} \\ &+ 3R \left( \frac{m_2}{m_3} \right) \frac{\phi}{1-\phi} - \ln(1-\phi). \end{aligned} \quad (26)$$

Motivated by these observations we shall assume in the remainder of this paper that first the excess properties of all hard sphere systems depend only upon  $\rho$  and  $m_1$  through to  $m_3$ , and that second  $\mu^{\text{ex}}$  is a polynomial of third order in  $R$ .

Table 1. Distribution function  $f(R)$ ,  $i$ th non-central moment  $m_i$ , and skewness  $v_3$  for log-normal, Schultz and triangular distributions. Here  $\bar{R}$  is the mean diameter and  $\sigma$  is the standard deviation in units of  $\bar{R}$ .

| $f(R)$  | $m_i$   | $v_3$                  |
|---|---|------------------------|
| $\frac{1 + \sigma^2}{\bar{R}[2\pi\ln(1 + \sigma^2)]^{1/2}} \exp\left\{\frac{-\ln^2[(1 + \sigma^2)^{3/2}(R/\bar{R})]}{2\ln(1 + \sigma^2)}\right\}$                         | $(1 + \sigma^2)^{i(i-1)/2}$   | $3\sigma^4 + \sigma^6$ |
| $\frac{1}{\bar{R}} \frac{(\sigma^{-2})^{\sigma^{-2}}}{\Gamma(\sigma^{-2})} \left(\frac{R}{\bar{R}}\right)^{\sigma^{-2}-1} \exp\left[-\sigma^{-2}\frac{R}{\bar{R}}\right]$ | $\prod_{k=0}^{i-1} (1 + k\sigma^2)$   | $2\sigma^4$            |
| $\frac{1}{6\sigma^2\bar{R}^2}(\sqrt{6}\sigma\bar{R} -  R - \bar{R} )$   | $\frac{1}{6\sigma^2(i+2)(i+1)} [(1 + \sqrt{6}\sigma)^{i+2} + (1 - \sqrt{6}\sigma)^{i+2} - 2]$ | 0                      |

### 3. Binary mapping

The small number of variables identified in hard sphere mixtures suggests a simple way to calculate the unknown properties of a polydisperse system. We look at an ‘equivalent’ system with equal values of  $\rho$  and  $m_1$  to  $m_3$  whose properties are known. From the discussion above, the excess properties of this simpler system must equal those of the unknown polydisperse mixture. Since a binary mixture has four degrees of freedom (the diameters and densities of each of the species) the simplest ‘equivalent’ system is a binary mixture. To establish the link between the two we shall find it more convenient to use the standardized central moments  $v_i$ :

$$v_i = \int dR f(R) \varepsilon^i, \quad (27)$$

where  $\varepsilon = (R - \bar{R})/\bar{R}$  is the fractional deviation of a particle’s diameter from its mean value  $\bar{R} = m_1$ . With this definition,  $v_2$  is simply the square of the conventionally defined polydispersity ( $v_2 = \sigma^2$ ) while  $v_3$  measures the skewness of the diameter distribution. Values of  $v_3$  for distributions which are of particular interest in colloid science are collected together in table 1. The relationship with the non-central moments  $m_i$  used above is

$$\begin{aligned} m_1 &= \bar{R}, \\ m_2 &= \bar{R}^2(1 + v_2), \\ m_3 &= \bar{R}^3(1 + 3v_2 + v_3). \end{aligned} \quad (28)$$

A polydisperse system may be described either in terms of the density  $\rho$  and the moments  $(m_1, m_2, m_3)$  or else in terms of  $\rho$ , the mean diameter  $\bar{R}$  and the central moments  $(v_2, v_3)$  whichever is more convenient. Using the central moment description it is easy to show that the binary mixture, defined in table 2, is ‘equivalent’ to a polydisperse system of density  $\rho$ , mean diameter  $\bar{R}$  and central moments  $(v_2, v_3)$  if the two parameters  $\delta$  and  $\Delta$

 Table 2. A binary mixture of hard spheres with a fixed value for the total number density of particles of  $\rho$  and a mean diameter of  $\bar{R}$ . The properties of the mixture are a function of the variables  $\delta$  and  $\Delta$ .

