Three hard spheres in a spherical cavity

Ignacio Urrutia[a)]
Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Av. Rivadavia 1917, RA-1033, Buenos Aires, Argentina and Departamento de Física de la materia condensada, Comisión Nacional de Energía Atómica, Av. Gral. Paz 1499 (RA-1650) San Martín, Buenos Aires, Argentina

(Received 28 March 2011; accepted 18 June 2011; published online 13 July 2011)

This work is devoted to furthering the understanding of few- and many-body inhomogeneous systems in the framework of the statistical mechanics of fluids. The three-body system consisting in three hard spheres (HS) confined in a spherical cavity at constant temperature is studied. Its canonical ensemble partition function and thermodynamic properties (such as the free energy, pressures, and fluid-substrate surface tension) are analytically obtained as a function of the cavity radius. This is the first time that a three-body fluid-like system is exactly solved. Symmetry relations between this system and its dual system composed of three HS surrounding a hard spherical object are analyzed. They allow to analytically obtain the canonical partition function of the dual system and its thermodynamic properties. Finally, the behavior of the many-body system of HS in contact with a hard spherical wall in the low density limit, is studied, focusing on the curvature dependence of the fluid-substrate surface tension and finding exact expressions for the Tolman's length and the second order term in curvature. © *2011 American Institute of Physics*. [doi:10.1063/1.3609796]

I. INTRODUCTION

The exact study of few-body systems played an important role in the development of several branches of the physical science. Some examples are the two-body mutually orbiting system in classical and relativistic mechanics, as well as the one electron atom in quantum mechanics. On the contrary, the few-body systems were largely ignored in statistical mechanics. Recently, the statistical mechanical properties of several two-body systems of simple particles were exactly determined.[1–4] These works analytically evaluate the partition function of two confined particles and trace the path to the thermodynamic interpretation of its properties in an exact framework. The novel thermodynamic approach enables the exact evaluation of the thermodynamic properties without claiming the usual thermodynamic limit that only applies to systems of many particles in large volumes.[3] In the first instance such a treatment was focused on hard potentials but later it was extended to more realistic interactions.[4]

The present work is part of a series of papers whose main goal is to advance in the understanding of the statistical mechanics and thermodynamic properties of fluid-like small inhomogeneous systems of confined particles. In particular, this work is devoted to obtain the exact solution of the three-body system of hard spheres (HS) confined in a hard wall spherical cavity (HSC), the 3-HS-HSC system, and also to establish a connection between this and other systems.

The structure of the paper is as follows: Sec. II is devoted to analytically obtain the canonical ensemble partition function of the 3-HS-HSC system over all density ranges going from the smallest radius, or caging limit, to $R \to \infty$. The canonical partition function for its dual, or conjugated, system composed of 3-HS outside a hard spherical object is also presented. In Sec. III, the thermodynamic properties of both systems and the symmetries between them are analyzed. There the exact curvature dependence of their fluid-substrate surface tension is derived. In addition, the HS many-body system in contact with hard spherical substrates is studied in the low density limit, both for the concave and convex curved surfaces. An interesting result presented in this section is the exact dependence of the (fluid-substrate) Tolman's length up to the first order in density. Finally, the main conclusions are summarized in Sec. IV.

II. PARTITION FUNCTION

I consider a system composed of $N = 3$ particles confined in some region of the space by the action of an external potential $\varphi = \sum \varphi(\mathbf{r}_i)$. Each pair of particles interacts via a two-body potential $\phi(\mathbf{r}_{ij})$, which produces an interaction potential between particles $\phi = \sum \phi(\mathbf{r}_{ij})$. The classical canonical partition function of such a system is given by

$$Q = \Lambda^{-3D}\, \mathrm{I}_3\, Z_3, \tag{1}$$

$$Z_3 = \iiint e_{\mathrm{A}} e_{\mathrm{B}} e_{\mathrm{C}} e_{\mathrm{AB}} e_{\mathrm{BC}} e_{\mathrm{AC}}\, d\mathbf{r}_{\mathrm{A}} d\mathbf{r}_{\mathrm{B}} d\mathbf{r}_{\mathrm{C}}\ , \tag{2}$$

where Z_3 is the configuration integral (CI), $\Lambda = \mathrm{h}/(2\pi m\, k_B T)^{1/2}$ is the thermal de Broglie wavelength, T denotes the temperature, $\beta = (k_B T)^{-1}$ is the inverse temperature, k_B is the Boltzmann constant, h is the Planck's constant, and D is the dimension of the space. I_3 in Eq. (1) is a constant factor equal to $1/3!$ or 1 for the case of identical indistinguishable particles or distinguishable particles, respectively. In Eq. (2) $e_{ij} = \exp[-\beta\phi(\mathbf{r}_{ij})]$, $e_i = \exp[-\beta\varphi(\mathbf{r}_i)]$, with $e_i = 0$ if the i-particle is outside of the confinement region and the domain of the integrals is

a)Author to whom correspondence should be addressed. Electronic mail: iurrutia@cnea.gov.ar.

the complete space. This convention about the integration domain is adopted for all the spatial integrals in the present work. The thermodynamic connection is established by relating in the usual way the partition function to the Helmholtz free-energy,

$$F = -\beta^{-1} \ln(Q). \tag{3}$$

The CI of an N-particles system can be expressed in terms of the CI of the k-particles system with $1 \leq k \leq N$. Thus, for three particles is

$$Z_3 = -2Z_1^3 + 3Z_1 Z_2 + \tau_3, \tag{4}$$

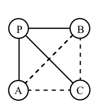
$$Z_2 = Z_1^2 + \tau_2, \tag{5}$$

where the τ_k are the cumulants or semi-invariants of Thiele [also called Ursell functions[5], (p. 135)]. τ_k is an integral over the available configuration space of k-particles[5] (p. 126). In the theory of real gases it is assumed that $\tau_k \equiv k! V b_k$, where V represents the *volume* of the system. In particular, for homogeneous systems in a large enough V the k-th-cluster integral $b_k = b_k(\infty)$ is a pure function of T (independent of both V and the shape of the vessel). In this work it is used the notation $\tau_k \equiv k! Z_1 b_k(p)$ to emphasize that $b_k(p)$ and τ_k depend on the characteristics of the vessel that confines the system, herefrom the *pore*. This dependence is produced by the external potential and implicitly contains the geometrical attributes associated with the shape of the pore.

