# Chemical potential and surface free energy of a hard spherical particle in hard-sphere fluid over the full range of particle diameters

Ruslan L. Davidchack ^1, a) and Brian B. Laird <sup>2, 3</sup>

<sup>1)</sup>School of Computing and Mathematical Sciences, University of Leicester, Leicester, LE1 7RH, UK

<sup>2)</sup>Department of Chemistry, University of Kansas, Lawrence, KS 66045, USA

<sup>3)</sup> Freiburg Institute for Advanced Studies, Albert Ludwigs Universität, Freiburg Germany

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The excess chemical potential  $\mu^{\text{ex}}(\sigma,\eta)$  of a test hard spherical particle of diameter  $\sigma$  in a fluid of hard spheres of diameter  $\sigma_0$  and packing fraction  $\eta$  can be computed with high precision using Widom's particle insertion method [J. Chem. Phys. **39**, 2808 (1963)] for  $\sigma$  between 0 and just larger than 1 and/or small  $\eta$ . Heyes and Santos [J. Chem. Phys. **145**, 214504 (2016)] showed analytically that the only polynomial representation of  $\mu^{\text{ex}}$  consistent with the limits of  $\sigma$  at zero and infinity has a cubic form. On the other hand, through the solvation free energy relationship between  $\mu^{\text{ex}}$  and the surface free energy  $\gamma$  of hard-sphere fluid at a hard spherical wall, we can obtain precise measurements of  $\mu^{\text{ex}}$  for large  $\sigma$ , extending up to infinity (flat wall) [J. Chem. Phys. **149**, 174706 (2018)]. Within this approach, the cubic polynomial representation is consistent with the assumptions of Morphometric Thermodynamics. In this work, we present measurements of  $\mu^{\text{ex}}$  that combine the two methods to obtain high-precision results for the full range of  $\sigma$  values from zero to infinity, which show statistically significant deviations from the cubic polynomial form. We propose an empirical functional form for  $\mu^{\text{ex}}$  dependence on  $\sigma$  and  $\eta$  which better fits the measurement data while remaining consistent with the analytical limiting behaviour at zero and infinite  $\sigma$ .

# I. INTRODUCTION

The hard-sphere (HS) fluid was the first (Alder and Wainwright) and remains one of the most studied systems in molecular simulations. This is because, on one hand, due to its simplicity, it is amenable to theoretical treatment (e.g., via integral equations or density-functional theories). On the other hand, it is sufficiently rich to manifest crystal nucleation and a solid-fluid phase transition with increasing density and thus serves as a test case for theoretical study of these important phenomena.

The bulk monodisperse HS fluid with sphere diameter  $\sigma_0$  can be characterized by the equation of state (EOS). which determines the fluid pressure p as a function of number density  $\rho$  or packing fraction  $\eta = \frac{\pi}{6}\sigma_0^3\rho$ . (From here on, we will use  $\sigma_0$  as the unit of length and thus set  $\sigma_0 = 1$ .) Another important quantity is the chemical potential  $\mu$  or, more precisely, the excess chemical potential  $\mu^{\text{ex}}(\eta)$ , which is the difference between the chemical potential of the HS fluid and that of the ideal gas with the same density. More generally, we are interested in the excess chemical potential  $\mu^{\text{ex}}(\sigma, \eta)$  of a spherical particle of diameter  $\sigma$  immersed in the HS fluid with packing fraction  $\eta$ , which becomes the excess chemical potential of the host fluid when  $\sigma = 1$ . This quantity is related to the probability  $P(\sigma, \eta)$  of successful insertion (i.e., without overlap with other spheres) of the particle at a random uniformly distributed location in the bulk HS fluid

as follows

$$\mu^{\text{ex}}(\sigma,\eta) = -\beta^{-1} \ln P(\sigma,\eta) \tag{1}$$

where  $\beta = 1/k_{\rm B}T$  is the inverse temperature and  $k_{\rm B}$  is the Boltzmann constant. (Because of the trivial dependence of the HS EOS on temperature, in what follows we set  $\beta = 1$ .) Based on this relationship, the excess chemical potential can be calculated in a simulation by the so-called Widom's particle insertion method.<sup>1</sup> Unfortunately, because the probability of a successful particle insertion decreases rapidly with increasing  $\sigma$  and/or  $\eta$ , this method yields accurate results only for moderate particle diameters and fluid packing fractions.

In their recent paper,<sup>2</sup> Heyes and Santos used Widom's particle insertion method in the formulation of Labík and Smith<sup>3</sup> to calculate  $\mu^{\text{ex}}(\sigma,\eta)$  for  $0 < \eta \leq 0.5$  and  $0 < \sigma \leq 1.1$ . Within the precision of their results, they showed that the excess chemical potential can be expressed as a cubic polynomial in  $\sigma$ :

$$\mu^{\text{ex}}(\sigma,\eta) = c_0(\eta) + c_1(\eta)\sigma + c_2(\eta)\sigma^2 + c_3(\eta)\sigma^3.$$
(2)

This form is widely adopted by researchers and appears in several well-known theoretical descriptions of the HS fluid such as, for example, Percus-Yevick (PY) integral equation<sup>4</sup>, the Scaled Particle Theory (SPT)<sup>5</sup> or the Density Functional Theory.<sup>6</sup> The following *exact* expressions for  $c_0(\eta)$  and  $c_1(\eta)$  can be derived by considering the limit  $\sigma \to 0$ :

$$c_0(\eta) = -\ln(1-\eta), \quad c_1(\eta) = \frac{3\eta}{1-\eta},$$
 (3)

while several approximate expressions for  $c_2(\eta)$  and  $c_3(\eta)$  can be found in the literature.<sup>2</sup> Currently, the most accurate analytical approximation known to the authors is the