|                         | Species 1                                   | Species 2                                   |
|-------------------------|---|---|
| Number density $\rho_i$ | $\rho \frac{(1 - \Delta)}{2}$               | $\rho \frac{(1 + \Delta)}{2}$               |
| Diameter $R_i$          | $\bar{R} \frac{(1 + \delta)}{(1 - \Delta)}$ | $\bar{R} \frac{(1 - \delta)}{(1 + \Delta)}$ |

are chosen so that

$$\begin{aligned} \delta &= \frac{2v_2^2 - v_3}{(4v_2^3 + v_3^2)^{1/2}}, \\ \Delta &= \frac{v_3}{(4v_2^3 + v_3^2)^{1/2}}. \end{aligned} \quad (29)$$

The two systems are then statistically equivalent, in the sense that both have the same set of first moments and so, following the arguments of section 2, identical excess thermodynamic properties. With this formalism the pressure of a polydisperse mixture,  $P_p$  is equal to that of an equivalent binary system  $P_b$  of diameter ratio  $\alpha$  and composition  $x_1$  (the fraction of large spheres):

$$\begin{aligned} &\beta \bar{R}^3 P_p(\rho \bar{R}^3, v_2, v_3) \\ &= \beta \bar{R}^3 P_b\left(\rho \bar{R}^3, \alpha = \frac{(1 - \delta)(1 - \Delta)}{(1 + \delta)(1 + \Delta)}, x_1 = \frac{1 - \Delta}{2}\right). \end{aligned} \quad (30)$$

This identity is, of course, exact by construction if the equation of state is a function only of the first three diameter moments. This simplification, as we have seen, is exact for low densities, and furthermore is displayed by many of the successful fluid equations of states which describe hard spheres at high densities. In

the following section we shall assume furthermore that this identity is also valid for crystalline phases.

#### 4. Polydisperse solid

The starting point for any calculation of phase equilibria is knowledge of the pressure and the chemical potentials. If the excess free energy is solely a function of the central moments  $v_i$  then the thermodynamic conditions of equilibrium between two phases  $A$  and  $B$  may be expressed concisely in terms of the moment chemical potentials [9, 10],  $\mu_i^{\text{ex}} = \partial f^{\text{ex}} / \partial p v_i$ , as

$$\begin{aligned} \mu_i^{\text{ex}}(A) &= \mu_i^{\text{ex}}(B) \text{ for } i = 0, 1, 2, \text{ etc.} \\ P(A) &= P(B). \end{aligned} \quad (31)$$

The moment potentials are physically just the coefficients of the polynomial describing the  $\varepsilon$  dependence of the conventional particle potential, as is seen readily from the expansion

$$\mu^{\text{ex}}(R) = \frac{\delta f^{\text{ex}}}{\delta p f(R)} = \sum_i \frac{\partial f^{\text{ex}}}{\partial p v_i} \frac{\delta v_i}{\delta f(R)} = \sum_i \mu_i^{\text{ex}} \varepsilon^i. \quad (32)$$

To calculate the pressure and moment potentials of the polydisperse crystal we look at the binary substitutionally disordered crystal which is isostructural with the polydisperse crystal. It is well known that a bi-disperse hard sphere system of very different sizes phase separates in the solid state. Computer simulation [23] and density functional calculations [24] have suggested that only for a diameter ratio above a limiting ratio  $\alpha^* \sim 0.82$  is the substitutionally disordered crystal stable. Consequently the mapping described in section 3 will remain valid only for sufficiently narrow distributions such that