Now I will consider the CI of 3-HS confined by a hard wall potential in a physical region $\Omega \subset \mathbb{E}$, where $\mathbb{E} = \mathbb{R}^3$ is the euclidean space and Ω is its subset. Particularly, I will focus on a spherical cavity given by $\Omega = \Omega_{\text{sph}}$, which defines the 3-HS-HSC system. To keep a simple notation I fix the hard repulsion distance between particles σ as the unit length ($\sigma = 1$). Therefore, the radius of the empty cavity is $R + 1/2$, being R the effective radius. For this system one can write

$$e_i(\mathbf{r}) = \begin{cases} 1, & \text{if } \mathbf{r} \in \Omega_{\text{sph}} \\ 0, & \text{if } \mathbf{r} \notin \Omega_{\text{sph}}\,. \end{cases} \tag{6}$$

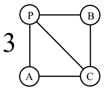
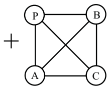
It is a unit-step *in*-function, being $e_i = 1$ if the i-particle is in the spherical pore and zero otherwise. On the other hand, e_{ij} is a unit-step *out*-function, for which $e_{ij} = 1$ if the j-particle is outside of the hard-core of the i-particle and zero otherwise. For the HS-HSC system $Z_1(R)$ and $Z_2(R)$ are known functions.[2] Equation (4) shows that the knowledge of τ_3 allow obtaining the analytic expression for $Z_3(R)$. The graph representation of the CI given in Eq. (2) is

$Z_3 =$  , (7)

where the continuous lines indicate the *in*-bonds, while the dashed lines are used to mark the *out*-bonds. The cumulant τ_3 is obtained from Eq. (7) by replacing

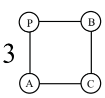
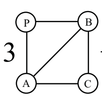
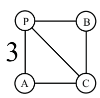
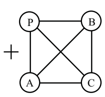
$$e = 1 + f, \tag{8}$$

for each e_{ij}-bond and taking only the ABC connected graphs, or ABC-clusters, which consist of graphs that are at least simply connected by f_{ij}-bonds. Since each topologically different labeled ABC-cluster appears once time in τ_3,

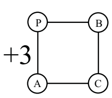
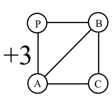
$\tau_3 = 3$  $+$  ,

$$= \iiint e_A e_B e_C (3 f_{BC} f_{AC} + f_{AB} f_{BC} f_{AC})\, d\mathbf{r}_A d\mathbf{r}_B d\mathbf{r}_C, \tag{9}$$

where the factor 3 results from the three different clusters with the same value. Note that $-f_{ij}$ is an *in*-function and I have adopted a convention in which each f_{ij}-bond involves an implicit -1 factor. Hence, the left hand side graph in Eq. (9) is positive, but the right hand side one is negative. This latter graph, the fully connected or star graph of four vertex, is the most difficult integral to be analytically solved. In the last years, the term $B_4^{[1]}(s)$ one of the three parts of the fourth virial coefficient for a HS binary fluid mixture (with hard repulsion diameters $\sigma_1 = 1$ and $\sigma_2 = s$) was analytically evaluated. The expression for $B_4^{[1]}(s)$ was first obtained by Blaak[6] for $0 \leq s \leq 2/\sqrt{3} - 1$. Recently, Labík and Kolafa presented the expression for $B_4^{[1]}(s)$ in the range $s \geq 2/\sqrt{3} - 1$ (see Eqs. (6) and (32) in Refs. 7 and 8). $B_4^{[1]}(s)$ relates to the 3-HS-HSC system through the replacement $s = 2R - 1$ and the relation[7]

$8B_4^{[1]}(R) = -3$  -3  $+3$  $+$  . (10)

From Eqs. (9) and (10) it follows that

$\tau_3 = 8\, B_4^{[1]}(R) + 3$  $+3$  . (11)

The analytical expression for all the non-star graphs that appear in Eqs. (9)–(11) were already calculated and are summarized in Appendix.[6] From Eqs. (4), (10), and (11) it is possible to obtain the analytical expressions for τ_3, the star-graph, and Z_3. By introducing the minimum pore radius $R_{\min} = 1/\sqrt{3}$, Z_3 can be written as

$$Z_3 = \begin{cases} h, & \text{if } R \geq 1 \\ h + \Delta\tau_3, & \text{if } R_{\min} \leq R < 1 \\ 0, & \text{if } 0 \leq R < R_{\min}, \end{cases} \tag{12}$$

$$h = \frac{\pi^2}{70}\left[\frac{1}{9} q (65 + 183R^2 - 342R^4 + 240R^6) - \frac{9}{2} p_1 (5 + 12R^2) + p_2 R (105 - 280R^2 + 840R^4 - 1152R^6 + 640R^8)\right], \tag{13}$$

$$q = \sqrt{3R^2 - 1}, \quad p_1 = \arctan(2q), \quad p_2 = \arctan(q/R), \tag{14}$$

$$\Delta\tau_3 = \frac{64}{945}\pi^3(-10 + 81R^2 - 105R^3 + 105R^6 - 81R^7 + 10R^9), = -\frac{128}{189}\pi^3(1-R)^5\left(1 + 5R + \frac{69}{10}R^2 + 5R^3 + R^4\right), \tag{15}$$

where for $0 \leq R < R_{\min}$ the three particles do not fit in the pore and in consequence $Z_3(R) = 0$. Equation (12) shows that $Z_3(R)$ is a continuous non-analytic function with two non-analytic points at $R = R_{\min}$ and $R = 1$. For the case $R = 1$ there is a discontinuity in its fifth-order derivative. The analytic behavior of Z_3 in the caging limit $R \to R_{\min}$ (with $R \gtrsim R_{\min}$) is given by

$$Z_3 = \frac{9216\, 3^{3/4}\sqrt{2}}{385}\pi^2\left(R - \frac{1}{\sqrt{3}}\right)^{11/2}\left[1 - \frac{3}{4*13}\times\left(R - \frac{1}{\sqrt{3}}\right)\right] + O\left[\left(R - \frac{1}{\sqrt{3}}\right)^{15/2}\right], \tag{16}$$

that is discontinuous in its sixth-order derivative at $R = R_{\min}$. On the other hand, the expression of τ_3 is

$$\tau_3 = \begin{cases} \frac{2\pi^3}{945}\left(320 - 2592R^2 + 3465R^3 - 1890R^5 + 2592R^7 - 1440R^9\right) + h + \Delta\tau_3\,\Theta(1-R), & \text{if } R \geq R_{\min} \\ \frac{2\pi^3}{27}R^3\left(3 - 54R^2 + 96R^3 - 32R^6\right), & \text{if } \frac{1}{2} \leq R < R_{\min} \\ \frac{128\pi^3}{27}R^9, & \text{if } 0 \leq R < \frac{1}{2}, \end{cases} \tag{17}$$

where $\Theta(R)$ is the Heaviside unit-step function and $\tau_3(R)$ is a continuous non-analytic function with three non-analytic points at $R = 1/2$, $R_{\min}$ and $R = 1$. The dependence of the star-graph on R is presented in Appendix.

