

# Free-volume approximations for predicting the phase behaviour of asymmetric hard-sphere mixtures

Henk N W Lekkerkerker<sup>1</sup> and S Martijn Oversteegen

Van 't Hoff Laboratory for Physical and Colloid Chemistry, Debye Research Institute,  
Utrecht University, PO Box 80051, 3508 TB Utrecht, The Netherlands

E-mail: h.n.w.lekkerkerker@chem.uu.nl

Received 2 May 2002

Published 27 September 2002

Online at [stacks.iop.org/JPhysCM/14/9317](http://stacks.iop.org/JPhysCM/14/9317)

## Abstract

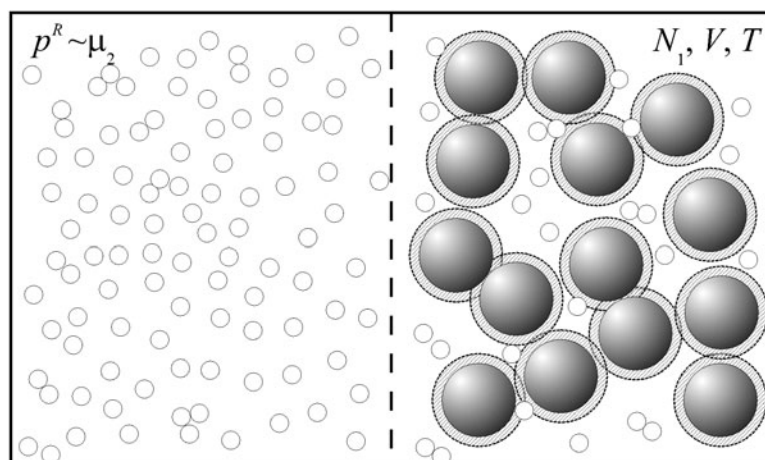
Two different levels of the free-volume approximation for the calculation of the phase diagram of an asymmetric hard-sphere mixture are compared to direct simulations of the phase behaviour. The mean-field-level free-volume approach, where only the statistically pre-averaged free volume is accounted for, is already in satisfactory agreement with the simulation results. Taking correlations into account within the free-volume approach improves the agreement with the solid branch of the phase diagram but, remarkably, this version performs somewhat worse for the fluid branch.

## 1. Introduction

Jean-Pierre Hansen has made wide-ranging, significant and lasting contributions to the theory of the liquid state. His timely book *Theory of Simple Liquids* [1] written together with Ian McDonald was an instant classic. With its authority and range of topics treated, it has been of great service both to newcomers entering the field of liquid state theory as well as to experienced researchers seeking a comprehensive and critical coverage of the topic.

The equilibrium properties of colloidal suspensions may be treated in the same way as in simple liquids by considering the colloidal particles as 'supramolecules' [2]. Onsager [3] showed that in applying statistical mechanics to such mesoscopic particles one must use the potential of the average forces that act between these particles. This paper is devoted to a few remarks on the use of this so-called potential of mean force in a problem that was first raised and treated by Biben and Hansen [4, 5], i.e., the phase behaviour of asymmetric binary hard-sphere mixtures. Until 1991 it was generally believed that hard-sphere mixtures are stable with respect to phase separation into two fluid phases. Indeed, at least within the Percus–Yevick closure of the Ornstein–Zernike equation and using the compressibility theorem to calculate the thermodynamic quantities, this is true [6, 7]. However, Biben and Hansen [4, 5] showed

<sup>1</sup> Author to whom any correspondence should be addressed.



**Figure 1.** A schematic representation of the essence of the free-volume theory. The small spheres in the reservoir on the left, with a pressure  $p^R$  or, equivalently, chemical potential  $\mu_2$ , are brought into equilibrium with the  $N_1$  large colloids in a volume  $V$  at temperature  $T$  on the right. The centres of mass of the small particles  $\bar{r}^{N_2}$  can only access the 'white' areas of the system, the so-called free volume  $V_{\text{free}}$ .

that starting from the Rogers–Young closure [8], which is known to be more accurate for hard spheres than the Percus–Yevick closure, such mixtures for diameter ratios larger than 5 do seem to become unstable at sufficiently high volume fractions. A direct experimental test of the prediction of Biben and Hansen is obviously not an easy task as hard-sphere atoms do not exist in reality. However, one can prepare (almost) monodisperse spherical colloidal particles whose short-ranged harshly repulsive interparticle forces closely approximate that of hard spheres [9, 10]. As indicated above, Onsager [3] has shown that the thermodynamic properties of such suspensions are the same as those of the hypothetical hard-sphere atomic system. A detailed discussion of colloid–atom analogies has been given by Pusey [11]. Over the last 10 years a number of experiments have been done on asymmetric binary mixtures of colloidal particles with diameter ratio 5 or higher [12–17], and they support the existence of demixing. However, these experiments have made it clear that such systems do not separate into two fluid phases but into a fluid and a crystal phase [15–17].