$$\frac{(1-\delta)(1-\Delta)}{(1+\delta)(1+\Delta)} > \alpha^*. \quad (33)$$

For a Schultz distribution, for instance, this condition is satisfied by distributions with normalized widths  $v_2^{*1/2} = 0.10$  or less. Presumably crystalline phases with broader diameter distributions will be mechanically unstable. For a sufficiently narrow distribution ( $v_2 < v_2^*$ ) the pressure of the polydisperse crystal  $P_p$  may then be equated to the pressure of the equivalent binary substitutional crystal  $P_b$ , from equation (30). For further analysis clearly it is desirable to represent the polydisperse pressure by an analytical function of  $\rho$ ,  $v_2$  and  $v_3$ . In the limiting situations where either  $v_2$  or  $\rho \rightarrow 0$  the dimensionless polydisperse pressure  $\beta \bar{R}^3 P_p$  must converge to the well known monodisperse limit  $\beta \bar{R}^3 P_{\text{mono}}$  (for which we use the hard sphere crystal EOS described by Young and Alder [25]). Therefore we have used the following general form for the poly-

disperse pressure:

$$\begin{aligned} \beta \bar{R}^3 P_p(\rho \bar{R}^3, v_2, v_3) &= \beta \bar{R}^3 P_{\text{mono}}(\rho \bar{R}^3) \\ &+ \sum_{i,j,k} C_{i,j,k} (\rho \bar{R}^3)^i (10^4 v_2)^j (v_3/v_2^2)^k, \end{aligned} \quad (34)$$

where we take  $i, j \geq 1$  and  $k \geq 0$ . This functional form was fitted to 2499 solid state pressures, calculated from equation (30) and the simulation data of Kranendonk and Frenkel for the bi-disperse crystal [26], on an equally spaced grid of values

$$\begin{aligned} 1.0 &\leq \rho \bar{R}^3 \leq 1.2, \\ 0.0 &\leq (v_2)^{1/2} \leq 0.09, \\ -3 &\leq v_3/v_2^2 \leq 3, \end{aligned} \quad (35)$$

which span the region where a polydisperse crystal is expected to be mechanically stable [4, 5]. The fitted coefficients  $C_{i,j,k}$  are given in table 3. Since the functions to which we fit are not orthogonal the coefficients are strongly correlated. Consequently we have quoted the coefficients with a large number of digits to minimize the effects of round-off errors. The maximum absolute error in the fit to  $\beta \bar{R}^3 P$  is in the region of 0.005.

To evaluate the moment chemical potentials we note that, from the Widom insertion principle [27], the chemical potential in a binary crystal  $\mu_b^{\text{ex}}$  may be regarded,

Table 3. Coefficients  $C_{i,j,k}$  for the polynomial fit defined in equation (34) for the pressure of the polydisperse crystal.

| $i$ | $j$ | $k$ | $C_{i,j,k}$            |
|-----|-----|-----|------------------------|
| 1   | 1   | 0   | 2.387 574 730 54E+00   |
| 2   | 1   | 0   | - 3.245 594 701 55E+00 |
| 3   | 1   | 0   | - 8.378 147 624 76E-01 |
| 4   | 1   | 0   | 1.739 954 321 08E+00   |
| 1   | 2   | 0   | 1.694 840 738 32E-04   |
| 2   | 2   | 0   | - 1.408 827 614 92E-03 |
| 4   | 2   | 0   | 1.329 270 610 91E-03   |
| 2   | 3   | 0   | - 6.506 832 296 54E-08 |
| 4   | 3   | 0   | 4.425 767 430 97E-07   |
| 1   | 2   | 1   | - 6.146 520 969 27E-04 |
| 2   | 2   | 1   | 7.434 642 398 15E-04   |
| 4   | 2   | 1   | - 1.276 976 547 31E-04 |
| 2   | 3   | 1   | 1.920 875 038 81E-07   |
| 4   | 3   | 1   | - 8.288 283 721 38E-08 |
| 4   | 1   | 2   | - 1.041 204 072 15E-06 |
| 1   | 2   | 2   | - 1.197 462 451 84E-05 |
| 2   | 2   | 2   | 1.878 247 293 88E-05   |
| 4   | 2   | 2   | - 6.918 060 118 77E-06 |
| 1   | 3   | 2   | 6.220 680 202 96E-08   |
| 2   | 3   | 2   | - 6.536 346 104 12E-08 |

formally at least, as a continuous function of  $R$ . Consequently the size-dependent chemical potential must have the functional form