The one-body density distribution $\rho(\mathbf{r})$ develops a homogeneous density central plateau for $R > 2$, which extends in the region $0 \leq r \leq R - 2$. This homogeneous density is given by

$$\rho_h(r) = 3Z_3^{-1}Z_2(R, l = R - 1), \tag{18}$$

where $Z_2(R, l)$ corresponds to the CI of the 2-HS-HSC with a central hard core with radius l.[9] Equation (18) also gives for $R > 1$ the density at the center of the pore, $\rho_0(R)$, which is zero for $R_{\min} < R < 1$. The density plateau is superimposed on a constant pressure plateau. It is interesting to mention that in a region of constant density the several different definitions for the pressure tensor converge to a unique and well defined scalar pressure. Indeed, for systems of two confined HS it was demonstrated that the scalar pressure in the plateau region is equal to the thermodynamic pressure.[3] Other important characteristic of $\rho(\mathbf{r})$ is its contact value $\rho_c = \rho(r = R)$, which is related to Z_3 by[9]

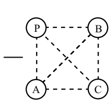
$$\rho_c = 3^{-1}\left(4\pi R^2\right)^{-1} Z_3^{-1}\partial Z_3/\partial R. \tag{19}$$

A. The dual system

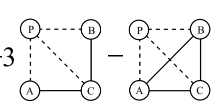
In the paragraphs above it was solved the CI of 3-HS confined in a spherical cavity, that is in a region where $\Omega = \Omega_{\rm sph}$. However, the analysis developed in Eqs. (1)–(9) can also be successfully applied to non-spherical cavities and unbounded regions of the space. Here, I consider 3-HS confined in the complement set of $\Omega_{\rm sph}$ defined as $\Omega = \bar{\Omega}_{\rm sph} = \mathbb{E}\backslash\Omega_{\rm sph}$ (note that for physical purposes the inclusion of the common boundary in $\Omega_{\rm sph}$ or $\bar{\Omega}_{\rm sph}$ has not relevance). This Ω region corresponds to the exterior of a hard spherical object (HSO) and thus defines the 3-HS-HSO system. In order to establish the relationship between the CI functions associated with the 3-HS-HSC and the 3-HS-HSO systems, I introduce the notation $\tilde{Z}_N$ for the CI of an N-particles system confined in $\bar{\Omega}_{\rm sph}$ and $\tilde{\tau}_i$ for its i-th order cumulant. Therefore, for the 3-HS-HSO it follows that

$$\tilde{Z}_3 = -2\tilde{Z}_1^3 + 3\tilde{Z}_1\tilde{Z}_2 + \tilde{\tau}_3. \tag{20}$$

Note that, if e_i given in Eq. (6) were re-defined as: $e_i(\mathbf{r}) = 1$ if $\mathbf{r} \in \Omega$ and zero otherwise, all the graph notation in Eqs. (7)–(11) would be still valid for the $\bar{\Omega}_{\rm sph}$-constrained system. However, I keep Eq. (6) unmodified to relate all the graph description to the $\Omega_{\rm sph}$ region. Thus, the CI of the 3-HS-HSO system is

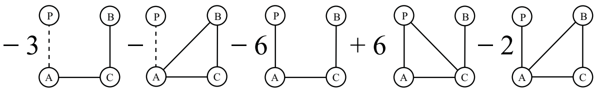
$\tilde{Z}_3 = -$  , (21)

where each dashed line between the pore and a particle is an f_i-bond that corresponds to the f_i function. The functions f_i and e_i are related to each other by Eq. (8). It is evident that $-f_i$ is an *out*-function ($f_i(\mathbf{r}) = -1$ if $\mathbf{r} \notin \Omega_{\rm sph}$ and zero otherwise). In this context, Eq. (9) for 3-HS-HSO is

$\tilde{\tau}_3 = -3$  . (22)

Using Eq. (8) each f_i-bond is replaced to obtain

$$\tilde{\tau}_3 = -8B_4^{[1]}$$



(23)

where $B_4^{[1]}$ is the same term that appears in Eq. (10). The graphs in Eq. (23) are reducible because they have articulation nodes.[5] The irreducible graphs in terms of which these reducible graphs can be factorized are summarized in the Appendix. The obtained expression for $\tilde{\tau}_3$ is

$$\tilde{\tau}_3 = \begin{cases} \frac{9\pi^2}{2}V_\infty + \frac{\pi^3}{3780}\big(1345 - 23652R^2 - 27720R^3 \\ +15120R^5 - 20736R^7 + 11520R^9\big) - h\,\Theta(R - R_{\min}), & \text{if } R \geq \frac{1}{2} \\ \frac{9\pi^2}{2}V_\infty + \frac{2\pi^3}{27}\left(-243R^3 + 192R^6 - 64R^9\right), & \text{if } 0 \leq R < \frac{1}{2}, \end{cases} \tag{24}$$

where V_∞ is the volume of $\mathbb{R}^3$. Thus, given that $\tilde{Z}_1$ and $\tilde{Z}_2$ are known[2,3] Eq. (20) provides the exact analytical expression for $\tilde{Z}_3$ in the range $R > 0$. The complete expression for $\tilde{Z}_3$ due to its extension is not presented.

III. THERMODYNAMICS

In Refs. 3 and 4 it was developed a thermodynamic approach suitable to study the properties of few-body inhomogeneous systems in the case that its partition function (and therefore its free energy, F) is analytically known. Here, I briefly present the procedure followed in those works and apply it to study the 3-HS spherically confined system.

Basically, the thermodynamic description for both few- and many-body inhomogeneous systems in a unified approach is done by introducing a set of thermodynamic measures **M**. These measures are generalizations of the concept of extensive variables, which characterize the spatial region where the fluid is confined. Typically, **M** includes the measures of volume and area although the surfaces curvature, edges length and some length parameters characterizing the geometry of the confinement cavity can be also taken into consideration. To implement this thermodynamic approach it is necessary to unambiguously define each measure that belongs to **M**. Additionally, it is necessary to introduce a decomposition rule in order to identify the dependence of the free energy on the elements of **M**. It must be noted that the definition of both **M** and the decomposition rule are not innocuous to the obtained thermodynamic properties.

To study the fluid-like system under spherically symmetric conditions I analyze two different sets of thermodynamic measures. In the first case I select $\mathbf{M} = \{V, A, \mathsf{J}, \mathsf{K}, R\}$ where V, A, J, and K represent the measures of the volume, area, and the mean and Gaussian extensive-like curvatures, respectively. The adopted definitions and their values for the region $\Omega = \Omega_{sph}$ are $V \equiv Z_1 = 4\pi R^3/3$, $A \equiv \int |\nabla e_A(\mathbf{r})|\, d\mathbf{r} = 4\pi R^2$, $\mathsf{J} = -4\pi \int r^2 \mathsf{j}(r)\partial_r e_A dr = 8\pi R$, and $\mathsf{K} = \frac{1}{2}4\pi \int r^2 \mathsf{k}(r)|\partial_r e_A| dr = 4\pi$ with $\mathsf{j}(r) = 2r^{-1}$ and $\mathsf{k}(r) = r^{-2}$. The same definitions were also utilized in the study of a few-body spherically inhomogeneous system of interacting particles.[4] The set **M** is complemented with a decomposition rule, which identifies the components of each measure in τ_i. I adopt the rule