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<sup>&</sup>lt;sup>a)</sup>Author to whom correspondence should be addressed; Electronic mail: r.davidchack@le.ac.uk

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Boublik-Carnahan-Starling-Kolafa (BCSK) expression<sup>2,7</sup> in the form (2) with (3) and

$$c_{2}(\eta) = 8\ln(1-\eta) + \eta \frac{22 - 21\eta + 4\eta^{2}}{2(1-\eta)^{2}},$$
  

$$c_{3}(\eta) = -\frac{16}{3}\ln(1-\eta) - \eta \frac{13 - 43\eta + 27\eta^{2} - 2\eta^{3}}{3(1-\eta)^{3}}.$$
 (4)

Note that the exact expression for  $c_2(\eta)$  in the expansion of  $\mu^{\text{ex}}(\sigma, \eta)$  in powers of  $\sigma$  can be derived within the SPT framework<sup>8</sup>

$$c_2(\eta) = \frac{3\eta(2+\eta)}{2(1-\eta)^2}$$

However, as shown by Heyes and Santos<sup>2</sup>, this expression (which they label 'PY-c') is not as accurate as that in (4) when compared to the coefficients in (2) obtained from the least-squares fit to the simulation data.

From the perspective of solvation thermodynamics, the excess chemical potential of a test particle is equivalent to its *solvation free energy* (at infinite dilution), which can be represented as the sum of volume and surface contributions:

$$\mu^{\rm ex}(\sigma,\eta) \equiv F_{\rm solv} = p(\eta)V_{\sigma} + \gamma(\sigma,\eta)A_{\sigma} \,, \qquad (5)$$

where  $p(\eta)$  is the pressure of the HS fluid,  $V_{\sigma} = \frac{\pi}{6}\sigma^3$ and  $A_{\sigma} = \pi\sigma^2$  are the volume and surface area of the spherical particle, respectively, and  $\gamma(\sigma, \eta)$  is the *surface* free energy.

For a general non-planar surface S, the surface free energy depends on its curvature, which can be characterized by the average mean  $\bar{H}_S$  and Gaussian  $\bar{K}_S$  curvatures of the surface. Formally, this dependence can be represented by a Taylor series in powers of the mean and Gaussian curvatures:<sup>9</sup>

$$\gamma_S(\eta) = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} a_{ij}(\eta) \bar{H}_S^i \bar{K}_S^j, \tag{6}$$

where the coefficients  $a_{ij}(\eta)$  depend only on the packing fraction of the surrounding fluid. For a spherical surface with diameter  $\sigma$ ,  $\bar{H}_{\sigma} = 2\sigma^{-1}$  and  $\bar{K}_{\sigma} = 4\sigma^{-2}$  and the  $\sigma$ -dependence of  $\gamma(\sigma, \eta)$  can be formally expressed as the Taylor series in powers of  $\sigma^{-1}$ :

$$\gamma(\sigma,\eta) = \sum_{n=0}^{\infty} \gamma_n(\eta) \sigma^{-n}, \qquad (7)$$

where  $\gamma_0$  is the surface free energy of the HS fluid at a planar wall,  $\gamma_1 = -\gamma_0 \delta$  is related to the *Tolman length*  $\delta$ , while  $\gamma_2 = 4(k + \kappa)$  is related<sup>10</sup> to the sum of the socalled *bending rigidity* k and *Gaussian curvature rigidity*  $\kappa$ .

Note that the  $\sigma$ -dependence of  $\gamma$  (and correspondingly  $\mu^{\text{ex}}(\sigma, \eta)$  in (5)) is significantly simplified<sup>11</sup> under fairly general conditions of *Hadwiger's theorem*,<sup>12,13</sup> which states that any motion-invariant, continuous, and

additive functional of a convex bounding surface S in three dimensions can be written as a linear combination of its volume  $V_S$ , area  $A_S$ , integrated mean curvature  $C_S = A_S \overline{H}_S$ , and the Euler characteristic  $X_S = A_S \overline{K}_S$ . The solvation free energy  $F_{\rm solv}$  is a functional that is obviously motion-invariant and continuous, while additivity can be considered a good approximation if the scale of the surface is much bigger than the intrinsic length scale (correlation length) of the fluid. Therefore, if such an assumption holds, then the solvation free energy of any shape S depends only on the four simple *morphometric* measures  $V_S$ ,  $A_S$ ,  $C_S$ , and  $X_S$ , while the corresponding four linear coefficients depend only on the thermodynamic state of the solvent, and thus can be determined in simple geometries, such as, for example, planar, cylindrical, and spherical surfaces. This greatly simplifies the determination of  $F_{\rm solv}$  for solutes with complex shapes. Hence it is important to determine the range of applicability of such a simplified approach, which is referred to as Morphometric Thermodynamics (MT).<sup>14,15</sup>

If S is a spherical surface of diameter  $\sigma$ , then the MT expression for its solvation free energy is

$$F_{\text{solv}} = F_V V_\sigma + F_A A_\sigma + F_C C_\sigma + F_X X_\sigma ,$$
  
$$= F_V \frac{\pi}{6} \sigma^3 + F_A \pi \sigma^2 + F_C 2\pi \sigma + F_X 4\pi . \quad (8)$$