$$\beta\mu_b^{\text{ex}}(R) = b_0 + b_1R + b_2R^2 + b_3R^3, \quad (36)$$

where the chemical potential is defined in terms of the probability  $W(R)$  for inserting an arbitrary size test sphere into the crystal from the expression  $\beta\mu_b^{\text{ex}}(R) = -\ln W(R)$ . From the discussion above, it follows that the probability  $W(R)$  should be equal at *any* value of  $R$  for the polydisperse and the *equivalent* binary crystal. With this identification equation (36) may be simplified further by using the known [28] exact small and large  $R$  limits for  $\mu^{\text{ex}}(R)$ . These constraints fix two of the four unknown coefficients in equation (36),

$$\begin{aligned} b_0 &= -\ln(1 - \phi), \\ b_3 &= \frac{\pi}{6}\beta P. \end{aligned} \quad (37)$$

The remaining unknown coefficients ( $b_1$  and  $b_2$ ) in the polynomial for  $\mu^{\text{ex}}(R)$  (equation (36)) may be determined by looking at particles with sizes equal to those of the two species in the binary crystal, for which the chemical potentials are known from the data of Kranendonk and Frenkel [26]. Values for  $b_1$  and  $b_2$  together with equation (37) fix the size dependence of the polydisperse potential as a function of the density  $\rho R^3$  and the two central moments  $v_2$  and  $v_3$ . We have determined the central moment chemical potentials  $\mu_i^{\text{ex}}$  (defined in equation (32)) using the simulation data of Kranendonk and Frenkel [26] as input and fitted the results to the following expressions:

$$\begin{aligned} \beta\mu_0^{\text{ex}}(\rho\bar{R}^3, v_2, v_3) &= \beta\mu_{\text{mono}}^{\text{ex}}(\rho\bar{R}^3) \\ &+ \sum_{i,j,k} D_{i,j,k} (\rho\bar{R}^3)^i (10^4 v_2)^j (v_3/v_2^2)^k, \\ \beta\mu_1^{\text{ex}}(\rho\bar{R}^3, v_2, v_3) &= \sum_{i,j,k} G_{i,j,k} (\rho\bar{R}^3)^i (10^4 v_2)^j (v_3/v_2^2)^k, \\ \beta\mu_2^{\text{ex}}(\rho\bar{R}^3, v_2, v_3) &= \sum_{i,j,k} H_{i,j,k} (\rho\bar{R}^3)^i (10^4 v_2)^j (v_3/v_2^2)^k, \end{aligned} \quad (38)$$

where  $\mu_{\text{mono}}^{\text{ex}}$  is the excess chemical potential of the monodisperse hard sphere crystal (obtained from [25]). The fitted coefficients are given in tables 4–6. The third moment potential  $\mu_3^{\text{ex}}$  is given in terms of the expression for  $b_3$  (equation (37)) as

$$\beta\mu_3^{\text{ex}} = \frac{\pi}{6}\beta\bar{R}^3 P_p. \quad (39)$$

where  $P_p$  is the polydisperse pressure.

In figure 2 we show the effect of  $\sigma$  on the pressure calculated for a polydisperse system. Two features are striking. First, the effect of increasing polydispersity is

Table 4. Coefficients  $D_{i,j,k}$  for the polynomial fit defined in equation (38) for the zero order central moment  $\beta\mu_0^{\text{ex}}$  of the polydisperse crystal.