This was first suggested by Lekkerkerker and Stroobants [18] and worked out in more detail by Poon and Warren [19] guided by work on the phase behaviour of colloidal polymer mixtures [20]. That work was based on a mean-field-level free-volume approximation of the potential of mean force. In this paper we consider free-volume approximations of the potential of mean force for an asymmetric hard-sphere mixture and compare the results for the phase behaviour to extensive computer simulations [21–23].

## 2. Free-volume approximations of the potential of mean force

A convenient way to study the phase behaviour of asymmetric binary hard-sphere mixtures is to use the semi-grand potential  $\Omega(N_1, V, T, \mu_2)$ , where  $N_1$  denotes the number of large spheres,  $V$  the volume,  $T$  the temperature, and  $\mu_2$  the chemical potential of the small particles (see figure 1). The semi-grand potential  $\Omega$  can be obtained from the semi-grand canonical

partition function  $\Xi$ :

$$\Omega = -k_B T \ln \Xi \quad (1)$$

which can be written as

$$\Xi = \sum_{N_2=0}^{N_2^{\max}} z_2^{N_2} Q_{N_1 N_2}. \quad (2)$$

Here  $z_2 = e^{\mu_2/k_B T}$  is the activity of the small spheres and  $Q_{N_1 N_2}$  is the canonical partition function of  $N_1$  large spheres and  $N_2$  small spheres:

$$Q_{N_1 N_2} = \frac{1}{\Lambda^{3N_1} N_1! \Lambda^{3N_2} N_2!} \int e^{-[U_{N_1} + U_{N_2} + \psi]/k_B T} d\vec{R}^{N_1} d\vec{r}^{N_2}. \quad (3)$$

In the above equation  $U_{N_1}$  is the interaction potential between  $N_1$  large hard spheres,  $U_{N_2}$  is the interaction potential between the  $N_2$  small hard spheres, and  $\psi$  is the interaction potential between  $N_1$  large hard spheres and  $N_2$  small hard spheres. Onsager [3] has shown that the semi-grand canonical partition function can formally be written as

$$\Xi = \frac{1}{\Lambda^{3N_1} N_1!} \int e^{-[U_{N_1} + \omega]/k_B T} d\vec{R}^{N_1} \quad (4)$$

where  $\omega$  is the potential of mean force. To derive an exact expression for  $\omega$  is in general impossible but useful approximations may be obtained. For the problem at hand, i.e., a mixture of large and small hard spheres, the free-volume approximation yields a useful expression for  $\omega$ . The free-volume approximation is based on realizing that the factor  $e^{-\psi/k_B T}$  in (3) limits the integration over  $\vec{r}_i$  ( $i = 1, 2, \dots, N_2$ ) to the free volume  $V_{\text{free}}(\vec{R}^{N_1})$  (see figure 1). Hence, it is a reasonable assumption to write

$$\frac{1}{\Lambda^{3N_2} N_2!} \int e^{-[U_{N_2} + \psi]/k_B T} d\vec{r}^{N_2} = Q_{N_2}(V_{\text{free}}). \quad (5)$$