$$\tau_i/i! = Z_1 b_i(p) = V\,b_i - A\,a_i + \mathsf{J}\,c_{i,\mathsf{J}} + \mathsf{K}\,c_{i,\mathsf{K}} + S_i(R^{-1}), \tag{25}$$

where $\{b_i, a_i, c_{i,\mathsf{J}}, c_{i,\mathsf{K}}\}$ are constant coefficients and $S_i(R^{-1})$ is a series in positive powers of R^{-1}. This first approach focus on the extensive-like thermodynamic variables used to describe curved interfaces.[10,11] Using Eqs. (4), (17), and (25) I obtain for the 3-HS-HSC system with $R > 1$,

$$Z_3 = V^3 + 6V^2 b_2 + 6Vb_3 - 6VA\,a_2 + 6V\mathsf{J}\,c_{2,\mathsf{J}} + 6V\mathsf{K}\,c_{2,\mathsf{K}} - 6A\,a_3 + 6\mathsf{J}\,c_{3,\mathsf{J}} + 6\mathsf{K}\,c_{3,\mathsf{K}} + 6V\,S_2(R^{-1}) + 6S_3(R^{-1}), \tag{26}$$

where $S_3(R^{-1})$ is represented by an odd power series in R^{-1},

$$S_3(R^{-1}) = \frac{\sqrt{3}\pi^2}{16}\left(\frac{R^{-1}}{60} + \frac{7R^{-3}}{14400} + \frac{R^{-5}}{28224} + \frac{449R^{-7}}{121927680} + \ldots\right). \tag{27}$$

Table I lists the known coefficients of τ_2 and τ_3 taken from Refs. 3 and 9 and from the series representation of Eq. (17), respectively. The coefficients b_2 and b_3 are universal and describe the properties of the bulk HS systems up to order

TABLE I. The components of τ_2 and τ_3.

i	b_i	a_i	$c_{i,\mathsf{J}}$	$c_{i,\mathsf{K}}$	$S_i(R^{-1})$
2	$-2\pi/3$	$-\pi/8$	0	$-\pi/(2^4 3^2)$	0
3	$3\pi^2/4$	$\frac{137}{560}\pi^2$	$\frac{9\pi\sqrt{3}+16\pi^2}{1536}$	$\frac{781}{36288}\pi^2$	$\neq 0$

three in density,[5] while the coefficients a_2 and a_3 being also universal describe the wall-fluid interface in the limit of low curvature. In a previous work,[3] I verified that $c_{2,\mathsf{J}} = 0$ also apply to cuboidal and cylindrical confinements and thus one can expect that both $c_{2,\mathsf{J}}$ and $c_{3,\mathsf{J}}$ to be universal. On the other hand, I determined that $c_{2,\mathsf{K}}$ is not the same coefficient for spherical and cylindrical cavities. I conjecture that the non-universal behavior of $c_{2,\mathsf{K}}$ extends to $c_{3,\mathsf{K}}$.

In what follows, I underline some interesting features regarding Eq. (26), which resume in Z_3 the statistical mechanical properties of the 3-HS-HSC system. Z_3 is a polynomial function of the set of variables $\{V, A, \mathsf{J}, \mathsf{K}\}$ and also includes a non-polynomial dependence on R. It contains pure volumetric terms and pure terms that depend on the other extensive-like measures $\{A, \mathsf{J}, \mathsf{K}\}$ together with mixed dependencies. A constant term is present in Z_3, which is related to the Gaussian curvature K. On the other hand, there is not a logarithmic term proportional to $\ln(R)$. Higher order terms in the curvature like $S_2(R^{-1})$ are needed to describe the properties of the system and they could be mixed with $\{V, A, \mathsf{J}, \mathsf{K}\}$. It is expected that these general properties to be not an artifact of the three-body system, but rather they should also apply to Z_N for any N. For example, all the mentioned features for Z_3 were also obtained in an exploratory analysis of the 4-HS system.[12] In particular, new terms proportional to A^2 and $A\,\mathsf{K}$ are present in the CI of this system.

Although the complete thermodynamic description of the 3-HS-HSC system may be done on the basis of $\mathbf{M} = \{V,\ A,\ \mathsf{J},\ \mathsf{K},\ R\}$, in order to obtain a simple description it is preferable to use $\mathbf{M} = \{V,\ A,\ R\}$. Therefore, I adopt the definitions for V and A given above and the decomposition rule

$$\tau_i/i! = Z_1 b_i(p) = V\,b_i - A\,a_i(R)\,, \tag{28}$$

$$a_i(R) = a_i - c_{i,\mathsf{J}}\,\mathsf{j} - c_{i,\mathsf{K}}\,\mathsf{k} - S_i(R^{-1})/A(R), \tag{29}$$

with $\mathsf{j} = \mathsf{j}(R) = 2R^{-1}$ and $\mathsf{k} = \mathsf{k}(R) = R^{-2}$. Thus, for $R > 1$ the CI takes the form

$$Z_3 = V^3 + 6V^2 b_2 + 6V b_3 - 6V A\,a_2(R) - 6A\,a_3(R). \tag{30}$$

Even though Eq. (28) may be used for any value of R, the analytic expressions for Z_3 and τ_3 in Eqs. (12) and (17) reveal that Eq. (29) only applies to $R > 1$. To implement a decomposition rule for the full region of physical interest $R > R_{\min}$, the Eqs. (28)–(30) must be supplemented with a decomposition rule for $\Delta\tau_3$ [see Eq. (12)]. By relating $\Delta\tau_3$ to the area term the full range decomposition rule is given by Eqs. (28) and (30) and

$$a_3(R) = a_3 - c_{3,\mathsf{J}}\,\mathsf{j} - c_{3,\mathsf{K}}\,\mathsf{k} - \frac{S_3(R^{-1})}{A(R)} - \frac{\Delta\tau_3}{6A(R)}\,\Theta(1-R). \tag{31}$$

Using the thermodynamic connection given in Eq. (3) it is obtained the total reversible work due to an infinitesimal variation of the radius, $dw = \mathcal{F}_R\,dR = P_w dV$, where $\mathcal{F}_R = -dF/dR$ is the scalar force and P_w is the pressure-for-work.[4] In fact, for a hard-wall fluid-substrate interaction P_w is the wall-pressure, which coincides with the contact density

$$\beta P_w = -\beta\frac{dF}{dR}\left(\frac{dV}{dR}\right)^{-1} = \rho_c. \tag{32}$$

