The importance of correlations in free-volume models for depletion phenomena

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Abstract

Two different levels of the free-volume approximation for describing one-dimensional mixtures of hard rods of two different lengths are analysed and tested against the exact solution. The mean-field level free-volume approach, where only the statistically pre-averaged free volume of the larger rods is accounted for, yields a spurious phase transition. Taking correlations into account not only gives better quantitative results, it also shows qualitative right physics, i.e., no phase transition. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

The stability of colloidal mixtures is an important issue for many industrial applications and in food science. Many theories have been put forward for a fundamental understanding of demixing phenomena in binary colloidal mixtures. Asakura and Oosawa [1] first proposed a theory for mixtures of large hard colloids with non-adsorbing ideal polymers based on effective pair-potentials. Their theory has been elaborated by Vrij [2] and adapted by Gast et al. [3].

Lekkerkerker et al. [4] proposed a so-called free-volume theory to describe the phase behaviour of colloid/polymer mixtures. A key quantity in this theory is the statistically averaged available volume of an unperturbed system of hard colloids in equilibrium with a reservoir of polymers of given activity. This effectively reduces the model to a

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mean-field level. The phase-diagrams obtained from this mean-field free-volume model relate well to those found experimentally [5,6] and from computer simulations [7,8].

According to a study by Lebowitz and Rowlinson [9], using Percus–Yevick integral relations, mixtures of asymmetric hard spheres are stable with respect to demixing. However, using a different closure, Biben and Hanssen [10] showed that phase-separation may be expected. These contradicting results have stimulated experimental work [11–13], theoretical analysis [14,15], and simulations [15–17].

The mean-field free-volume theory has also been applied to asymmetric colloid/colloid mixtures [18,19]. In order to test this version of the free-volume theory for these kinds of mixtures, Lekkerkerker and Widom [20] compared the mean-field free-volume approximation for a binary mixture of one-dimensional hard spheres (rods) with the exact result. Although this mean-field free-volume theory holds well for mixtures of the asymmetric rods over the whole volume-fraction range of the large colloids, it shows a spurious phase transition above a certain activity of the smaller species. In this paper we show that this is an artifact of the mean-field approach and not of the free-volume approximation as such. By including correlations that are averaged out on the mean-field level in the free-volume theory not only better quantitative results but also qualitative right physics, i.e., no phase transition, are found.

In Section 2 we briefly derive the exact solution and elaborate on the expressions of the free-volume theory with correlations as well as those in the mean-field approximation. In Section 3 we show that although the ordering of the semi-grand potentials is determined by the level of approximation, the stability predicted by the different approaches only follows from the pressure and chemical potential of the larger species. Finally, we discuss in Section 4 the importance of correlations in free-volume models for binary colloid mixtures.

2. Theory for one-dimensional mixtures of asymmetric hard colloids

2.1. Exact result

Consider N_1 hard rods of length a and N_2 rods of length b on a line of length $L > N_1a + N_2b$ at given temperature T. The appropriate partition function to describe this system is the canonical $Q(N_1, N_2, L, T)$, given by

$$Q(N_1, N_2, L, T) = \frac{1}{\Lambda_1^{N_1} \Lambda_2^{N_2} N_1! N_2!} [L - (N_1a + N_2b)]^{N_1+N_2} . \qquad (1)$$

Here, Λ_1 and Λ_2 are the de Broglie wavelengths of the respective rods. Introducing the 'volume' fractions

$$\eta_1 = \frac{aN_1}{L}, \quad \eta_2 = \frac{bN_2}{L} \qquad (2)$$

and the size ratio
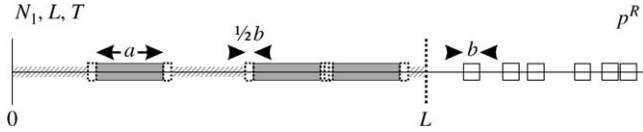
$$q = \frac{b}{a} \qquad (3)$$

Fig. 1. A certain configuration of N_1 hard particles of type 1 of length a on a line of length L is to be brought in equilibrium with a reservoir of hard particles 2 of length $b < a$ with a given reservoir pressure p^R. The dotted parts show the depletion or taboo zones which are excluded for particles 2. The hatched parts on the line shows L_{free}; the space available for particles 2 in this particular configuration.

we find for the chemical potentials of both species

$$\frac{\mu_1}{k_B T} = -\left(\frac{\partial \ln Q}{\partial N_1}\right)_{T,L,N_2} = \ln \frac{\Lambda_1}{a} + \ln \frac{\eta_1}{1 - \eta_1 - \eta_2} + \frac{q\eta_1 + \eta_2}{q(1 - \eta_1 - \eta_2)} , \tag{4}$$

$$\frac{\mu_2}{k_B T} = -\left(\frac{\partial \ln Q}{\partial N_2}\right)_{T,L,N_1} = \ln \frac{\Lambda_2}{b} + \ln \frac{\eta_2}{1 - \eta_1 - \eta_2} + \frac{q\eta_1 + \eta_2}{1 - \eta_1 - \eta_2} , \tag{5}$$

where k_B is the Boltzmann constant. For the pressure we find the generalized van der Waals-like expression [21]

$$\frac{p}{k_B T} = \left(\frac{\partial \ln Q}{\partial L}\right)_{T,N_1,N_2} = \frac{1}{b} \frac{q\eta_1 + \eta_2}{1 - \eta_1 - \eta_2} . \tag{6}$$