Note that (5) is not an exact relation, as it does not take into account the correlations created among the small particles by the presence of the large particles. Substituting the approximate result (5) in (3) and using this in turn in (2) we obtain

$$\Xi = \sum_{N_2=0}^{N_2^{\max}} \frac{z_2^{N_2}}{\Lambda^{3N_1} N_1!} \int Q_{N_2}(V_{\text{free}}) e^{-U_{N_1}/k_B T} d\vec{R}^{N_1} = \frac{1}{\Lambda^{3N_1} N_1!} \int e^{p^R V_{\text{free}}/k_B T} e^{-U_{N_1}/k_B T} d\vec{R}^{N_1} \quad (6)$$

where  $p^R$  is the pressure of the small particles in the reservoir with which the system is in equilibrium (see figure 1). Comparing (4) and (6) we see that in the free-volume approximation the potential of mean force is given by

$$\omega = -p^R V_{\text{free}}. \quad (7)$$

This approximate result could have been written down immediately by realizing that the potential of mean force is equal to the grand potential of the small particles in a fixed configuration of the large particles. Equation (6) can be written as

$$\Xi = Q_{N_1} \langle e^{p^R V_{\text{free}}/k_B T} \rangle_0 \quad (8)$$

where  $\langle \dots \rangle_0$  denotes an average over the canonical distribution of the large particles. From (8) it follows that

$$\Omega = F_0 - k_B T \ln \langle e^{p^R V_{\text{free}}/k_B T} \rangle_0 \quad (9)$$

where  $F_0$  is the Helmholtz free energy of the pure system of large hard spheres. An even simpler expression for the semi-grand potential is obtained by replacing in (9) the average of the

exponent by the exponent of the average (which is equivalent to a mean-field approximation). This eventually leads to

$$\Omega = F_0 - p^R \langle V_{\text{free}} \rangle_0. \quad (10)$$

### 3. Test of the approximations

For a one-dimensional mixture of hard rods of two different lengths, analytic expressions for the semi-grand potential can be obtained both for the exact case as well as for the two levels of the free-volume approximation, i.e. with correlations and mean field [24, 25]. The mean-field-level free-volume approach, where only the statistically pre-averaged free volume of the larger rods is accounted for (see (10)), yields a spurious phase transition. Taking correlations into account (see (9)) not only gives better quantitative results, it also shows qualitatively right physics, i.e., no phase transition. Although the phase separation found in the mean-field approximation cannot be attained in one dimension, it is nevertheless of interest because it shows the propensity towards phase separation in mixtures of hard particles of different sizes at high enough densities. As we will see, the phase separation is realized in three dimensions.

The semi-grand potential for a mixture of hard spheres cannot be calculated exactly, but extensive direct simulations of the phase behaviour of binary hard-sphere mixtures have been carried out by Dijkstra *et al* [22, 23]. In figure 2 the symbols give their results for a diameter ratio  $\sigma_2/\sigma_1 = 0.1$ .

The free-volume approximation with correlation (9) can also be obtained from simulation results in the literature [26] even although they are obtained for a model colloid–polymer mixture. For a diameter ratio  $\sigma_2/\sigma_1 < (\frac{2}{3}\sqrt{3} - 1) \approx 0.1547$  there are no multiple-overlap regions of excluded volume. Hence, the potential of mean force (7) takes the following simple form (see figure 1):

$$\omega = -p^R V_{\text{free}} = -p^R \left[ V - N_1 \frac{\pi}{6} (\sigma_1 + \sigma_2)^3 + \sum_{i < j}^{N_2} V_{\text{overlap}}(R_{ij}) \right] \quad (11)$$

