Empirical expressions of the pair correlation functions at contact and equation of state of the liquid hard-sphere mixtures at large size ratio

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Abstract

The virial–pressure equation of state of hard-sphere mixtures in the colloidal limit obtained from ad hoc expressions of the contact values of the pair correlation functions and the related question of the fluid–fluid phase separation are revisited. The sensitivity of the location of the binodal to the exponential behaviour of the contact value of the big spheres pair correlation function and its size ratio dependence are analyzed by considering a model for the mean force potential that is used to parameterise the contact value. Agreement with simulation data or accurate integral equations theories is improved when compared with previous approaches based on the virial–pressure equation of state.
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1. Introduction

Since the proposal of Biben and Hansen [1,2] that hard-sphere (HS) mixtures can phase separate, numerous works has been performed to establish the phase diagram of the HS mixture in the so-called colloidal range, i.e. when the size ratio R of the big and small hard spheres is large (see Refs. [3,4] for detail). The binary mixture of hard spheres with large difference in size is indeed the simplest model from which one can study important questions in the physics of complex fluids, such as the purely "entropic" phase transitions or the validity of the effective fluid approach. This model may also be used to analyze the behaviour of pseudo-binary mixtures of hard-sphere-like colloids. A quantitative description of the phase diagram is however a difficult task when the size asymmetry is large. On the one hand, sampling by computer simulation the configurations of the big

spheres is very inefficient in this case [3]. For the methods that use integrals equations now, the non-convergence problem in a large domain of the parameters space is a severe limitation [5,6], besides the need of very accurate closures. Dijkstra et al. (DvRE) computed the first reliable phase diagram of the binary HS mixture, in the colloidal range, in 1999 [3]. These authors performed Monte Carlo (MC) simulations of the true mixture to explore the fluid–solid phase transition but could not study the dense fluid region in the same way. Rather, they used the effective fluid approach and predicted in this way a metastable fluid–fluid phase transition. Very recently, Ayadim and Amokrane (AA [7]) solved the Ornstein-Zernike equations with a closure having a large enough convergence domain to permit exploration of the dense fluid region. They validated in this way the equivalence in practice between the true mixture of big and small spheres and the associated one component effective fluid of big spheres as introduced by the McMillan–Mayer theory [8]. These two studies [3,7] are complementary since the true mixture can be studied in the dense fluid range only from the integral equation method. As a consequence, the work of AA legitimates the use of analytical models to represent the effective interaction in asymmetric hard-sphere mixtures at large size ratio $R > 5$. Such models are, for instance, the depletion potential of Götzelmann

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et al. [9] or, more drastically, the corresponding effective sticky potential [10,11] for which simulations have been performed by Miller and Frenkel [12]. The latter model reproduces almost quantitatively the phase diagram of the HS fluid mixture and so the (metastable) fluid–fluid equilibrium in the colloidal limit.

It is however clear that both the computer simulation method and the integral equation approach involve a considerable amount of numerical work and hence cannot be used to rapidly estimate the phase diagram in specific situations. Numerous attempts [13–22] have thus been made to improve the analytical equation of state (EOS) of Boublik, Mansoori, Carnahan, Starling and Leland (BMCSL) [23,24] of HS mixtures in the regime of high size asymmetry. Indeed, this widely used EOS is accurate at small size asymmetry, but it does not predict any phase transition in the HS mixture fluid in the colloidal range. Among such attempts, the approach of Henderson et al. (here and after H et al.) [14,25,26] based on the virial–pressure EOS from the contact values g_{ij} of the pair correlation functions (pcf) has a special status. This approach involves analytical ad hoc corrections in order to get a better agreement of the g_{ij}s with the known simulation data, that do verify specific internal constraints in the colloidal limit (i.e. in the wall-particle limit the contact theorem: $1 + 4\eta_1 g_{11} = g_{12}$ and the behaviour $\ln g_{22} \approx R$, where the subscript 2 is for the large spheres and η_1 is the packing fraction of the small spheres). From any new ad hoc set of the three g_{ij}s, one can readily integrate the virial–pressure EOS to obtain the Gibbs energy of the mixture $G(P, x_2)$ versus P pressure and x_2 concentration. And so on, the equilibrium fluid–fluid line (or binodal) is deduced from the constant pressure $G(P, x_2)$ curve when a common tangent at two concentrations may be obtained. Although straightforward and appealing, the H et al. method is very sensitive to the ad hoc corrections and therefore questionable. As shown in our previous works [27,28] a binodal of the HS mixture can be obtained while the g_{ij}s verify only one of the two previous constraints. The virial–pressure binodals as obtained from the H et al. method were also found to be quantitatively poor, being systematically at too low packing fractions of the small spheres. On the contrary, the binodals obtained from some particular analytical EOS [17] were found almost at the correct packing fraction but with too small values of g_{22} in the colloidal limit (i.e. without exponential behaviour versus R). Indeed even three inaccurate g_{ij} contact values can combine in such a way so as to eventually produce a binodal.