It turns out to be convenient to introduce the abbreviations

$$x = \frac{q\eta_1}{1 - \eta_1}, \quad y = \frac{\eta_2}{1 - \eta_1} . \tag{7}$$

The pressure may then be written in its reduced form as

$$\bar{p} \equiv \frac{pb}{k_B T} = \frac{x + y}{1 - y} . \tag{8}$$

The reduced chemical potentials are given by

$$\overline{\mu_1} \equiv \frac{\mu_1}{k_B T} - \ln \frac{\Lambda_1}{a} = \ln \frac{x}{q} \frac{1}{1 - y} + \frac{x + y}{q(1 - y)} , \tag{9}$$

$$\overline{\mu_2} \equiv \frac{\mu_2}{k_B T} - \ln \frac{\Lambda_2}{b} = \ln \frac{y}{1 - y} + \frac{x + y}{1 - y} . \tag{10}$$

Now suppose that the binary mixture is in equilibrium with a reservoir of pure 2, being the smaller of the two species, i.e., $q < 1$. Let us therefore start with a line of length L containing N_1 particles 1 of length a each. We bring this line in equilibrium with a reservoir of particles 2 of length $b < a$ with a given reservoir pressure p^R. This is shown schematically in Fig. 1. The semi-grand potential is the appropriate state variable to describe such a system of species 1 in equilibrium with a reservoir of given pressure or, analogously, chemical potential of species 2 at a given temperature

$$\Omega(N_1, \mu_2, L, T) \equiv -k_B T \ln Q - \mu_2 N_2 = -pL + \mu_1 N_1 . \tag{11}$$

Relative to the Helmholtz free energy $F_0 = -p_0 L + \mu_1^\circ N_1$ of a system of pure 1, the reduced semi-grand potential is given by

$$\frac{\Omega - F_0}{N_1 k_B T} = \ln \frac{1}{1-y} - \frac{y(1+x)}{x(1-y)} \ . \tag{12}$$

The connection between the partitioning of particles 2 in the system, i.e., y in Eq. (12), with the imposed number of large particles, i.e., x, and the reservoir pressure, p^R, is found from the condition for chemical equilibrium, using Eqs. (10) and (8)

$$\overline{\mu_2}^R = \overline{\mu_2} \Rightarrow \ln w + w = \ln \frac{y}{1-y} + \frac{x+y}{1-y} \ , \tag{13}$$

where we defined the reduced pressure of the reservoir as

$$w \equiv \bar{p}^R = \frac{p^R b}{k_B T} \ . \tag{14}$$

The semi-grand potential turns out to be the appropriate state variable in the free-volume approaches of the subsequent sections.

The stability criterion of a binary mixture is equivalent to a Van der Waals-like loop where the pressure is determined by the volume fraction of large particles and the chemical potential of the smaller species or, equivalently the pressure of the reservoir [22]

$$\left(\frac{\partial \bar{p}}{\partial x}\right)_{\overline{\mu_2}} = \left(\frac{\partial \bar{p}}{\partial x}\right)_y - \frac{(\partial \bar{p}/\partial y)_x (\partial \overline{\mu_2}/\partial x)_y}{(\partial \overline{\mu_2}/\partial y)_x} = \frac{1}{1+xy} > 0 \ . \tag{15}$$

Since the reduced volume fractions x and y are always positive, it follows that the one-dimensional colloidal mixture is stable against demixing. The impossibility of a phase transition in one dimension may be proven more rigorously as has been done by van Hove for single component systems [23].

2.2. Free-volume approximations

As stated in Section 2.1, in the (N_1, μ_2, L, T)-ensemble the semi-grand potential, Ω, is the appropriate state variable. The grand canonical partition function can formally be written as [24,25]

$$\Xi(N_1, \mu_2, L, T) = \frac{1}{\Lambda_1^{N_1} N_1!} \int_0^L \cdots \int_0^L e^{-[U_{N_1} + \omega]/k_B T} \, dr_1 \cdots dr_{N_1} \ . \tag{16}$$

Here U_{N_1} is the effective interaction potential of the N_1 hard particles of type 1 at the positions r_i, $i = 1, \ldots, N_1$. The potential of mean force between the larger rods due to the presence of the smaller ones, ω, is formally the grand potential of the smaller particles in a fixed configuration of the larger. In the free-volume approach we approximate the grand potential by the work to insert a particle 2 from the reservoir against the pressure p^R into the system of purely 1 that has a total available volume L_{free}, i.e., we neglect

the influence of the larger particles on the configurations of the smaller ones

$$\omega = -p^R L_{free}(r_1 \cdots r_{N_1}) \,. \tag{17}$$

Note that this approximation becomes exact in the case where the small rods can penetrate each other. So, within the free-volume theory L_{free} is predominantly determined by the configurations of particles 1. It therefore seems a fair approximation to replace the actual free volume by its initial statistical mean, i.e., averaging out the correlations between the particles. Hence, on the mean-field level of the free-volume approach we take

$$\omega = -p^R \langle L_{free} \rangle_0 \,, \tag{18}$$

where the index '0' refers to the initial, unperturbed configuration. The latter is the free-volume approach as originally considered [4,18,19].