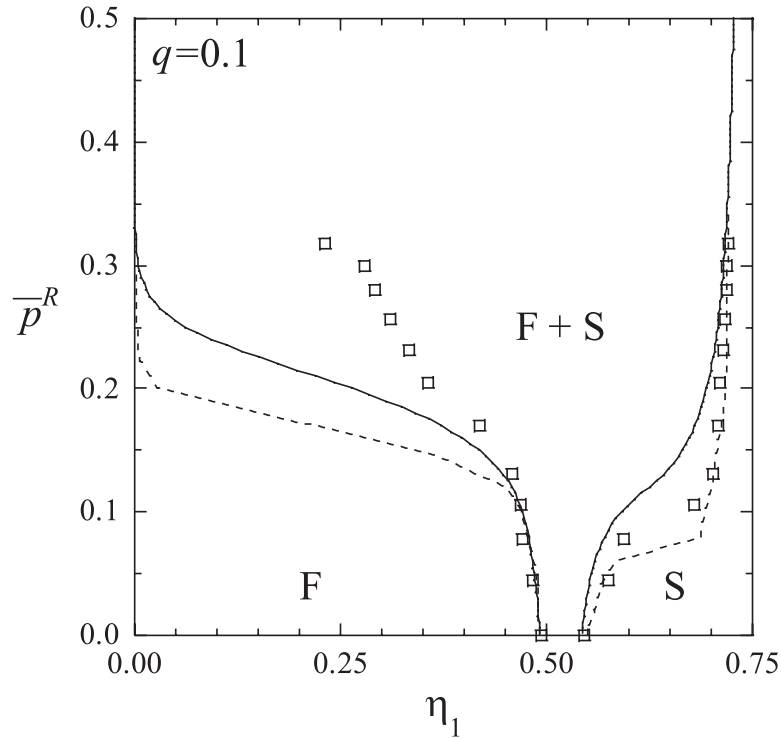
where

$$V_{\text{overlap}}(R_{ij}) = \begin{cases} \frac{\pi}{12} (\sigma_1 + \sigma_2 - R_{ij})^2 (2\sigma_1 + 2\sigma_2 + R_{ij}) & \sigma_1 < R_{ij} < \sigma_1 + \sigma_2 \\ 0 & R_{ij} \geq \sigma_1 + \sigma_2. \end{cases} \quad (12)$$

Here,  $R_{ij}$  is the distance between the centres of mass of two large particles  $i$  and  $j$ .

Computer simulations were carried out for the case of a colloid–polymer mixture where the polymer is modelled as a penetrable hard sphere, the Asakura–Oosawa–Vrij model [27, 28]. In that case  $p^R = \rho_p^R k_B T$  where  $\rho_p^R$  is the number density of polymers in the reservoir. In fact for  $\sigma_p/\sigma_1 < (\frac{2}{3}\sqrt{3} - 1)$  the potential of mean force given by (11) is exact for this model, whereas it is still an approximation for the case of binary mixture of hard spheres treated here. Hence, we can take the simulation results for the model colloid–polymer mixture, and on replacing  $\rho_p^R k_B T$  by  $p^R$  the results apply to the binary hard-sphere case within the free-volume approximation including correlations in the free volume. The results are given in figure 2 by the dotted curve.

We finally turn to the mean-field level of the free-volume approximation. In that case the grand potential can be calculated by using accurate, albeit still approximate, expressions for the Helmholtz free energy  $F_0$  of the pure system of large hard spheres in both the fluid and solid phases and the statistically pre-averaged free volume  $\langle V_{\text{free}} \rangle_0$  [18]. To calculate the phase



**Figure 2.** The phase diagram of an asymmetric mixture of spheres with a diameter ratio  $\frac{\sigma_2}{\sigma_1} = 0.1$  as a function of the reduced reservoir pressure  $\bar{p}^R = \frac{p^R}{k_B T} \frac{\pi}{6} \sigma_1^3$ . The symbols represent the (rescaled) simulation results [22, 23], the dotted curve [26] the free-volume approximation that accounts for the correlations in the free volume, and the solid curve the mean-field free-volume approximation.

diagram we need the chemical potential  $\mu_1$  and the pressure  $p$  which can be found from

$$\mu_1 = \left( \frac{\partial \Omega}{\partial N_1} \right)_{V, T, \mu_2} = \mu_1^o - p^R \left( \frac{d\alpha}{d\rho_1} \right) \quad (13)$$

$$p = - \left( \frac{\partial \Omega}{\partial V} \right)_{N_1, T, \mu_2} = p^o - p^R \left( \alpha - \rho_1 \frac{d\alpha}{d\rho_1} \right). \quad (14)$$

Here  $\mu_1^o$  and  $p^o$  are the chemical potential and pressure of the pure hard-sphere system, respectively, and

$$\alpha = \frac{\langle V_{\text{free}} \rangle_0}{V}$$

is the free-volume fraction. An approximate expression for  $\alpha$  can be obtained from the scaled particle theory [18]. The phase diagram is now obtained by equating the chemical potentials and pressure for different values of  $p^R$ . The results are represented in figure 2 by the solid curve.

The version of the free-volume theory that accounts for correlations performs better for the solid branch but, remarkably, the mean-field version performs better for the fluid branch of the phase diagram. This may be due to a fortuitous cancellation of errors. On the whole, the agreement of both free-volume theories with direct simulation of the phase behaviour of

binary hard-sphere mixtures is quite satisfactory for low values,  $\bar{p}^R = \frac{p^R}{k_B T} \frac{\pi}{6} \sigma_1^3 \lesssim 0.15$ , of the reduced pressure of the reservoir of small particles.