This latter expression provides the first equation-of-state (EOS) of the system and applies for $R > R_{\min}$. Based on Eqs. (3) and (12)–(16) it is possible to describe the properties of F and P_w in their non-analytic points. Near $R = 1$ I find $\beta\Delta F \simeq (1-R)^5\,\Theta(1-R)$ and

$$\beta\Delta P_w \simeq (1-R)^5\ \Theta(1-R)\,. \tag{33}$$

Besides, near $R = R_{\min}$ it is evident a logarithmic divergence in the free energy $\beta F \simeq 11/2\ln(R - R_{\min})$ and an order one pole in P_w

$$\begin{aligned}\beta P_w &= \frac{33}{8\pi}(R - R_{\min})^{-1} - \frac{1719\sqrt{3}}{208\pi} + O(R - R_{\min}),\\ &\simeq \frac{11}{6}(v - v_{\min})^{-1}\,,\end{aligned} \tag{34}$$

where $v = V/3$ is the volume per particle. The properties given in Eqs. (32)–(34) link measurable properties in a molecular dynamic simulation of the system with the basic non-analytic behavior of Z_3, which suggests an interesting approach to the study of the exact properties for systems with $N > 3$. The other EOS are given by

$$\beta P \equiv -\beta\left.\frac{\partial F}{\partial V}\right|_{T,\mathbf{M}-V} = 3Z_3^{-1}\left[V^2 + V\,4b_2 + 2b_3 - A\,2a_2(R)\right], \tag{35}$$

$$\beta\gamma \equiv \beta\left.\frac{\partial F}{\partial A}\right|_{T,\mathbf{M}-A} = 6Z_3^{-1}\left[V\,a_2(R) + a_3(R)\right], \tag{36}$$

$$\beta C_R \equiv \beta\left.\frac{\partial F}{\partial R}\right|_{T,\mathbf{M}-R} = 6Z_3^{-1}A\,\left[V\,\partial_R a_2(R) + \partial_R a_3(R)\right], \tag{37}$$

where in the partial derivatives, $\mathbf{M} - M_i$ means that all the measures except M_i are held fixed. In Eqs. (35)–(37) P is the thermodynamic pressure, γ is the fluid-substrate surface tension, and C_R describes the work necessary to curve the fluid-substrate interface. The four EOS are related to each other via the Laplace-like equation that express the balance between them

$$-\Delta P \equiv P - P_w = \gamma\,\mathsf{j} + C_R\,A^{-1}. \tag{38}$$

Equation (38) is a direct consequence of Eq. (32) and the definitions of P, γ, and C_R given in Eqs. (35)–(37). Therefore, the equation of balance is still valid despite the fact that P, γ, and C_R could be not given by the right-hand side of Eqs. (35)–(37). In fact, it also applies to the N-HS-HSC fluid system without restriction in the number of particles. From

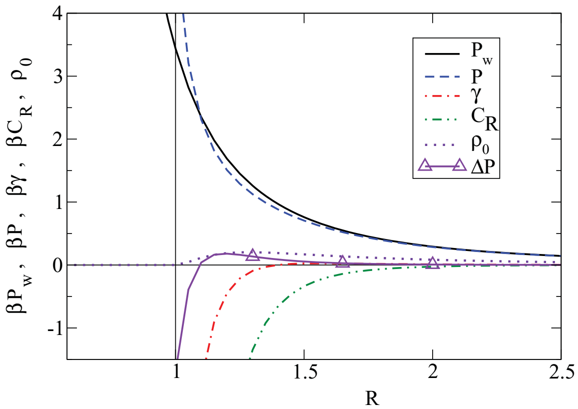


FIG. 1. The dependence on the size cavity parameter R of the thermodynamic EOS and other relevant functions for the 3-HS-HSC system.

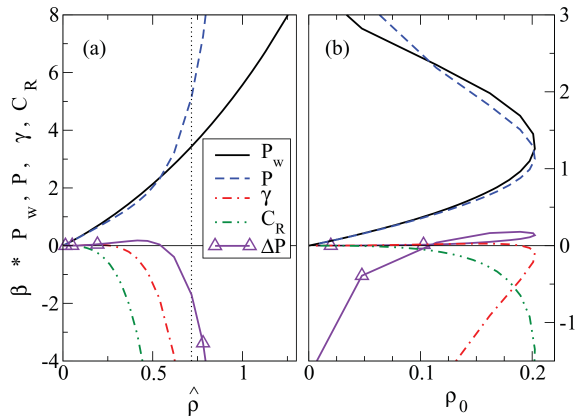


FIG. 2. Thermodynamic EOS for the 3-HS-HSC system. Subfigure (a) shows their dependence on the global density, while (b) displays the more complex dependence on the central density.

Eqs. (32) and (35) is clear that ΔP measures the magnitude of the inhomogeneous terms in dw. This suggests the introduction of the excess work $dw_e = \Delta P\, dV = dw - dw_V$ where dw_V is the work of volume and $w_e(R) = \int_\infty^R \Delta P\, dV$, where the lower limit corresponds to zero density.

In Fig. 1 it is plotted the dependence on R of P_w, P, γ, C_R, the difference of pressures ΔP, and the density $\rho_0(R)$. All the EOS diverge at $R = R_{\min}$ but they are continuous, smooth but non-analytic functions at $R = 1$. The density $\rho_0(R)$ goes to zero at $R = 1$ is smooth but non-analytic at $R = 2$ and has a maximum value $\rho_0(1.284) \simeq 0.2027$. Both pressures are monotonous functions but γ, C_R, and ΔP are not. The function $\beta\Delta P(R)$ has a zero at $R \simeq 1.092$ (where $\beta P = \beta P_w \simeq 2.418$) and reaches a maximum value $\beta\Delta P(1.189) \simeq 0.1809$. In addition, the function $\beta\gamma(R)$ has a zero at $R \simeq 1.396$ and a maximum value $\beta\gamma(1.564) \simeq 0.02615$. Finally, $R \simeq 0.9714$ corresponds to a null excess work $w_e(R) = 0$. It is also interesting to analyze the EOS as functions of the "rough" or global density $\hat{\rho} = 3/V$ and the central density ρ_0, which are plotted in Figs. 2(a) and 2(b), respectively. The vertical dotted line included in Fig. 2(a) shows the value $\hat{\rho}(R = 1) \simeq 0.7162$, for comparison the maximum density value is $\hat{\rho}(R_{\min}) \simeq 3.721$. The general picture of Fig. 2(a) agrees with the features shown in Fig. 1. On the contrary, Fig. 2(b) shows a more complex behavior for the dependence of the EOS on ρ_0, which includes bi-valued functions and a closed loop for ΔP. The ΔP curve intersects itself at $\rho_0 \simeq 0.1079$ and $\beta\Delta P \simeq 0.01419$ where its two branches have a positive slope. This intersection corresponds to macroscopically different states, one is moderately inhomogeneous with $R \simeq 1.816$, $\hat{\rho} = 0.1196$ and $(\rho_c - \rho_0)/\rho_0 \simeq 2.710$, while the other is strongly inhomogeneous with $R \simeq 1.095$, $\hat{\rho} = 0.5455$ and $(\rho_c - \rho_0)/\rho_0 \simeq 21.20$. It is worthwhile to note that all the plotted magnitudes in Fig. 2(b) evolve along the axis $\rho_0 = 0$ for $R_{\min} < R < 1$.