Comparing this expression to (5) and (7), we see that  $F_V = p(\eta)$ ,  $F_A = \gamma_0(\eta)$ ,  $F_C = \frac{1}{2}\gamma_1(\eta)$ , and  $F_X = \frac{1}{4}\gamma_2(\eta)$ , with all higher order terms in (7) equal to zero. So, the MT expression for the excess chemical potential takes the form

$$\mu_{\rm MT}^{\rm ex}(\sigma,\eta) = \pi \gamma_2(\eta) + \pi \gamma_1(\eta)\sigma + \pi \gamma_0(\eta)\sigma^2 + \frac{\pi}{6}p(\eta)\sigma^3 \quad (9)$$

In a recent paper<sup>10</sup> we have presented high-precision measurements of the HS fluid surface free energy of the HS fluid at cylindrical and spherical walls of different diameters. The purpose of this work was to test the limits of applicability of the MT assumptions. While we observed deviations from the MT at the cylindrical wall, we were not able to detect such deviations in case of the spherical wall within the precision of the simulations. The main reason is that the precision of the Gibbs-Cahn method which we used to determine  $\gamma(\sigma, \eta)$ is higher for surfaces with larger area (i.e., for cylinders) and spheres with larger diameter  $\sigma$ ), while deviations from the MT are expected to be observed for convex surfaces with small areas, where the additivity assumption of Hadwiger's theorem may no longer hold. In Ref. 10, using weighted least-squares fit of the Gibbs-Cahn results for a spherical wall to a cubic polynomial in  $\sigma^{-1}$ , we obtained estimates of  $\gamma_n(\eta)$ , n = 0, 1, 2, 3, in (7) and found that  $\gamma_0(\eta)$  is consistent with the flat-wall results obtained in Ref. 16, while deviations of  $\gamma_3(\eta)$  from zero were not statistically significant.

Note that if the cubic polynomial dependence of  $\mu^{\text{ex}}(\sigma,\eta)$  on  $\sigma$  were valid for all  $\sigma \in [0,\infty)$ , then  $\pi\gamma_1(\eta)$  and  $\pi\gamma_2(\eta)$  in (9) would have to be equal to the exactly

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FIG. 1. Differences (scaled by  $\eta^{-2}$  for greater clarity) between coefficients of the cubic polynomial expressions (2) and (9) with respect to  $\sigma$  for the excess chemical potential. The coefficients  $\gamma_1(\eta)$  and  $\gamma_2(\eta)$  were obtained from the simulation results for  $\gamma(\sigma, \eta)$  of HS fluid at a hard spherical wall,<sup>10</sup> while  $c_0(\eta)$  and  $c_1(\eta)$  are defined in (3).

known expressions (3) for  $c_1(\eta)$  and  $c_0(\eta)$ , respectively, in (2). In Figure 1 we plot the differences  $\pi \gamma_1(\eta) - c_1(\eta)$ and  $\pi \gamma_2(\eta) - c_0(\eta)$ , which show statistically significant differences between these parameters in the cubic polynomial expressions (2) and (9), especially for  $\pi \gamma_1(\eta) - c_1(\eta)$ at larger  $\eta$ . (The coefficients  $\gamma_1(\eta)$  and  $\gamma_2(\eta)$  were obtained in Ref. 10, as explained above.) Therefore, the cubic polynomial dependence cannot be valid in the whole range of  $\sigma$  values, although it appears to be a reasonably good approximation at small  $\eta$ . Perhaps, as a compromise, the following reference expression can be taken as a reasonable cubic polynomial approximation for the excess chemical potential

$$\mu_{\rm ref}^{\rm ex}(\sigma,\eta) = c_0(\eta) + c_1(\eta)\sigma + \pi\gamma_0(\eta)\sigma^2 + \frac{\pi}{6}p(\eta)\sigma^3 \quad (10)$$

where  $c_0(\eta)$  and  $c_1(\eta)$  are given by (3),  $\gamma_0(\eta)$  is the surface free energy of HS fluid at a planar hard wall, and  $p(\eta)$  is given by the HS fluid EOS. Such an expression exhibits correct asymptotic behaviour both at small and large  $\sigma$ .

Widom's particle insertion method, via the link (5) between  $\mu^{\text{ex}}$  and  $\gamma$ , allows us to obtain results at spherical surfaces with small diameters, and is thus complementary to the Gibbs-Cahn method. By combining the results obtained by these two methods, we should be able to test the dependence of  $\mu^{\text{ex}}$  on  $\sigma$  over the full range of  $\sigma$  values from 0 to  $\infty$ .

In this paper we report the results for  $\mu^{\text{ex}}(\sigma, \eta)$  which clearly show deviation from the expression (10), as well as from the general cubic polynomial dependence (2) tested by Heyes and Santos.<sup>2</sup> To achieve this, we have combined the results from Ref. 10 for  $\sigma = 1, 2, 3, 4, 10, 20, \infty$  with



FIG. 2. Top: Excess chemical potential  $\mu^{\text{ex}}(\sigma,\eta)$  of spherical particle with diameter  $\sigma$  immersed in the HS fluid with sphere diameter 1 and packing fraction  $\eta$  obtained from molecular simulations using Widom's particle insertion method. Error bars are smaller than the size of the dots.