| $i$ | $j$ | $k$ | $D_{i,j,k}$           |
|-----|-----|-----|-----------------------|
| 1   | 1   | 0   | 4.972 795 952E + 00   |
| 2   | 1   | 0   | - 1.115 877 719E + 01 |
| 3   | 1   | 0   | 7.254 490 173E + 00   |
| 4   | 1   | 0   | - 1.020 223 113E + 00 |
| 2   | 2   | 0   | - 2.915 092 900E - 03 |
| 3   | 2   | 0   | 3.550 802 611E - 03   |
| 4   | 2   | 0   | - 5.512 759 696E - 04 |
| 2   | 3   | 0   | - 1.310 283 588E - 07 |
| 3   | 3   | 0   | 4.750 313 909E - 07   |
| 2   | 1   | 1   | - 2.613 788 868E - 06 |
| 1   | 2   | 1   | - 1.029 201 075E - 03 |
| 2   | 2   | 1   | 1.801 003 695E - 03   |
| 3   | 2   | 1   | - 8.635 348 552E - 04 |
| 4   | 2   | 1   | 9.387 749 902E - 05   |
| 2   | 3   | 1   | 3.747 694 880E - 07   |
| 3   | 3   | 1   | - 2.749 597 974E - 07 |
| 1   | 2   | 2   | - 1.392 407 811E - 05 |
| 2   | 2   | 2   | 3.011 842 029E - 05   |
| 3   | 2   | 2   | - 1.633 843 239E - 05 |
| 1   | 3   | 2   | 5.966 026 102E - 08   |
| 2   | 3   | 2   | - 6.148 884 367E - 08 |

Table 5. Coefficients  $G_{i,j,k}$  for the polynomial fit defined in equation (38) for the first central moment  $\beta\mu_1^{\text{ex}}$  of the polydisperse crystal.

| $i$ | $j$ | $k$ | $G_{i,j,k}$             |
|-----|-----|-----|-------------------------|
| 0   | 0   | 0   | - 1.797 103 3849E + 03  |
| 1   | 0   | 0   | 5.320 803 395 5E + 03   |
| 2   | 0   | 0   | - 5.232 166 877 0E + 03 |
| 3   | 0   | 0   | 1.739 132 353 2E + 03   |
| 0   | 1   | 0   | 1.979 820 767 6E + 00   |
| 1   | 1   | 0   | 2.164 916 510 5E + 00   |
| 2   | 1   | 0   | - 1.077 331 676 6E + 01 |
| 3   | 1   | 0   | 6.719 731 981 8E + 00   |
| 1   | 2   | 0   | - 1.214 058 780 0E - 03 |
| 2   | 2   | 0   | - 1.450 220 359 8E - 03 |
| 3   | 2   | 0   | 3.116 085 953 8E - 03   |
| 1   | 3   | 0   | 7.987 846 102 9E - 07   |
| 0   | 1   | 1   | - 1.075 139 058 0E + 00 |
| 1   | 1   | 1   | 3.343 026 977 8E + 00   |
| 2   | 1   | 1   | - 3.493 330 035 7E + 00 |
| 3   | 1   | 1   | 1.229 479 231 7E + 00   |
| 1   | 2   | 1   | - 1.300 693 699 8E - 03 |
| 2   | 2   | 1   | 1.278 460 548 9E - 03   |
| 1   | 3   | 1   | 3.035 809 994 7E - 07   |
| 0   | 2   | 2   | 7.132 580 982 5E - 04   |
| 1   | 2   | 2   | - 1.897 021 263 2E - 03 |
| 2   | 2   | 2   | 1.655 220 311 4E - 03   |
| 3   | 2   | 2   | - 4.717 358 524 2E - 04 |
| 1   | 3   | 2   | - 4.034 913 604 2E - 08 |

Table 6. Coefficients  $H_{i,j,k}$  for the polynomial fit defined in equation (38) for the second central moment  $\beta\mu_2^{\text{ex}}$  of the polydisperse crystal.