For a one-dimensional system, as considered in the present paper, both levels of the free-volume approximation can be determined analytically.

2.2.1. Mean-field free-volume approximation

By inserting the pre-averaged free-volume of the initial configurations of particles 1 into Eq. (16), we obtain the following expression for the semi-grand partition function of the mean-field free-volume approximation

$$\Xi(N_1, \mu_2, L, T) \approx \frac{1}{\Lambda_1^{N_1} N_1!} \int_0^L \cdots \int_0^L e^{-[U_{N_1} - p^R \langle L_{free} \rangle_0]/k_B T} \, dr_1 \cdots dr_{N_1}$$

$$= Q_{N_1} e^{p^R \langle L_{free} \rangle_0 / k_B T} \,. \tag{19}$$

Here Q_{N_1} is the canonical partition function of a system of pure particles 1 and the subscript 0 refers to the pre-averaged initial configurations of a system of pure particles 1.

We will obtain the mean free-volume by averaging the exact free-volume. Due to the hard interactions, particles of type 2 cannot come closer to the particles 1 than $\frac{1}{2}b$ on both sides of the particle. This $\frac{1}{2}b$ is the so-called depletion zone around each particle 1. Consequently, the effective volume excluded by the N_1 particles 1 is $N_1(a+b)$. However, the total free volume may be overestimated for the case when the depletion zones overlap. This error must be restored. Hence, the initial free volume available for particles 2 in a given configuration of particles 1 is given as

$$L_{free} = L - N_1(a+b) + \sum_{i=1}^{N_1-1} [a + b - (r_{i+1} - r_i)] \theta(a + b - (r_{i+1} - r_i)) \,. \tag{20}$$

The Heaviside function $\theta(z)$ counts the overlapping free volumes when particles $i+1$ and i in the given configuration are less than $a+b$ apart ($\theta(z > 0)=1$ and $\theta(z \leqslant 0)=0$). In Eq. (20) we neglected the boundary terms when the depletion zones overlap with the ends of the line. Moreover, we do not correct for the few configurations $r_i < \frac{1}{2}a$ and $r_i > L - \frac{1}{2}a$ where the particles 1 exceed the length of the line. In principle this small error can be corrected for by considering the boundaries as fixed 'particles' on $r_0 = 0$ and $r_{N_1+1} = L$ [26].

Now the mean free-volume may be derived from Eq. (20), where averaging over the Heaviside step functions $\theta(z)$ amounts to the number density distribution $\rho g(r)$ of all N_1 particles

$$\langle L_{free} \rangle_0 = L - N_1(a + b) + N_1 \int_a^{a+b} \rho g(r)[a + b - r] \, dr . \tag{21}$$

The number density distribution has been derived by Zernike and Prins [27], and reads between a and $2a$ as

$$\rho g(r) = \frac{N_1}{L - N_1 a} \exp\left[-\frac{(r - a)N_1}{L - N_1 a} \right] . \tag{22}$$

Substitution of Eq. (22) in (21) yields after performing the integration

$$\langle L_{free} \rangle_0 = L \frac{q}{x + q} \, e^{-x} . \tag{23}$$

Here, we used the abbreviations q and x as introduced in Eqs. (3) and (7). The pre-averaged free volume, as given by Eq. (23), can, following the Widom insertion theorem, also be derived in the dilute limit from N_2/z_2 [20]. The activity $z_2 = e^{\mu_2/k_B T}/\Lambda_2$ of the particles in the reservoir can, in turn, be determined from Eq. (5) with $\eta_2 = 0$.

We derive the chemical potential from Eq. (19) as

$$\frac{\mu_1}{k_B T} = -\left(\frac{\partial \ln \Xi}{\partial N_1} \right)_{T, L, \mu_2} = \frac{\mu_1^\circ}{k_B T} - \frac{p^R a}{k_B T} \left(\frac{\partial \langle L_{free} \rangle_0 / L}{\partial \eta_1} \right)_L . \tag{24}$$

Here, we used the fact that a constant chemical potential of the smaller species 2 is equivalent to a constant reservoir pressure.