Therefore, the method of H et al. is relevant only if all the expressions of the g_{ij}s, at all concentration and size ratio are in accordance with simulation data, and verify also the selected physical constraints of the colloidal limit to make the corresponding EOS reliable. For the reasons recalled above, MC simulations and/or integral equations for the true mixture can hardly be used to achieve this goal especially at very large size ratio, high packing fraction of the big spheres or close to the critical domain. On the other hand, the effective fluid approach is feasible, but it gives only the contact value g_{22} and that also with numerical difficulties at very large size ratio. Consequently, the method of H et al. may be useful in the colloidal domain provided one can find analytical expressions which are, at least, in agreement with simulations and/or accurate integral equations results,

in the domain where these methods can be performed. For this purpose, guidelines are useful to parameterise the contact value g_{22}. A step in this direction is to consider several new approximate expressions of the contact values g_{22} which, basically, rest on the model of potential of mean force, to calculate the corresponding binodals and to compare them with the simulation data of the effective fluid. The aim of this work is thus to explore more systematically this route and to point out the sensitivity of the binodal to presumably more accurate expressions of g_{22} (i.e. which better agree with the available simulation data).

This paper is hence organised as follows: first we present the various sets of parameterised g_{ij}s which are used in this work, then, in Section 3, we discuss step by step the sensitivity of the binodals to the various approximate expressions of these contact values g_{22}. From the systematic comparison of the binodals and the corresponding g_{22} with simulation data we finally discuss the expressions which better correlate binodals with accurate contact values.

2. Expressions of the contact values

The original ad hoc formula of H et al. [14], gives exceedingly large contact values of the big spheres pcf due to the behaviour of the exponential terms in g_{22}. Later, Cao et al. [25] proposed a novel expression which includes a damping factor. But we also found that the corresponding pressure–virial EOS produced only very qualitative binodals at various size ratio $10 < R < 30$ [27]. Finding the optimal combination of the terms in the expression of g_{22} remains, therefore, to be done. In order to explore more systematically this route, we begin here with other new expressions of H et al. [26] and attempt to parameterise them by using the known analytical expression of the mean force potential. We thus consider various schemes, where g_{11} and g_{12} have the same expressions but where g_{22} differs only slightly, and test them versus simulation data.

The first scheme here labelled HB1, corresponds to the H et al. [26] expressions:

$$g_{11}^{HB1} = g_{11}^{BMCSL} \tag{1a}$$

$$g_{12}^{HB1} = g_{12}^{BMCSL} \frac{\delta_2^2 d_1^2}{(1-\delta_3)^3} + \frac{R^2-1}{(R+1)^2} - \frac{\delta_2^3 d_1^3}{(1-\delta_3)^3} \frac{R^3-1}{(R+1)^3} \tag{1b}$$

$$g_{22}^{HB1} = g_{22}^{BMCSL} + f_1(x_A) \tag{1c}$$

where $f_1(x) = \exp(x) - 1 - x$, and x_A expression is [26]:

$$x_A = \frac{3(\delta_2 d_2 - \delta_3)}{2} = \frac{3}{2}\eta_1\left(\frac{1-y}{y}\right) \tag{1d}$$

$\delta_n = (\pi/6)\rho(x_1 d_1^n + x_2 d_2^n)$, ρ is the number density and d_k is the hard-sphere diameter of the k species. $\eta_k = (\pi/6)\rho x_k d_k^3$ is the corresponding packing fraction and $y = d_1/d_2 = 1/R$.

In this work we also consider the development of g_{22}, labelled HB2:

$$g_{22}^{HB2} = g_{22}^{BMCSL} + f_2(x_A) \tag{1e}$$

where $f_2(x) = \exp(x) - 1 - x - x^2/2$.