Bottom: Estimated relative relative confidence intervals of the simulation results,  $S(\sigma, \eta)/\mu^{\text{ex}}(\sigma, \eta)$ .

the newly obtained high-precision results from Widom's particle insertion method<sup>3</sup> (essentially repeating the simulations of Heyes and Santos,<sup>2</sup> but with much larger computing budget and extended range of  $\sigma$  values up to  $\sigma = 4$  for small  $\eta$ ).

The rest of the paper is organized as follows. In the next Section, we describe the details of our simulations and the obtained results, followed by the analysis of the results in Section III, and the summary in Section IV.

## **II. SIMULATION DETAILS AND RESULTS**

The HS fluid systems were simulated using the molecular-dynamics algorithm of Rapaport.<sup>17</sup> We prepared well-equilibrated systems at packing fractions  $\eta = 0.01, 0.02, \ldots, 0.49, 0.50$  and several system sizes (cubic simulation box volume  $V = L^3$  with  $L \approx 17, 20, 25, 34$ , and 42).

During the simulation of each system, a random uni-

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formly distributed location was generated at regular intervals and the distance  $d_{\min}$  from this location to the nearest sphere was determined. If  $d_{\min} > 1/2$ , then a spherical particle with diameter  $\sigma \leq 2d_{\min} - 1$  can be successfully inserted at this location. To record this insertion event, a  $\sigma$ -dependent histogram was used with bins  $\sigma_k = 0.01k, \ k = 1, \ldots, 400$ , and 1 was added to all bins with  $\sigma_k \leq \sigma$ . At the end of the simulation, the probability of successful insertion  $P(\sigma_k, \eta)$  is measured as the ratio  $p_k = n_k/n_{\rm tot}$  of the value  $n_k$  in bin k to the total number of insertion attempts  $n_{\rm tot}$ .

Because counting insertions can be viewed as a Bernoulli process, the 95% confidence interval in the measurement of  $P(\sigma_k, \eta)$  can be estimated as  $s_k = 2\sqrt{\frac{p_k(1-p_k)}{n_{\text{tot}}}}$ . The estimated excess chemical potential is then calculated as

$$\mu_L^{\text{ex}}(\sigma_k, \eta) = -\ln p_k \pm \frac{s_k}{p_k},\tag{11}$$

where the subscript L indicates the simulated system size. When examining the results for different L at fixed  $\sigma$  and  $\eta$ , we observed a linear dependence of  $\mu_L^{\text{ex}}$  on  $L^{-3}$ (i.e., the inverse volume or number of simulated spheres). Therefore, to account for the system size effects, we calculated the weighted least-squares approximation of  $\mu_L^{\text{ex}}$ vs  $L^{-3}$  to a straight line and took the value of the straight line approximant at  $L^{-3} = 0$  as the measured value of the excess chemical potential  $\mu^{\text{ex}}(\sigma_k, \eta) = \mu_{\infty}^{\text{ex}}(\sigma_k, \eta)$ . The 95% confidence interval,  $S(\sigma_k, \eta)$ , for this value was also estimated using standard regression analysis.

The majority of the computational effort was focused on systems with  $L \approx 25$  and 42, where  $n_{\text{tot}} \approx 10^{14}$  for each simulated system. For  $\eta \leq 0.14$  we obtained the results for  $\sigma$  values up to 4.0, while for larger  $\eta$  the results were limited to the range of  $\sigma_k$  where  $n_k \geq 5$ . The results for  $\mu^{\text{ex}}(\sigma_k, \eta)$ , together with the relative size of the estimated confidence interval,  $S(\sigma_k, \eta)/\mu^{\text{ex}}(\sigma_k, \eta)$ , are shown in Figure 2.

During the simulations, we have also measured the compressibility factor,  $z = p/\rho$ , from the collisional virial. The size effect was taken into account in the same way as for the excess chemical potential. As shown in the top panel of Figure 3, the obtained results are consistent with and more precise than those of Kolafa, Labík, and Malijevský,<sup>18</sup> as well as more recent results of Pieprzyk *et al.*<sup>19</sup>.

Fitting the simulation data to a polynomial in terms of  $x = \eta/(1 - \eta)$ , we obtained the following empirical expression

$$z_{\rm fit}(x) = 1 + 4x + 6x^2 + z_3x^3 - 0.867384x^4 + 1.0598991x^5 - 0.8542136x^6 + 0.9972434x^8 - 0.8407042x^9 + 0.1507499x^{12} + 0.0532314x^{20} - 0.0469318x^{21}.$$
(12)

where

$$z_3 = \frac{3}{70\pi} \left[ 529\pi - 1377 \arccos(1/3) + 146\sqrt{2} \right]$$
  
= 2.36476838...



FIG. 3. Top: Simulation data (presented relative to the empirical expression (12) and scaled by  $\eta^{-1}$  for greater clarity) for the compressibility factor of the HS fluid at different packing fractions from Refs. 18, 19, and this work. Error bars represent estimated 95% confidence intervals (i.e., twice the estimated standard deviations) of the data values.

Bottom: Same data as in the top panel together with different empirical expressions.

The coefficients up to the cubic term were fixed at their exact values known from the virial expansion,<sup>20</sup> while others were obtained by the weighted least-squares fit to the combined simulation data from Refs. 18, 19, and this work. The powers of x were chosen to minimize the number of terms necessary to obtain the expression that agrees with the simulation data within the statistical error at all the densities up to  $\rho = 1.03$  ( $\eta = 0.5393$ ), as can be seen in the bottom panel of Figure 3.