The reduced chemical potential of pure 1 in Eq. (24) can be found from Eq. (9) with $y = 0$. The derivative in Eq. (24) is straightforwardly found from Eq. (23), using Eqs. (2) and (7). Hence, the reduced chemical potential reads

$$\overline{\mu_1} = \ln \frac{x}{q} + \frac{x}{q} + \left[\frac{1 + x}{q} + 1 \right] we^{-x} . \tag{25}$$

Analogously, we find the pressure from Eq. (19) as

$$\frac{p}{k_B T} = \left(\frac{\partial \ln \Xi}{\partial L} \right)_{T, N_1, \mu_2} = \frac{p_0}{k_B T} + \frac{p^R}{k_B T} \left(\frac{\partial \langle L_{free} \rangle_0 / L}{\partial L} \right)_{N_1} . \tag{26}$$

The derivative of the mean free-volume is again found from Eq. (23), using Eqs. (2) and (7). The pressure p_0 of a system of pure 1 is given by the Tonks equation of state [28] (cf. Eq. (6) with $\eta_2 = 0$). The reduced pressure is consequently given by

$$\bar{p} = x + (1 + x)we^{-x} . \tag{27}$$

Like in the preceding sections, the reduced semi-grand potential can be obtained from the derived chemical potential and pressure

$$\frac{\Omega - F_0}{N_1 k_B T} = -\frac{w}{x} e^{-x} . \tag{28}$$

From the roots $(\partial \bar{p}/\partial x)_w = 1 - xw\mathrm{e}^{-x} = 0$ and $(\partial^2 \bar{p}/\partial x^2)_w = (x-1)w\mathrm{e}^{-x} = 0$, we find a critical point at $w_c = \mathrm{e}$ and $x_c = 1$. That is, for reduced reservoir pressures greater than the base of the natural logarithm, e, we find phase-transitions on the mean-field level of the free-volume approximation. However, we have proven analytically in Section 2.1 that the one-dimensional mixtures of asymmetric hard colloids cannot phase-separate. It therefore seems legitimate to question the validity of the free-volume approximation. However, the spurious phase-transition may also be due to the mean-field approximation imposed when pre-averaging the free-volume, i.e., going from Eqs. (20) to (23). Consequently, we account for the correlated free-volume in the next section.

2.2.2. Correlated free-volume approximation

By inserting Eq. (17) into Eq. (16), we obtain the following expression for the semi-grand partition function of the correlated free-volume approximation

$$
\Xi(N_1, \mu_2, L, T) = \frac{1}{\Lambda_1^{N_1} N_1!} \int_0^L \cdots \int_0^L \mathrm{e}^{-[U_{N_1} - p^R L_{free}]/k_B T} \, \mathrm{d}r_1 \cdots \mathrm{d}r_{N_1}
$$

$$
= Q_{N_1} \langle \mathrm{e}^{p^R L_{free}/k_B T} \rangle_0 .
\tag{29}
$$

Here Q_{N_1} is again the canonical partition function of a system of pure particles 1. The subscript '0' in the second line again refers to the fact that we consider the unperturbed free volume of N_1 particles of type 1.

Substitution of the expression for the free-volume in which the correlations have not been averaged out, Eq. (20), into the semi-grand partition function, Eq. (29), yields, introducing $z_i = r_{i+1} - r_i$

$$
\Xi = \frac{1}{\Lambda_1^{N_1}} \mathrm{e}^{p^R[L - N_1(a+b)]/k_B T} \frac{1}{N_1!} \int_0^L \cdots \int_0^L \mathrm{e}^{-\sum \varphi(r_{i+1} - r_i)/k_B T} \, \mathrm{d}r_1 \cdots \mathrm{d}r_{N_1}
$$

$$
= \frac{1}{\Lambda_1^{N_1}} \mathrm{e}^{-p^R N_1(a+b)/k_B T} \mathrm{e}^{p^R L/k_B T} \int_0^{z_2} \mathrm{e}^{-\varphi(z_1)/k_B T} \, \mathrm{d}z_1 \cdots \int_0^L \mathrm{e}^{-\varphi(z_{N_1})/k_B T} \, \mathrm{d}z_{N_1} .
\tag{30}
$$

Here $\varphi(z)$ is the effective pair-potential which comes from the hard interactions of particles 1 and the overlapping depletion zones due to the hard interactions between particles of types 1 and 2

$$
\varphi(z) = \begin{cases} \infty & \text{for } z \leqslant a, \\ -p^R[a + b - z] & \text{for } a < z < a + b, \\ 0 & \text{for } z \geqslant a + b. \end{cases}
\tag{31}
$$

This potential, as drawn in Fig. 2, has the form of a 'classical' Asakura–Oosawa depletion potential. The depth of the potential is directly related to p^R or the activity of the small particles 2.

It turns out to be convenient to go over to the isobaric ensemble since this implies the following Legendre transformation

$$
\Omega_p \equiv \Omega + pL = \mu_1 N_1 .
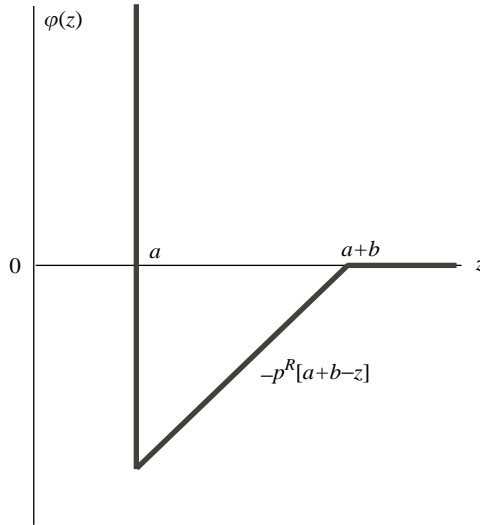\tag{32}
$$

Fig. 2. Effective pair-potential $\varphi(z)$ as a function of the particle separation z. The repulsive part is due to the mutual hard interactions of particles of type 1. The attractive part stems from the overlap of depletion zones, which in turn arises from the hard interaction between particles of types 1 and 2.