| $i$ | $j$ | $k$ | $H_{i,j,k}$           |
|-----|-----|-----|-----------------------|
| 0   | 0   | 0   | - 1.592 587 102E + 03 |
| 1   | 0   | 0   | 4.708 423 777E + 03   |
| 2   | 0   | 0   | - 4.632 828 411E + 03 |
| 3   | 0   | 0   | 1.538 993 488E + 03   |
| 0   | 1   | 0   | - 9.746 903 189E - 01 |
| 1   | 1   | 0   | 9.090 570 281E + 00   |
| 2   | 1   | 0   | - 1.568 524 068E + 01 |
| 3   | 1   | 0   | 7.635 577 376E + 00   |
| 1   | 2   | 0   | 5.858 690 060E - 04   |
| 2   | 2   | 0   | - 3.894 632 807E - 03 |
| 3   | 2   | 0   | 3.724 822 978E - 03   |
| 1   | 3   | 0   | 6.385 702 771E - 07   |
| 0   | 1   | 1   | - 1.060 209 846E + 00 |
| 1   | 1   | 1   | 3.306 204 721E + 00   |
| 2   | 1   | 1   | - 3.462 990 053E + 00 |
| 3   | 1   | 1   | 1.221 108 119E + 00   |
| 1   | 2   | 1   | - 8.742 177 575E - 04 |
| 2   | 2   | 1   | 5.538 426 804E - 04   |
| 3   | 2   | 1   | 2.942 647 615E - 04   |
| 1   | 3   | 1   | 2.783 232 803E - 07   |
| 0   | 2   | 2   | 7.099 636 534E - 04   |
| 1   | 2   | 2   | - 1.887 268 984E - 03 |
| 2   | 2   | 2   | 1.641 798 433E - 03   |
| 3   | 2   | 2   | - 4.649 114 167E - 04 |
| 1   | 3   | 2   | - 3.703 404 903E - 08 |

very different for a crystalline as compared with a fluid system. For a crystal, increasing  $\sigma$  raises the pressure, while in a fluid the converse is true. Second, the pressure of a polydisperse crystal is very sensitive to even a relatively moderate level of polydispersity, whereas by contrast the pressure of a fluid phase is fairly insensitive to  $\sigma$ . Figure 3 shows that similar trends are also seen in the dependence of the moment chemical potentials on  $\sigma$ .

### 5. Conclusions

We have investigated the virial expansion of a continuous polydisperse system of hard spheres. Our analysis shows that the polydisperse virial coefficients are a function of the total hard sphere number density and the first three moments,  $m_1$  through to  $m_3$ , of the normalized diameter distribution. This observation has two important consequences. First of all, it demonstrates that, at least for low densities, the excess free energy (above that of the polydisperse ideal gas) is purely a function of a *finite* set of moments. Second, the excess portion of the particle chemical potential is a third-order polynomial of the particle diameter.

In order to reduce the strictly infinite number of equations for polydisperse coexistence to a finite set, previous

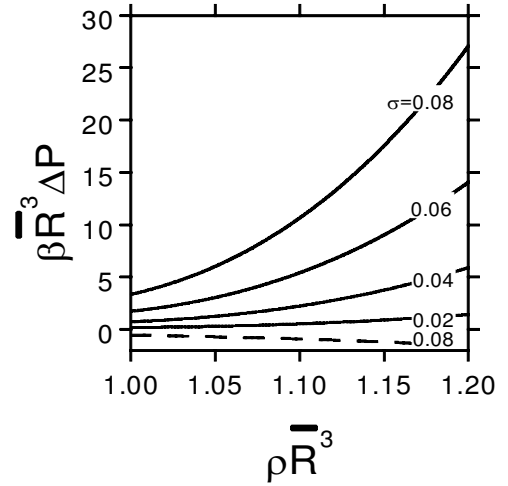


Figure 2. Variation in pressure  $\Delta P = P_p - P_{\text{mono}}$  with density for a polydisperse crystal for different levels of polydispersity  $\sigma$ . The reduced pressure  $\bar{\rho}R^3 \Delta P$  is calculated from equation (34). The degree of skewness is fixed at  $v_3 = 2\sigma^4$ . The dashed line shows, for comparison, the pressure of the polydisperse fluid ( $\sigma = 0.08$ ) calculated from the BMCSL equation of state [21, 22].

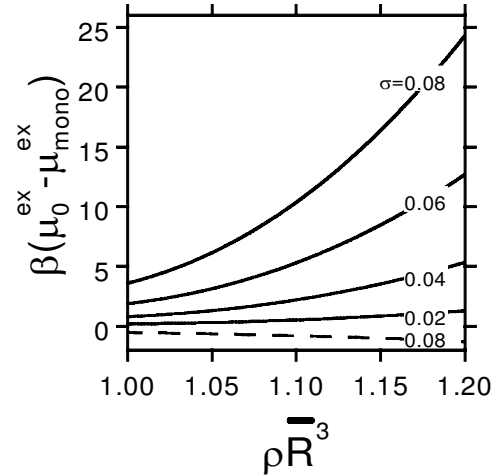


Figure 3. Effect of density  $\bar{\rho}R^3$  on the zero order moment potential  $\beta(\mu_0^{\text{ex}} - \mu_{\text{mono}}^{\text{ex}})$  for different levels of polydispersity  $\sigma$ . The solid lines depict results for the crystalline phase while the dashed line shows, for comparison, the results for the fluid phase. The curves are calculated from equations (38) and (A 1).