In Figure 4, we compare the current results for  $\mu^{\text{ex}}(\sigma,\eta)$  with  $\sigma = 1, 2, 3$  and 4 to those obtained from the results for  $\gamma(\sigma,\eta)$  using the Gibbs-Cahn integration<sup>10</sup> and (5), with the pressure  $p(\eta)$  given by (12). Based on this comparison we conclude that i) the results obtained by the two methods agree within the error bar for majority of the data; ii) the two methods are complementary in that Widom's particle insertion method has higher precision at smaller  $\sigma$  and  $\eta$ , while the Gibbs-Cahn integration is more precise at larger  $\sigma$  and  $\eta$ ; iii) The BCSK expression is quite accurate at  $\sigma = 1$  for both low and high  $\eta$ , but becomes less accurate with increasing  $\eta$  for  $\sigma > 1$ .

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FIG. 4. Difference (scaled by  $\eta^{-2}$ ) between the excess chemical potential  $\mu^{\text{ex}}(\sigma, \eta)$  measured in simulations (black circles for Gibbs-Cahn integration<sup>10</sup> and red triangles for Widom's method used in this work) and the BCSK expression.



FIG. 5. Deviation (scaled by  $\eta^{-2}$ ) of  $\gamma_0^{\text{fit}}(\eta)$  in (13) from the MD simulation data<sup>16</sup>  $\gamma_0^{\text{MD}}(\eta)$ . Error bars show the 95% confidence intervals of the simulation data and filled circles show the deviations.

#### ANALYSIS OF RESULTS III.

In this Section we analyse the deviation of the excess chemical potential obtained in molecular simulations from the reference expression (10), where  $p(\eta)$  is given by (12) and  $\gamma_0(\eta)$  obtained from the precise Gibbs-Cahn measurements presented in Ref. 16. To facilitate



Deviations (scaled by  $\sigma^{-2}$ ) of the excess chemi-FIG. 6. cal potential simulation results from the expression (10) for  $\eta = 0.12$ . The results from the Widom's particle insertion simulations are shown in red. The results from the Gibbs-Cahn integration are shown with black open circles. The dotted green line represents the BCSK expression and the solid blue line and dots represent large- $\sigma$  correction (17) with  $a_0 = 2.2776 \times 10^{-3}$  and  $b_1 = 1.5087$ .

the analysis, we use the weighted least-squares approximation to the simulation data<sup>16</sup> to obtain the following polynomial expression for  $\gamma_0(x)$ ,  $x(\eta) = \eta/(1-\eta)$ ,

$$\pi \gamma_0^{\text{fit}}(x) = 3x + \frac{9}{2}x^2 - \frac{81}{70}x^3 - 0.87992x^4 + 3.58153x^5 - 4.06093x^6 + 5.68225x^8 - 6.48896x^9 + 2.32409x^{10} - 0.02681x^{33}, \quad (13)$$

where the first three coefficients were fixed at their exact values known from the virial expansion. As in the case of (12), the powers of x were chosen to minimize the number of terms. Figure 5 shows the deviation of the above expression from the simulation data. The above expression is used in the reference expression (10) to which we compare the excess chemical potential simulation results presented in this work.

As an example, the difference (scaled by  $\sigma^{-2}$ ) between the measured excess chemical potential and that obtained from the reference expression (10) is shown for  $\eta = 0.12$ in Figure 6. Similar behaviour is observed at other values of  $\eta$ , except the very high values as discussed later. We see a statistically significant deviation from the reference expression for all finite values of  $\sigma$ . The deviation is largest at small  $\sigma$  (due to the scaling), but appears to converge to a finite value as  $\sigma$  tends to zero, which indicates consistency of the simulation results with the values of  $c_0(\eta)$  and  $c_1(\eta)$  given by (3).

We also plot the scaled difference between the BCSK and reference expressions, which looks like a straight line with respect to  $\sigma$  because  $c_0(\eta)$  and  $c_1(\eta)$  are the same in both expressions, so

$$\frac{\mu_{\text{BCSK}}^{\text{ex}} - \mu_{\text{ref}}^{\text{ex}}}{\sigma^2} = c_2(\eta) - \pi \gamma_0(\eta) + [c_3(\eta) - \frac{1}{6}\pi p(\eta)]\sigma.$$
(14)

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6

5

4

3

2

0

FIG. 7.

0

0.1

 $C_l(\sigma, \eta)$  coefficients

In order for this expression to converge to 0 as  $\sigma \to \infty$ , m and n must satisfy the condition m < n.

 $a_0(\eta)\eta^{-3}$ 

 $a_0^{\mathrm{fit}}(\eta)\eta^{-3}$ 

0.3

 $\eta$ 

from the nonlinear weighted least-squares approximation to

the Widom results for  $\sigma \ge 0.6$  and Gibbs-Cahn results. The errorbars denote estimated confidence intervals. The fitted

Coefficients of the large- $\sigma$  correction (17) obtained

0.4

(15)