In the last step we used Eq. (11). The isobaric semi-grand partition function is found from

$$\Xi_p(N_1, \mu_2, p, T) = \int_0^\infty e^{-pL/k_BT} \Xi(N_1, \mu_2, L, T)\, dL$$

$$= \frac{1}{\Lambda_1^{N_1}} e^{-p^R N_1(a+b)/k_BT} \int_0^\infty e^{-[p-p^R]L/k_BT}\, dL$$

$$\times \int_0^{z_2} e^{-\varphi(z_1)/k_BT}\, dz_1 \cdots \int_0^L e^{-\varphi(z_{N_1})/k_BT}\, dz_{N_1}. \tag{33}$$

If we again neglect the (same) boundary terms, we can write the length of the line as $L = \sum_i z_i$. Consequently, the integrals in Eq. (33) may be rewritten as repeated integrals over all z_i, all containing the same argument. Hence, according to Fubini's theorem, the order of the integration may be reversed which eventually leads to

$$\Xi_p = \frac{1}{\Lambda_1^{N_1}} e^{-p^R N_1(a+b)/k_BT} \left(\int_0^\infty e^{-[p-p^R]\,z/k_BT} e^{-\varphi(z)/k_BT}\, dz \right)^{N_1}$$

$$\equiv \frac{1}{\Lambda_1^{N_1}} e^{-p^R N_1(a+b)/k_BT} J(s)^{N_1}. \tag{34}$$

This defines $J(s)$ as the integral in parentheses. In fact, going from Eqs. (33) to (34) is the convolution theorem of a Laplace transform. Hence, we may regard $J(s)$ as the Laplace transform of the Boltzmann weights of the effective pair-potential, in which

we find the inverse length as an excess pressure

$$s = \frac{p - p^R}{k_B T} . \tag{35}$$

Using Eq. (31) for the effective potential, the Laplace transform $J(s)$ can be made explicit as

$$J(s) \equiv \int_0^\infty e^{-sz} e^{-\varphi(z)/k_B T} \, dz = \frac{e^{-as}}{s} \left[\frac{bse^w + we^{-bs}}{bs + w} \right] . \tag{36}$$

Here, we used the reduced reservoir pressure w as introduced in Eq. (14).

Using Eq. (32), we obtain the reduced chemical potential of the large colloid from Eqs. (34) and (36)

$$\overline{\mu_1} \equiv \frac{\mu_1}{k_B T} - \ln \frac{\Lambda_1}{a} = \frac{-\ln \Xi_p}{N_1} - \ln \frac{\Lambda_1}{a} = \ln a + \frac{p^R(a + b)}{k_B T} + \ln J(s)$$

$$= \ln \frac{bs}{q} + \frac{bs + w}{q} - \ln \frac{bs + we^{-(bs+w)}}{bs + w} . \tag{37}$$

Here $q = b/a$ is again the size ratio as defined in Eq. (3). The reduced pressure can be found straightforwardly from Eqs. (14) and (35) as

$$\bar{p} \equiv \frac{pb}{k_B T} = \frac{(p - p^R)b}{k_B T} + \frac{p^R b}{k_B T} = bs + w . \tag{38}$$

The value of the excess pressure s at a given reservoir pressure w, number of particles 1 on the line, x, and temperature T, can be found from the equation of state. Using Eqs. (34) (or Eq. (37)) and (35), the average length per particle is given by

$$\frac{L}{N_1} = \left(\frac{\partial L}{\partial N_1} \right)_{T, p, \mu_2} = \left(\frac{\partial \mu_1}{\partial p} \right)_{T, N_1, p^R} = \left(\frac{\partial \mu_1}{\partial s} \right)_{T, p^R} \left(\frac{\partial s}{\partial p} \right)_{T, p^R} = -\frac{J'(s)}{J(s)}$$

$$= a + \frac{1}{s} - \frac{bw[1 - (bs + w + 1)e^{-(bs+w)}]}{(bs + w)[bs + we^{-(bs+w)}]} . \tag{39}$$

In the second line we used Eq. (36) to evaluate the derivative $J'(s)$ with respect to s. With the use of the definitions of the volume fractions, Eq. (2), we may rewrite Eq. (7) as $x = N_1 b/(L - N_1 a)$. Substitution in Eq. (39) consequently yields, after rearranging of terms

$$\frac{1}{x} = \frac{1}{bs} - \frac{w[1 - (bs + w + 1)e^{-(bs+w)}]}{(bs + w)[bs + we^{-(bs+w)}]} . \tag{40}$$

We note that for a system of pure particles 1, i.e., no activity of the reservoir, $w = 0$, Eq. (40) reduces to $bs = x$. As we expected this is again the Tonks equation of state as can be seen from Eqs. (7) and (35) to write this more explicit.