#### 4. Summary and conclusions

The use of the potential of mean force to study thermodynamic properties of colloidal suspensions has a long and celebrated history. A notable example is the Derjaguin–Landau–Verwey–Overbeek potential for the electric double-layer repulsion [2, 30]. In recent years, great interest has developed in phase-separation processes in mixed colloidal suspensions. Here, the potential of mean force is also a useful tool for describing the thermodynamics of these systems [23]. In this paper we have tested two different levels of the free-volume approximation to the potential of mean force for the phase diagram of an asymmetric mixture of hard spheres with a diameter ratio of 0.1. The agreement with direct computer simulations of the phase diagram is particularly satisfactory given the simplicity of the mean-field-level approximation.

#### References

- [1] Hansen J P and McDonald I R 1976 *Theory of Simple Liquids* (London: Academic)
- [2] Vrij A, Nieuwenhuis E A, Fijnaut H M and Agterof W G M 1978 *Faraday Discuss.* **65** 101
- [3] Onsager L 1933 *Chem. Rev.* **13** 73
- [4] Biben T and Hansen J P 1991 *Phys. Rev. Lett.* **66** 2215
- [5] Biben T and Hansen J P 1991 *J. Phys.: Condens. Matter* **3** 65
- [6] Lebowitz J J and Rowlinson J S 1964 *J. Chem. Phys.* **41** 133
- [7] Vrij A 1978 *J. Chem. Phys.* **69** 1742
- [8] Rogers F J and Young D A 1984 *Phys. Rev. A* **30** 999
- [9] Antl L, Goodwin J W, Hill R D, Ottewill R H, Owens S W and Papworth S 1986 *Colloids Surf.* **17** 67
- [10] Vrij A, Jansen J W, Dhont J K G, Pathmamanoharan C, Kops-Werkhoven M M and Fijnaut H M 1983 *Faraday Discuss. Chem. Soc.* **76** 19
- [11] Pusey P N 1991 *Liquids, Freezing and Glass Transition* ed J-P Hansen, D Levesque and J Zin-Justin (Amsterdam: North-Holland) p 759
- [12] Sanyal S, Easwar N, Ramaswamy S and Sood A K 1992 *Europhys. Lett.* **18** 107
- [13] van Duijneveldt J S, Heinen A W and Lekkerkerker H N W 1993 *Europhys. Lett.* **21** 369
- [14] Kaplan P D, Rouke J L, Yodh A G and Pine D J 1994 *Phys. Rev. Lett.* **72** 582
- [15] Dinsmore A D, Yodh A G and Pine D J 1995 *Phys. Rev. E* **52** 4045
- [16] Steiner U, Meller A and Stavans J 1995 *Phys. Rev. Lett.* **74** 4750
- [17] Imhof A and Dhont J K G 1995 *Phys. Rev. Lett.* **75** 1662
- [18] Lekkerkerker H N W and Stroobants A 1993 *Physica A* **195** 387
- [19] Poon W C K and Warren P B 1994 *Europhys Lett.* **28** 513
- [20] Lekkerkerker H N W, Poon W C K, Pusey P N, Stroobants A and Warren P B 1992 *Europhys Lett.* **20** 559
- [21] Dijkstra M, van Roij R and Evans R 1998 *Phys. Rev. Lett.* **81** 2268
- [22] Dijkstra M, van Roij R and Evans R 1999 *Phys. Rev. Lett.* **82** 117
- [23] Dijkstra M, van Roij R and Evans R 1999 *Phys. Rev. E* **59** 5744
- [24] Lekkerkerker H N W and Widom B 2000 *Physica A* **285** 483
- [25] Oversteegen S M and Lekkerkerker H N W 2002 *Physica A* **310** 181
- [26] Dijkstra M, Brader J M and Evans R 1999 *J. Phys.: Condens. Matter* **11** 10 079
- [27] Asakura S and Oosawa F 1954 *J. Chem. Phys.* **22** 1255
- [28] Vrij A 1976 *Pure Appl. Chem.* **48** 471
- [29] Derjaguin B V and Landau L D 1941 *Acta Phys. Chim. URSS* **14** 633
- [30] Verwey E J W and Overbeek J Th G 1948 *Theory of the Stability of Lyophobic Colloids* (Amsterdam: Elsevier) (reprinted in 1999 (New York: Dover))