τ

 $b_1(\eta)$ ₮

 $b_1^{\text{fit}}(\eta)$ 

₫

0.2

When we tried to determine coefficients  $a_i$  and  $b_k$  by weighted least-squares approximation for the whole range of  $\sigma$  values, we found that the small- $\sigma$  behaviour is difficult to approximate using small m and n. On the other hand, the deviations from the reference expression at  $\sigma$ larger than about 0.6 can be well approximated by the simple Padé approximant with m = 0 and n = 1. (This can be seen in Figure 6 for  $\eta = 0.12$ , where we used the Widom results for  $\sigma > 0.6$  and Gibbs-Cahn results in the non-linear weighted least-squares approximation to determine  $a_0$  and  $b_1$ .) Therefore, we model the deviations of the simulation results from the MT expression as the sum of the large- $\sigma$  and small- $\sigma$  corrections

$$\frac{\mu^{\text{ex}}(\sigma,\eta) - \mu^{\text{ex}}_{\text{ref}}(\sigma,\eta)}{\sigma^2} = C_l(\sigma,\eta) + C_s(\sigma,\eta), \qquad (16)$$

where

$$C_l(\sigma, \eta) = \frac{a_0(\eta)}{1 + b_1(\eta)\sigma} \,. \tag{17}$$



FIG. 8. Coefficients of the small- $\sigma$  correction (18) obtained from the nonlinear weighted least-squares approximation to the Widom results for  $\sigma \leq 1.0$ . The errorbars denote estimated confidence intervals. The fitted curves are polynomials in  $x = \eta/(1 - \eta)$  given by (26).

The small- $\sigma$  correction is fast decaying with increasing  $\sigma$ , as can be seen in Figure 6, so we model it with an exponential function

$$C_s(\sigma, \eta) = d(\eta) e^{-\sigma/\delta(\eta)}.$$
(18)

To obtain the coefficients  $a_0(\eta)$  and  $b_1(\eta)$  in (17), we used the Widom results for  $\sigma \geq 0.6$  and Gibbs-Cahn results<sup>10</sup> in the nonlinear weighted least-squares approximation of the expression  $[\mu^{ex}(\sigma,\eta) - \mu^{ex}_{ref}(\sigma,\eta)]\hat{\sigma}^{-2}$  at each  $\eta$ . Thus obtained values of  $a_0(\eta)$  (scaled by  $\eta^{-3}$ ) and  $b_1(\eta)$  for all  $\eta$  are shown in Figure 7 together with the following expressions obtained via weighted least-squares approximation to polynomials in  $x = \eta/(1-\eta)$ 

$$a_0^{\text{fit}}(x)\eta^{-3} = 0.9292 + 2.4542x + 3.6897x^2 - 5.5175x^3 + 3.3412x^4 ,$$
  

$$b_1^{\text{fit}}(x) = 1.7694 - 2.5851x + 5.437x^2 - 2.2655x^3 - 1.5928x^4 .$$
(19)

It is interesting to consider how the large- $\sigma$  correction is reflected in the Taylor series (7) of  $\gamma(\sigma, \eta)$  by comparing the terms  $\gamma_n(\eta)$  to their exactly known virial  $expansions^{21,22}$ 

$$\pi\gamma_1(\eta) = 3\eta + 3\eta^2 + \left(\frac{81\sqrt{3}}{16\pi} + \frac{24}{35}\right)\eta^3 + \mathcal{O}(\eta^4), (20)$$

$$\pi\gamma_2(\eta) = \eta + \frac{1}{2}\eta^2 + \left(\frac{81\sqrt{3}}{16\pi} - \frac{289}{105}\right)\eta^3 + \mathcal{O}(\eta^4), (21)$$

$$\pi\gamma_3(\eta) = \frac{9\sqrt{3}}{20\pi}\eta^3 + \mathcal{O}(\eta^4).$$
(22)

From the expression  $\mu_{\rm ref}^{\rm ex}(\sigma,\eta) + C_l(\sigma,\eta)\sigma^2$  we have

$$\pi \gamma_1(\eta) = c_1(\eta) + \frac{a_0(\eta)}{b_1(\eta)}, \qquad (23)$$

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FIG. 9. Deviation of the measured excess chemical potential,  $\mu^{\text{ex}}(\sigma,\eta)$ , from different empirical expressions,  $\mu^{\text{ex}}_{\text{emp}}(\sigma,\eta)$ , relative to the estimated standard deviation of the simulation results,  $S(\sigma,\eta)$ : a)  $\mu^{\text{ex}}_{\text{emp}}(\sigma,\eta) = \mu^{\text{ex}}_{\text{BCSK}}(\sigma,\eta)$ ; b)  $\mu^{\text{ex}}_{\text{emp}}(\sigma,\eta) = \mu^{\text{ex}}_{\text{ref}}(\sigma,\eta)$ ; c)  $\mu^{\text{ex}}_{\text{emp}}(\sigma,\eta) = \mu^{\text{ex}}_{\text{ref}}(\sigma,\eta) + C_l(\sigma,\eta)\sigma^2$ ; d)  $\mu^{\text{ex}}_{\text{emp}}(\sigma,\eta) = \mu^{\text{ex}}_{\text{ref}}(\sigma,\eta) + C_l(\sigma,\eta)\sigma^2$ .

$$\pi \gamma_2(\eta) = c_0(\eta) - \frac{a_0(\eta)}{b_1^2(\eta)}, \qquad (24)$$

$$\pi \gamma_3(\eta) = \frac{a_0(\eta)}{b_1^3(\eta)} \,. \tag{25}$$

Given the Taylor series for  $c_1(\eta) = 3\eta/(1-\eta) = 3\eta + 3\eta^2 + 3\eta^3 + \mathcal{O}(\eta^4)$  and  $c_0(\eta) = -\ln(1-\eta) = \eta + \frac{1}{2}\eta^2 + \frac{1}{3}\eta^3 + \mathcal{O}(\eta^4)$ , we see that the virial and the reference expressions match for the  $\eta$  and  $\eta^2$  terms for all  $\gamma_n(\eta)$ , n = 1, 2, 3. The  $\eta^3$  coefficient in (20) is  $\approx 3.4768$  compared to  $3 + 0.9292/1.7694 \approx 3.5251$  from (23) and (19). For  $\gamma_2(\eta)$  we get the  $\eta^3$  coefficient  $\approx 0.03872$  from (21) compared to  $1/3 - 0.9292/1.7694^2 \approx 0.03658$  from (24) and (19). Finally, the  $\eta^3$  coefficient is  $\approx 0.2481$  from (22) compared to  $0.9292/1.7694^3 \approx 0.1677$  from (25). This comparison demonstrates a fairly good agreement between the empirical expressions obtained from fitting the simulation data and the virial expressions for  $\gamma_n(\eta)$  in (7).