From the expressions found for the pressure and the chemical potential of particles 1, we obtain for the reduced semi-grand potential

$$\frac{\Omega - F_0}{N_1 k_B T} = \ln \frac{bs}{x} - \frac{bs + w - x}{x} - \ln \frac{bs + we^{-(bs+w)}}{bs + w} . \tag{41}$$

The Helmholtz free energy $F_0 = -p_0 L + \mu_1^\circ N_1$ of a system of pure 1 is derived from the exact solution as derived in Section 2.1.

The stability criterion $(\partial \bar{p}/\partial x)_{\overline{\mu_2}} = (\partial \bar{p}/\partial x)_w > 0$ can from Eq. (38) be written as $(\partial bs/\partial x)_w > 0$, which can be obtained from implicit differentiation of Eq. (40)

$$
\left(\frac{\partial bs}{\partial x}\right)_w = [bs(bs + w)(bs + we^{-(bs+w)})]^2 /
$$

$$
[x^2 e^{-(bs+w)}\{bs^5 we^{(bs+w)} + 2bsw^3(1 + e^{(bs+w)}) + w^4
$$

$$
+ bs^3 we^{(bs+w)}(w + 2)^2 + bs^4 e^{(bs+w)}(e^{(bs+w)} + 2w(w + 1))
$$

$$
+ 2bs^2 w^2 (1 + e^{(bs+w)}(w + 2))\}] > 0 .
$$

Since the excess and reservoir pressures, s and w, are positive quantities, it is easily seen that mixtures of hard rods do not phase-separate on the correlated level of the free-volume approximation.

3. Results for one-dimensional mixtures of asymmetric hard colloids

In the previous sections we derived expressions for the semi-grand potential, chemical potential of the larger particles 1, and pressure. Since their functional form differ, we would like to make a qualitative comparison between the exact solution and both levels of the free-volume approximation. In this section we will show the aforementioned state variables as a function of the larger particles 1 for the size ratio $q = \frac{1}{4}$. This size ratio is greater than in most applications (typically $q \simeq 0.1$) and is far from the limit where both free-volume approaches go to the exact solution ($q = 0$). We consider three reservoir pressures: one well below ($w = 0.2$), one below ($w = 1.0$), and an other above ($w = 4.0$) the critical value of the mean-field free-volume approximation ($w_c = e$).

3.1. Semi-grand potential

The numerical results for the semi-grand potential of the exact solution, as given by Eq. (12), the free-volume approximation accounting for correlations, Eq. (41), and the mean-field free-volume approximation, Eq. (28), are shown in Fig. 3 by the solid, dotted, and dashed lines, respectively. All lines neatly vanish upon increasing volume fraction; when the system is filled with particles of type 1, particles of type 2 cannot enter the system irrespective of the reservoir pressure and the reduced semi-grand potential must go to the value of a system of purely 1.

Both levels of the free-volume approximation work very well for low reservoir pressures and deviate from the exact solution upon increasing p^R. The free-volume approximation accounting the correlations, Eq. (41), is always in between the exact solution, Eq. (12), and the mean-field free-volume approximation, Eq. (28). Using the Gibbs–Bogoliubov inequality [29],

$$
Q_{N_1} \langle e^{p^R L_{free}/k_B T} \rangle_0 \geqslant Q_{N_1} e^{p^R \langle L_{free} \rangle_0 / k_B T} . \tag{42}
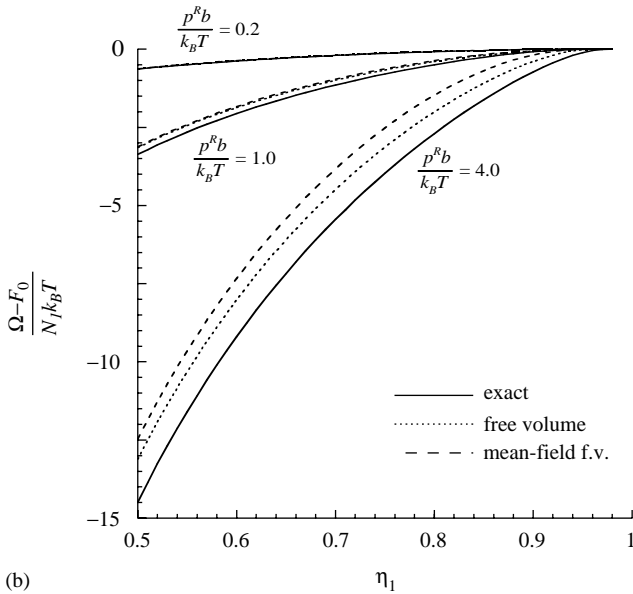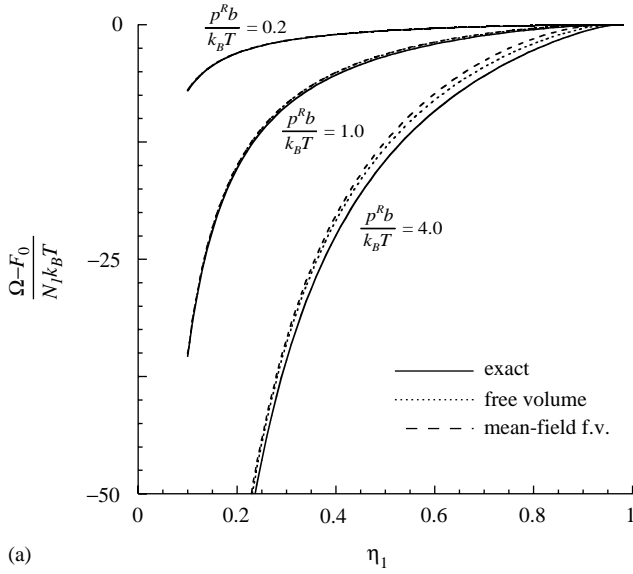$$