Finally, I extract the dependence on the curvature of the fluid-substrate surface tension. For the case of a flat substrate or wall, the surface tension of a fluid-substrate interface, γ_∞, is obtained from Eq. (36) by replacing $a_i(R) = a_i$ but keeping unmodified the factor Z_3^{-1}.[3] Thus, for the 3-HS-HSC system the ratio between both surface tensions is

$$\frac{\gamma(R)}{\gamma_\infty} - 1 = \frac{[a_2(R) - a_2]\, V + a_3(R) - a_3}{a_2 V + a_3},$$
$$= -\frac{1}{V}\frac{c_{3,\mathsf{J}}}{a_2 + a_3/V}\,\mathsf{j} - \frac{c_{2,\mathsf{K}} + c_{3,\mathsf{K}}/V}{a_2 + a_3/V}\,\mathsf{k} + O(R^{-3}),$$
$$= \delta_\mathsf{j}\,\mathsf{j} + \delta_\mathsf{k}\,\mathsf{k} + O(R^{-3}), \tag{39}$$

where δ_j and δ_k are the coefficients of $2R^{-1}$ and R^{-2}, respectively.

A. Many-body systems

The procedure developed to obtain Eq. (39) may be also implemented for systems composed of N particles with $N > 3$. Briefly, from the expression for Z_N in terms of τ_i given by Eq. (22.23) in Ref. 5 (p. 135) [which is similar to Eqs. (4) and (5)] together with the assumption that Eqs. (25) and (28) hold for τ_i, one can derive an expression for Z_N similar to Eq. (30). Using the surface tension definition in Eq. (36) one can derive $\gamma(R)$ and γ_∞ [see the comments above Eq. (39)]. Finally, from the ratio of both surface tensions one find the curvature dependence of the surface tension. Following this approach and making a careful analysis of the terms that scale with N, I found

$$\frac{\gamma(R)}{\gamma_\infty} - 1 = -\frac{\nu\, c_{3,\mathsf{J}}}{a_2}\hat{\rho}\,\mathsf{j} + \Bigg[-\frac{c_{2,\mathsf{K}}}{a_2} + \nu\left(\frac{c_{2,\mathsf{K}} a_3}{a_2^2} - \frac{c_{3,\mathsf{K}}}{a_2}\right)\hat{\rho}\Bigg]\mathsf{k} + \ldots, \tag{40}$$

where $\nu = 1 - 2N^{-1}$ and the higher order term is $(\mathsf{j} + \mathsf{k})\, O(\hat{\rho}^2) + O(R^{-3})\, O(\hat{\rho})$. In addition

$$\beta\gamma_\infty = \nu' a_2 \hat{\rho}^2 - \left(4 a_2 b_2 \nu''' - a_3 \nu''\right)\hat{\rho}^3 + \ldots, \tag{41}$$

where $\nu' = 1 - N^{-1}$, $\nu'' = \nu'\nu$ and $\nu''' = \nu'(1 - \frac{3}{2}N^{-1})$. In the limit $N \to \infty$, one can obtain the third order dependence on the density of the fluid-wall surface tension

$$\beta\gamma_\infty = a_2 \hat{\rho}^2 - (4 a_2 b_2 - a_3)\,\hat{\rho}^3 + \ldots, \tag{42}$$

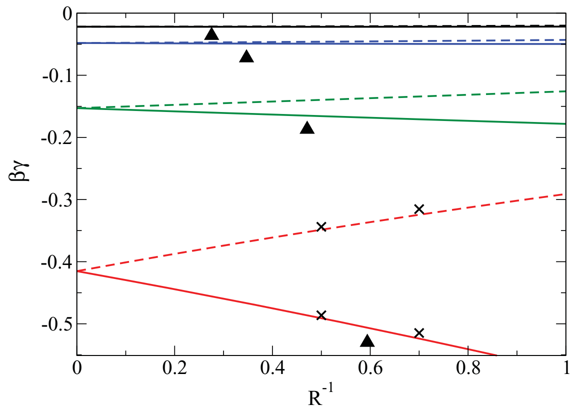


FIG. 3. Dependence of the low density expansion for the fluid-substrate surface tension on the radius of the spherical substrate. The continuous lines correspond to $\beta\gamma$ for the HS fluid in contact with a concave hard substrate ($\mathsf{j} > 0$), while dashed lines draw $\beta\gamma$ for the fluid in contact with a convex substrate ($\mathsf{j} < 0$). From top to bottom the curves correspond to the global densities $\hat{\rho} = 0.05$, $\hat{\rho} = 0.1$, $\hat{\rho} = 0.25$, and $\hat{\rho} = 0.5$. The triangles approximately indicate the place where the continuous curves leave to be valid and the crosses show some $\beta\gamma$ values obtained by assuming $\delta_{\mathsf{k}} = 0$.

or $\beta\gamma_\infty \simeq -0.39267\hat{\rho}^2 - 0.87534\hat{\rho}^3$, which coincides with the previously known exact result.[13–15] It is interesting to mention that such results were obtained in the study of the HS fluid in contact with a planar hard wall using the virial expansion in the grand canonical ensemble, which shows the consistency of the present approach. In addition, I obtained the first order dependence of the surface tension on both curvatures

$$\frac{\gamma(R)}{\gamma_\infty} - 1 = \delta_{\mathsf{j}}\,\mathsf{j} + \delta_{\mathsf{k}}\,\mathsf{k} + \ldots, \tag{43}$$

where the delta coefficients are given up to first order in density by

$$\delta_{\mathsf{j}} = -\frac{c_{3,\mathsf{J}}}{a_2}\hat{\rho} = \left(\frac{3\sqrt{3}}{64} + \frac{\pi}{12}\right)\hat{\rho}, \tag{44}$$

$$\begin{aligned}\delta_{\mathsf{k}} &= -\frac{c_{2,\mathsf{K}}}{a_2} + \left(\frac{c_{2,\mathsf{K}}\,a_3}{a_2^2} - \frac{c_{3,\mathsf{K}}}{a_2}\right)\hat{\rho},\\ &= -\frac{1}{18} + \frac{1439\pi}{22680}\,\hat{\rho},\end{aligned} \tag{45}$$

i.e., $\delta_{\mathsf{j}} \simeq 0.34299\,\hat{\rho}$ and $\delta_{\mathsf{k}} \simeq -0.055555 + 0.19933\,\hat{\rho}$. It is the first time that this result is obtained. The fluid-substrate Tolman's length is the coefficient of j in Eq. (43),

$$\delta_{\mathrm{Tol}} \equiv \delta_{\mathsf{j}}. \tag{46}$$

Thus, in the case of a fluid in contact with a spherical concave substrate, δ_{Tol} is the coefficient of $2R^{-1}$ and is positive (note that the sign of δ_{Tol} may change by adopting a different convention). Figure 3 shows in continuous line the dependence of $\gamma(R)$ on both R^{-1} and the density for a HS fluid in contact with a concave spherical wall [given by Eqs. (42)–(45)]. In the low density regime, the large N and the small radius conditions cannot be simultaneously fulfilled. Therefore, I estimated the maximum value of R^{-1} where Eqs. (43)–(45) make sense, through the expression $R^{-1} \sim (4\pi\hat{\rho}/3N)^{1/3}$ with $N = 10$. This situation is plotted in Fig. 3 using triangles. The δ_{k} term has a little observable effect in the behavior of $\beta\gamma(R^{-1})$, as it is denoted by the crosses in Fig. 3 which mark the value of $\beta\gamma(R^{-1})$ at $R^{-1} = 0.5$ and at $R^{-1} = 0.7$ for $\hat{\rho} = 0.5$ under the assumption of $\delta_{\mathsf{k}} = 0$.