Another approach could be to use the virial expressions in order to fix the leading terms of polynomial approximations of  $a_0(\eta)$  and  $b_1(\eta)$ . From the virial expressions (20) and (21), the leading terms in (19) would be

$$a_0(\eta)\eta^{-3} = 0.7717 + \mathcal{O}(\eta),$$
  
 $b_1(\eta) = 1.6185 + \mathcal{O}(\eta).$ 

The  $\eta^3$  coefficient in (25) would now become  $0.7717/1.6185^3 \approx 0.182$ , which is somewhat closer to the value 0.2481 of the virial coefficient in (22), but doesn't match it exactly. In order to get the exact match for all exactly known virial coefficients, we would have to retain more terms in the Padé approximant (15), introducing at least two more parameters  $a_1(\eta)$  and  $b_2(\eta)$ . However, using a more complicated expression for the large- $\sigma$  correction makes the data fitting process less stable.

The coefficients of the small- $\sigma$  correction (18) were obtained from the nonlinear weighted least-squares approximation of the Widom results in the expression  $[\mu^{\text{ex}}(\sigma,\eta)-\mu^{\text{ex}}_{\text{ref}}(\sigma,\eta)]\sigma^{-2}-C_l(\sigma,\eta)$  at each  $\eta$  and  $\sigma \leq 1.0$ . The results are shown in Figure 8 together with the weighted least-square approximation to polynomials in  $x = \eta/(1-\eta)$ 

$$d^{\text{fit}}(x)\eta^{-3} = 0.5105 - 1.5467x + 11.285x^2 - 14.7402x^3 + 5.9413x^4,$$



FIG. 10. Oscillatory behaviour of excess chemical potential at large packing fractions. The reference expression and large- $\sigma$  correction are subtracted from the simulation results for greater clarity.

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fit(x) = 
$$0.1162 + 0.4183x - 2.6166x^2 + 5.4973x^3 - 5.281x^4 + 1.9846x^5$$
. (26)

The observed in Figure 8 scatter of the results for  $d(\eta)\eta^{-3}$  at  $\eta > 0.4$  is not due to statistical uncertainly of our measurements, but is rather related to the oscillatory behaviour of  $\mu^{\text{ex}}(\sigma,\eta)$  at large  $\eta$ , which we will discuss later. So, the simple exponential form of the small- $\sigma$  correction is well suited for  $\eta < 0.4$ , while for larger  $\eta$  a more complicated form of this correction is necessary to adequately fit the simulations.

The accuracy of different empirical expressions compared to the simulation results is shown in Figure 9, where the differences between the simulation results and the empirical expressions are shown relative to the estimated standard deviation of the simulation results,  $\frac{\mu^{\text{ex}}(\sigma,\eta)-\mu^{\text{ex}}_{\text{emp}}(\sigma,\eta)}{S(\sigma,\eta)}$ . We present the differences for four different empirical expressions: a) BCSK, given by (2) with the coefficients from (3) and (4); b) reference expression (10); c) reference expression with the large- $\sigma$  correction (17), where  $a_0(\eta)$  and  $b_1(\eta)$  are given by (19); d) reference expression with both large- $\sigma$  and small- $\sigma$  corrections (18), where the coefficients in the small- $\sigma$  correction are given by (26).

We see that the BCSK expression is quite accurate for  $\sigma = 1$ , but deviates from the simulation results for both smaller and larger  $\sigma$ . The reference expression is not accurate at larger  $\eta$ , but has correct asymptotic behaviour at small  $\eta$  and in the limits  $\sigma \to 0$  and  $\sigma \to \infty$ . The large- $\sigma$  correction to the reference expression gives accurate result for  $\sigma$  larger than about 0.6, while addition of the small- $\sigma$  correction restores accuracy also at smaller  $\sigma$  except at  $\eta$  larger than about 0.35, where we observe the emergence of oscillations. These oscillations are seen in more details in Figure 10 and are likely to be the pre-



FIG. 11. Consistency test (27) for the simulation data (denoted 'MD' in the legend) and several empirical expressions for the excess chemical potential: 'BCSK' refers to the BCSK expression (2-4), 'ref' is the reference expression (10), and 'ref +  $C_l$ ' is the reference expression plus the large- $\sigma$  correction  $C_l(\sigma, \eta)\sigma^2$  defined in (17), (19).

cursor of the emergent crystalline order in the HS fluid at packing fractions near the freezing value of  $\eta = 0.492$ .