Fig. 3. The reduced semi-grand potential as a function of the volume fraction of particle 1 for three values of the reduced reservoir pressure and a size ratio $q = \frac{1}{4}$. The solid lines give the exact result (Eq. (12)), the dotted lines the free-volume approximation (Eq. (41)), and the dashed lines the mean-field free-volume approximation (Eq. (28)).

We indeed expect from Eqs. (19) and (29) the semi-grand potential, $\Omega = -k_B T \ln \Xi$, of the mean-field approximation to be above the 'pure' free-volume approximation. The reason why the exact solution is below the free-volume approximations is less evident. We believe that the neglected presence of particles 2 in the system allows for more actual configurations than accounted for with the free-volume approximations. This reasoning yields that the order of the approximation determines the sequence of the reduced semi-grand potential, as shown in more detail in Fig 3b.

3.2. Pressure and chemical potential

In Fig. 4a the reduced pressure is displayed for the three reduced reservoir pressures. The solid line again shows the exact result as given by Eq. (8), the dotted line the free-volume approximation that includes all configurations, Eq. (38), and the dashed line the mean-field free-volume approximation, Eq. (27). For low reservoir pressures both levels of the free-volume approximation describe the exact result very well. Higher reservoir pressures cause the free-volume approximations to deviate from the exact description. The free-volume models always underestimate the real pressure owing to the nature of the approximation made. In the real system both particles 1 and 2 are present, whereas in the free-volume models the particles 2 do not interact. Therefore the excluded volume, and by that the pressure, is underestimated in the free-volume approximation.

For reservoir pressures greater than the base of the natural logarithm, $w > e$, the deviation on the mean-field level model is more dramatic. It clearly shows a van der Waals-like loop which predicts a phase separation as also derived analytically in Section 2.2.1. Although the deviation from the exact result of the free-volume approach on the correlated level becomes larger with higher w, they are both monotonically increasing functions as has been proven analytically in Sections 2.1 and 2.2.2, respectively. Consequently, the spurious phase transition of the mean-field free-volume model is due to the imposed pre-averaged available volume and not because of the free-volume approximation itself.

In the limits of low volume fractions of the greater particles 1, $\eta_1 \to 0$, all expressions for the pressure nicely go to the imposed reservoir pressure of the ideal interacting particles 2 in the system. In the case of close packed rods 1, $\eta_1 \to 1$, all pressures diverge as expected. In Section 2 we have shown analytically that all three kinds of expressions go to the Tonks equation for vanishing reservoir pressure, i.e., for $\eta_2 \to 0$.

The solid lines in Fig. 4b show the exact reduced chemical potentials of the large particles 1 as given by Eq. (9). The dotted and dashed lines give the reduced chemical potentials of both levels of the free-volume approximation as given by Eqs. (37) and (25), respectively. Like it has been found for the semi-grand potential and pressure, both levels of the free-volume approximation describe the exact behaviour very well for low reservoir pressures and deviate upon increasing reservoir pressures. However, unlike the semi-grand potential and pressure, there is no systematic deviation since the free-volume approximations cross the exact result. The intersection points shift slightly
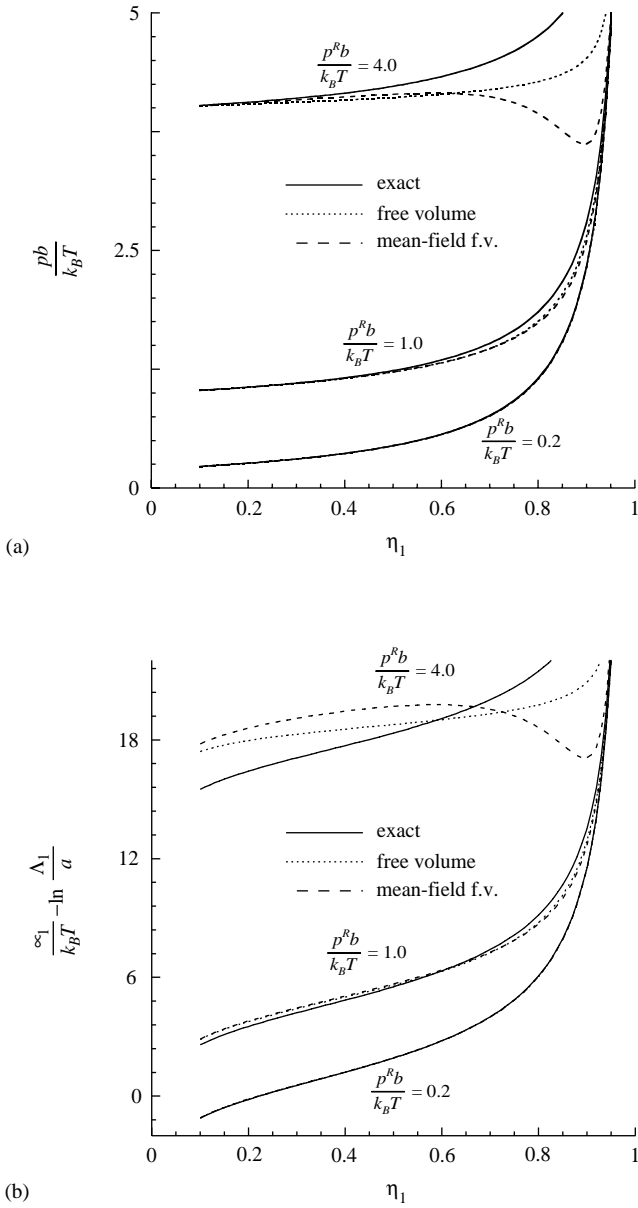
Fig. 4. (a) The reduced pressure and (b) chemical potential of the large particles 1 as a function of the volume fraction of particle 1 for three values of the reduced reservoir pressure and a size ratio $q = \frac{1}{4}$. The solid lines give the exact result (Eqs. (8) and (9)), the dotted lines the free-volume approximation (Eqs. (38) and (37)), and the dashed lines the mean-field free-volume approximation (Eqs. (27) and (25)).