B. In-out symmetry and the properties of the dual system

Here I discuss the similarities and differences between HS-HSC and HS-HSO, systems. In order to make this I introduce the following notation, which is used in this and next subsections: a measure X ($X \in \mathbf{M}$) without label refers to the system contained in the $\bar{\Omega}_{\mathrm{sph}}$ region, and X_{sph} denotes the same measure but it is referred to the system confined in Ω_{sph} the region. The extensive-like set of measures $\mathbf{M} = \{V, A, \mathsf{J}, \mathsf{K}, R\}$ applied to the system in $\bar{\Omega}_{\mathrm{sph}}$ and the same set applied to system in Ω_{sph} are related to each other by $V = V_\infty - V_{\mathrm{sph}}$, $A = A_{\mathrm{sph}}$, $\mathsf{J} = -\mathsf{J}_{\mathrm{sph}}$, and $\mathsf{K} = \mathsf{K}_{\mathrm{sph}}$, where V_∞ is the volume measure of the complete space. A second symmetry relation between the systems constrained to Ω_{sph} and $\bar{\Omega}_{\mathrm{sph}}$ involves the derivatives of the measures. For the Ω_{sph} confinement one obtain $\partial_R V_{\mathrm{sph}} = A_{\mathrm{sph}}$, $\partial_R A_{\mathrm{sph}} = \mathsf{J}_{\mathrm{sph}}$ and $\partial_R \mathsf{J}_{\mathrm{sph}} = \mathsf{K}_{\mathrm{sph}}$, while for the $\bar{\Omega}_{\mathrm{sph}}$ confinement one find $\partial_R V = -A$, $\partial_R A = -\mathsf{J}$, and $\partial_R \mathsf{J} = -\mathsf{K}$. Using Eq. (23) for the 3-HS-HSO system it follows that

$$\begin{aligned}\tilde{\tau}_3/3! = \tilde{Z}_1 b_3(p) &= V\,b_3 - A\,a_3 + \mathsf{J}\,c_{3,\mathsf{J}}\\ &\quad + \mathsf{K}\,c_{3,\mathsf{K}} + S_3(R^{-1})\,,\end{aligned} \tag{47}$$

where the coefficients $\{b_3, a_3, c_{3,\mathsf{J}}, c_{3,\mathsf{K}}\}$ are the same to those listed in Table I for the case of HSC. However, $S_3(R^{-1})$ is different to the expression given in Eq. (27) that herefrom I will rename $S_{3\,\mathrm{sph}}(R^{-1})$. Indeed, I find $S_3(R^{-1}) = -S_{3\,\mathrm{sph}}(R^{-1}) = S_{3\,\mathrm{sph}}(-R^{-1})$. The symmetry between Eqs. (25) and (47), and the known properties of $\tilde{\tau}_2$[3] show an interesting relation concerning τ_i and $\tilde{\tau}_i$. For $i = 1, 2, 3$ and $R > 1$ it is easy to demonstrate that

$$\tau_i(R)/i! - \tilde{\tau}_i(-R)/i! + V_\infty\,b_i = 0, \tag{48}$$

$$\begin{aligned}\tau_i(R)/i! + \tilde{\tau}_i(R)/i! - V_\infty b_i &= 2\\ \times \left[-a_i\,A_{\mathrm{sph}} + c_{i,\mathsf{K}}\mathsf{K}_{\mathrm{sph}} + S_{i\,\mathrm{sph}}(R^{-1})\big|_{\mathrm{even}}\right],\end{aligned} \tag{49}$$

$$\begin{aligned}\tau_i(R)/i! - \tilde{\tau}_i(R)/i! + V_\infty b_i &= 2\\ \times \left[b_i\,V_{\mathrm{sph}} + c_{i,\mathsf{J}}\mathsf{J}_{\mathrm{sph}} + S_{i\,\mathrm{sph}}(R^{-1})\big|_{\mathrm{odd}}\right],\end{aligned} \tag{50}$$

where $S_{i\,\mathrm{sph}}(R^{-1})|_{\mathrm{even\,(odd)}}$ implies that only the even (odd) powers of R^{-1} in $S_{i\,\mathrm{sph}}(R^{-1})$ are taken into account. Eqs. (48)–(50) constitute the third symmetry relation between both systems. I conjecture that this relation is also valid for $i > 3$ and a large enough R.

The symmetry between τ_i and $\tilde{\tau}_i$ may also be analyzed by adopting the second set of measures $\mathbf{M} = \{V, A, R\}$ along with the decomposition rule

$$\tilde{\tau}_i/i! = \tilde{Z}_1 b_i(p) = V\,b_i - A\,a_i(R)\,, \tag{51}$$

$$a_i(R) = a_i - c_{i,\mathsf{J}}\,\mathsf{j} - c_{i,\mathsf{K}}\,\mathsf{k} - S_i(R^{-1})/A(R), \tag{52}$$

with $\mathsf{j} = -\mathsf{j}_{\rm sph} = -2R^{-1}$ and $\mathsf{k} = \mathsf{k}_{\rm sph} = R^{-2}$. In such a case $\tilde{Z}_3$ becomes

$$\tilde{Z}_3 = V^3 + 6V^2 b_2 + 6V b_3 - 6V A\, a_2(R) - 6A\, a_3(R), \tag{53}$$

and Eqs. (49) and (50) take the form

$$\tau_i(R)/i! + \tilde{\tau}_i(R)/i! - V_\infty b_i = 2\left[-\, a_{i\,\rm sph}(R^{-1})\big|_{\rm even} A_{\rm sph}\right], \tag{54}$$

$$\tau_i(R)/i! - \tilde{\tau}_i(R)/i! + V_\infty b_i = 2 \times \left[b_i V_{\rm sph} - a_{i\,\rm sph}(R^{-1})\big|_{\rm odd} A_{\rm sph}\right]. \tag{55}$$