Considering HS binary mixtures, Smith and Labík<sup>23</sup> have derived the following consistency test for a HS fluid of diameter 1 mixed with infinitely diluted spheres of diameter  $\sigma$ :

$$\Delta_{\text{test}}(\eta) \equiv \left. \frac{1}{3} \frac{\partial \mu^{\text{ex}}(\sigma, \eta)}{\partial \sigma} \right|_{\sigma=1} + 1 - z(\eta) = 0. \quad (27)$$

In Figure 11, we show the deviation of this expression from zero for the simulation data, as well as several empirical expressions. The partial derivative for the simulation data is approximated by centered difference formula

$$\left. \frac{\partial \mu^{\mathrm{ex}}(\sigma,\eta)}{\partial \sigma} \right|_{\sigma=1} \approx \frac{\mu^{\mathrm{ex}}(1.01,\eta) - \mu^{\mathrm{ex}}(0.99,\eta)}{0.02},$$

while the empirical expressions are differentiated analytically. We use (12) for the compressibility factor  $z(\eta)$ . We see from the Figure that the simulation results are consistent with the test at all values of  $\eta$ . Among the empirical expressions, the reference expression (10) shows deviation from the test with increasing  $\eta$ , while the BCSK expression passes the test reasonably well, except at the highest  $\eta$ . The reference expression with the large- $\sigma$  correction,  $\mu_{\text{ref}}^{\text{ex}}(\sigma, \eta) + C_l(\sigma, \eta)\sigma^2$ , is better than the BCSK at small and moderate  $\eta$ , but exhibits similar deviation at large  $\eta$ . Adding the small- $\sigma$  correction does not change the behaviour, as its contribution is negligibly small at  $\sigma = 1$ .

In the last part of our analysis of the simulation results, we focus on  $\mu^{\text{ex}}(\sigma = 1, \eta)$ , which is the excess chemical potential of the HS fluid at packing fraction  $\eta$ . In Figure 12 we show the deviations (scaled by  $\eta^{-2}$  for greater

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FIG. 12. Differences (scaled by  $\eta^{-2}$ ) between the simulation results and different empirical expressions,  $\mu_{\rm emp}^{\rm ex}$  at  $\sigma = 1$ . In the legend, 'BCSK' refers to the BCSK expression, 'ref +  $C_l$ ' refers to  $\mu_{\rm ref}^{\rm ex}(1,\eta) + C_l(1,\eta)$ , and 'fit' refers to  $\mu_{\rm fit}^{\rm ex}(x(\eta))$  in (28). The error bars denote estimated 95% confidence intervals in the simulation results. A magnification of the middle part of the plot is shown in the inset.

clarity) of various empirical expressions from the simulations results. We see that  $\mu_{\rm ref}^{\rm ex}(1,\eta) + C_l(1,\eta)$  is more accurate than the BCSK expression, although the deviations exceed the statistical errors because of the use of polynomial approximations (19) for the coefficients of  $C_l$ in (17). The expression that is within the error bars of the simulation data for all  $\eta$  can be expressed as a polynomial with respect to  $x = \eta/(1 - \eta)$ 

$$u_{\rm fit}^{\rm ex}(x) = 8x + 7x^2 + 2.48813x^3 - 1.20146x^4 + 1.67614x^5 - 1.84192x^6 + 1.00149x^7 + 0.99064x^8 - 2.01853x^9 + 0.93424x^{10},$$
(28)

whose first two coefficients have been fixed at their exactly known values, while others obtained via the weighted least-square fit to the simulation results at  $\sigma = 1$ .

# IV. SUMMARY

We have performed a series of high-resolution molecular-dynamics (MD) simulations to determine via Widom's particle insertion method the excess chemical potential  $\mu^{\text{ex}}(\sigma,\eta)$  of a sphere of diameter  $\sigma$  immersed in the HS fluid with sphere diameter 1 and packing fraction  $\eta$ . From the considerations of Morphometric Thermodynamics (MT), the dependence of  $\mu^{\text{ex}}$  on  $\sigma$  has to follow a cubic polynomial with the  $\eta$ -dependent coefficients dictated by the limiting behaviour at  $\sigma \to \infty$ , which include the HS fluid equation of state  $p(\eta)$  and the surface free energy at a hard planar wall  $\gamma_0(\eta)$ . On the other, hand, the exactly known coefficients of the polynomial expansion in powers of  $\sigma$  near  $\sigma = 0$  differ from those predicted by the MT, so the cubic polynomial dependence of  $\mu^{\text{ex}}$ on  $\sigma$  is not consistent in the limits  $\sigma \to \infty$  and  $\sigma \to 0$ .

By combining the results of the Widom's particle insertion method with those from the Gibbs-Cahn method for calculating the surface free energy of the HS fluid at a spherical wall,<sup>10</sup> we observe deviation of the simulation results from the cubic polynomial dependence and propose empirical correction expressions for large and small  $\sigma$  which encode this deviation. Thus obtained empirical expression  $\mu_{\rm ref}^{\rm ex}(\sigma,\eta) + C_l(\sigma,\eta)\sigma^2 + C_s(\sigma,\eta)\sigma^2$ reproduces with high accuracy the simulation results, except in the large  $\eta$  region where the simulation results exhibit oscillations which could be a precursor of the crystalline structure in the HS fluid near the freezing transition.

### DATA AVAILABILITY

The simulation results for the excess chemical potential  $\mu^{\text{ex}}(\sigma,\eta)$  of a sphere of diameter  $\sigma$  immersed in the HS fluid with sphere diameter 1 and packing fraction  $\eta$  obtained via Widom's particle insertion method and the compressibility factor of the HS fluid at different  $\eta$  obtained from the collisional virial calculations are openly available in the University of Leicester Research Archive at https://doi.org/10.25392/ leicester.data.20278443.v1.

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