but in a highly non-linear way. Again the free-volume approximation that accounts for correlations is closer to the mean-field result than the exact solution.

The chemical potentials of type 1 show van der Waals loops for $w > e$ on the mean-field level whilst still crossing the exact result. On a correlated level, the free-volume model deviates for increasing reservoir pressure more from the exact solution but also remains a monotonic increasing function of the volume fraction. This once more demonstrates that the phase transition is an artefact of pre-averaging the available volume in the mean-field approximation and not of the free-volume approximation itself.

From Fig. 4b it can be seen that the chemical potentials diverge upon approaching close packing of particles 1. The reason why the divergence of the exact solution is always slower than the free-volume approximations also stems from the fact that the latter always underestimates the excluded volume. It can be shown that all three expressions for the chemical potentials of type 1 go to the chemical potential of pure 1 for dilute systems, i.e., $\mu_1 \to \mu_1^\circ$ if $\eta_2 \to 0$.

4. Discussion

We scrutinized the role of correlations in the free-volume approximation in mixtures of asymmetric hard colloids. To that end we compared for a one-dimensional system the exact result of Section 2.1, to that of the mean-field free-volume approximation, as derived in Section 2.2.1, and that of the correlated free-volume approximation, as derived in Section 2.2.2. In the free-volume approximation we consider the space that is initially available for particles from a reservoir and neglect their own presence. This makes the correlated free-volume approximation, i.e., accounting for each possible configuration of the larger colloid, exact in the case of mixtures of hard spheres with fully penetrable spheres, e.g. ideal polymers, for $q < 1$ [30]. On the mean-field level of the free-volume theory the available space has been pre-averaged.

As clearly shown in Fig. 3, both levels of the free-volume approximation give a very good description for the semi-grand potential of the system. The approximations lie above the exact result and this deviation increases for increasing reservoir activity. The correlated free-volume model is slightly closer to the exact solution than the mean-field free-volume approximation. We conclude that the level of the approximation determines the sequence of the semi-grand potential.

Owing to the small differences of the semi-grand potential between both free-volume approximations, it is tempting to use the simpler expressions of the mean-field theory. In this approach the semi-grand potential, Eq. (28), chemical potential, Eq. (25), and pressure, Eq. (27), can be determined straightforwardly as a function of the reservoir pressure and volume fraction of the large particles 1, whereas in the exact solution and when correlations are taken into account the implicit relations Eqs. (13) and (40) must be solved (numerically) to obtain the partitioning of particles 2 and excess pressure, respectively. However, as can be seen from Fig. 4, the mean-field approximation shows a loop in the pressure and chemical potential. This implies a spurious phase transition, since the exact result shows no demixing for one-dimensional mixtures. Accounting for

correlations in the free-volume approach, as has been done in Section 2.2.2, prevents the system from phase separation. The correlated free-volume approach shows the right qualitative and better quantitative behaviour for the semi-grand potential as well as its derivatives, the chemical potential of particles 1, and the pressure. Apparently correlations are important for a one-dimensional mixture of hard rods in order to obtain the correct physics.

The importance of correlations in higher dimensions is yet unclear. Although experiments [11–13], simulations [14,15], and other theories [10,15–17] confirmed the phase-transitions found by the mean-field free-volume theory from mixtures of asymmetric hard spheres [18,19], it is still not sure whether this is an artefact of the mean-field approach as shown in this paper. Progress can be made by introducing more exact expressions for the free volume [31,32]. This kind of mathematical challenging theories may be subject for future studies.

Acknowledgements

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