authors [9, 10] have *assumed* that  $F^{\text{ex}}$  can be approximated by a function of a finite number of moments. The current analysis demonstrates that the ‘finite moment’ assumption is exact for 3D hard spheres, at least in the region where the virial expansion is convergent (see text following equation (24)). Indeed, since the same simplification is apparent also in both the scaled particle and Percus–Yevick predictions, the finite moment approximation is probably a reasonable approximation at all densities.



One of the most interesting features of the prediction that  $F^{\text{ex}}$  depends on a small number of variables is that it allows the properties of a polydisperse system to be ‘mapped’ onto those of a much simpler binary mixture. Using this approach we have developed a physically reasonable model of a slightly polydisperse crystal. In the current paper we have extended our previous work [11] to include a description of the effect of both the width and the skewness of the diameter distribution. Furthermore, we present approximate analytical expressions for the pressure and moment potentials.

Finally, we stress that although we believe the microscopic foundation for the current model is reasonable it is undoubtedly somewhat arbitrary. For instance, it is difficult to believe that all of the distortion introduced into a crystalline lattice by a continuous range of different sized spheres can be reproduced by considering just two different sizes. However, we hope that the current results will stimulate further investigations into the structure of polydisperse crystals.

#### Appendix. Central moment potentials for the polydisperse fluid

The central moment chemical potentials  $\mu_i^{\text{ex}}$  for the BMCSL polydisperse fluid [21, 22] are given by the expressions:

$$\begin{aligned} \beta\mu_0^{\text{ex}} &= \frac{\pi}{6}\beta P_{BM}\bar{R}^3 - (2\bar{m}_2 + 1)(\bar{m}_2 - 1)^2 \ln(1 - \phi) \\ &\quad + 3(\bar{m}_1 + \bar{m}_2)\frac{\phi}{1 - \phi} + 3\bar{m}_2^2\frac{\phi}{(1 - \phi)^2} \\ &\quad + \bar{m}_2^3\frac{\phi(\phi - 2)}{1 - \phi}, \\ \beta\mu_1^{\text{ex}} &= \frac{\pi}{2}\beta P_{BM}\bar{R}^3 - 6(\bar{m}_2^3 - \bar{m}_2)^2 \ln(1 - \phi) \\ &\quad + 3(2\bar{m}_1 + \bar{m}_2)\frac{\phi}{1 - \phi} + 6\bar{m}_2^2\frac{\phi}{(1 - \phi)^2} \\ &\quad + 3\bar{m}_2^3\frac{\phi(\phi - 2)}{1 - \phi}, \\ \beta\mu_2^{\text{ex}} &= \frac{\pi}{2}\beta P_{BM}\bar{R}^3 - (6\bar{m}_2^3 - 3\bar{m}_2^2) \ln(1 - \phi) \\ &\quad + 3\bar{m}_1\frac{\phi}{1 - \phi} + 3\bar{m}_2^2\frac{\phi}{(1 - \phi)^2} + 3\bar{m}_2^3\frac{\phi(\phi - 2)}{1 - \phi}, \\ \beta\mu_3^{\text{ex}} &= \frac{\pi}{6}\beta P_{BM}\bar{R}^3 - 2\bar{m}_2^3 \ln(1 - \phi) \\ &\quad + \bar{m}_2^3\frac{\phi(\phi - 2)}{1 - \phi}, \end{aligned} \quad (\text{A } 1)$$

where  $\bar{m}_i$  is the moment ratio

$$\bar{m}_i = \frac{m_i}{m_3}\bar{R}^{3-i}. \quad (\text{A } 2)$$

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