The analytic expressions for the EOS of the 3-HS-HSO system are obtained easily from their definitions in Eqs. (32) and (35)–(37) and they are very similar to those found for the 3-HS-HSC system. The equilibrium condition between the EOS is given by the Laplace-like relation for the HSO confinement

$$\Delta P = P_w - P = \gamma\, \mathsf{j}_{\rm sph} + C_R\, A^{-1}, \tag{56}$$

which is similar to Eq. (38) and also apply to any number of particles. For the case $N \leq 3$ is

$$C_R A^{-1} = \partial_R \gamma - \beta\gamma\, C_R, \tag{57}$$

and then Eq. (56) may be rewritten as

$$\Delta P = \gamma\, \left(\mathsf{j}_{\rm sph} - \beta C_R\right) + \partial_R \gamma. \tag{58}$$

C. Many-body dual system

In Refs. 16 and 17 Henderson derived an *approximate* Laplace-like equation for a fluid in contact with a HSO (sometimes called impurity hard-particle, test particle or empty cavity in a bulk fluid), which is frequently considered as an exact sum rule.[18,19] He obtained

$$\Delta P = \gamma\, \mathsf{j}_{\rm sph} + \partial_R \gamma, \tag{59}$$

which differs from the exact Eqs. (56) and (58). From the comparison of his result with that in Eq. (58) it is apparent the missing term $\beta\gamma C_R$, which is of the order $\beta^{-1} O(A V^{-4} R^{-3})$ and positive.

To obtain the low density expansion of γ_∞ and the low curvature expansion of $\gamma(R)$ I follow the same procedure implemented above for the HS fluid in contact with a concave spherical wall. This reproduces the expressions given in Eqs. (40)–(46) but now for the HS fluid in contact with a convex spherical wall. The unique difference is that now $\mathsf{j} = -2R^{-1}$ and thus δ_{j} is the coefficient of $-2R^{-1}$. In summary, for a many-HS fluid system in contact with either a concave or convex spherical surface, the fluid-substrate Tolman's length and the second order term in curvature are given up to first order in density by

$$\delta_{\rm Tol} = 0.342\,99\, \hat{\rho}, \qquad \delta_{\mathsf{k}} = -0.055\,55 + 0.199\,33\, \hat{\rho}. \tag{60}$$

It is interesting to compare the exact results presented in this work with that obtained from the scaled particle theory (SPT). Taken into account[18] [Eqs. (4), (5) and (12), (13) therein], I obtain $\delta_{\rm Tol,SPT} = 0.261\,80\rho$ and $\delta_{\mathsf{k},\rm SPT} = -0.055\,556 + 0.143\,23\rho$, which up to zero order in density agrees with the exact result. There is not, however, a good agreement in the first order for which the discrepancy between both, the SPT and the exact results, is approximately of 25%. The fluid-substrate surface tension for a HS fluid in contact with a convex spherical wall is plotted in Fig. 3 using dashed lines. For a given density this graphic shows that the curves that correspond to concave and convex surfaces have negative and positive slope, respectively, as well as a linear dependence on R^{-1}.

The results, derived for the curvature dependence of the HS fluid-substrate surface tension may be extrapolated to the case of a HS fluid in contact with other hard curved substrates. By assuming that $c_{3,\mathsf{J}}$ is universal, i.e., it is the same coefficient for any constant curvature surface, the Eq. (43) also represents $\gamma(R)$ for a cylindrical surface (with $|\mathsf{j}| = R^{-1}$). In such a case Eq. (60) gives the Tolman's length up to the first order in density. Unlikewise, because of δ_{k} involves the coefficients $c_{2,\mathsf{K}}$ and $c_{3,\mathsf{K}}$ which are not universal, the Eqs. (45) and (60) do not gives δ_{k} for this system. However, for a HS fluid in contact with a cylindrical surface (with $\mathsf{k} = 0$), the curvature dependence of the surface tension involves a term of order $\mathsf{j}^2 = R^{-2}$.[3] Up to zero order in density it is $-\mathsf{j}^2 \frac{3}{8} c_{2\mathsf{k}}/a_2$ which is of the same order to that found in Eqs. (43) and (45). I propose that this latter statement is also valid for the first order term in density. That is, for a HS fluid in contact with a cylindrical surface the curvature dependence of the surface tension should be roughly given by

$$\gamma(R)_{\rm cyl} \approx \gamma_\infty[1 + \delta_{\rm Tol}\mathsf{j} + (-0.021 + 0.2\hat{\rho})\,\mathsf{j}^2], \tag{61}$$

with γ_∞ and $\delta_{\rm Tol}$ taken from Eqs. (42) and (60). This result together with the little effect produced by the second order term in curvature on the behavior of $\gamma(R)$, show that Fig. 3 (after renaming the ordinate axis as $|\mathsf{j}|/2$) not only describes $\gamma(R)$ for the HS fluid in contact with a spherical substrate, but also it can be considered to describe the case of a cylindrical surface both, for the convex and concave cases.

IV. FINAL REMARKS

The analysis of the statistical mechanical properties presented in this work concerning few-body systems of HS determine the relationship between two types of spherical confinement: the closed hard spherical cavity and the unbounded hard spherical object.

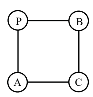
This in-out symmetry for spherical boundaries is stated in Eqs. (48)–(50). The studied many-body systems composed of HS in contact with spherical walls revealed that the concavity/convexity of the hard surface is linked with the in-out symmetry. This is an interesting point because the symmetry involves a global property while the curvature of a surface is a local property. To the best of my knowledge, the curvature dependence of the fluid-substrate surface tension, specifically, the expression for $\delta_{\rm Tol}$ given in Eqs. (43)–(46) and (60), concern new results never published in the literature up to present. The approximate sum-rule given in Eq. (59) is often assumed to be an exact relation in the literature. This point, however, should be analyzed in more detail because the higher order terms in the curvature may produce measurable consequences. The exact results presented in the current work are useful to test several approximations involved in the theories of inhomogeneous fluids. In particular, those concerning the curvature dependence of the fluid-substrate surface tension may contribute to further understand the still controversial behavior of the Tolman's length in the fluid-substrate interface.

ACKNOWLEDGMENTS

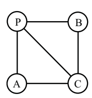
This work was supported in part by the Argentina grants UBACyT x099 and CONICET-PIP 0546. The author thanks Gabriela Castelletti for helpful discussions.

APPENDIX: ANALYTIC EXPRESSIONS OF SEVERAL GRAPHS

This appendix summarizes the analytic expressions for the integrals that correspond to three particles labeled-clusters in a spherical pore which are represented by irreducible four-nodes graphs. Note that the convention used in this work for the implicit sign of each graph is as follows: a term -1 is involved in both, each continuous-line between particles (an f_{ij}-bond) and each dashed line between p and a particle (an f_i-bond). On the other hand, there is not a negative term related to dashed lines between particles (e_{ij}-bonds) and continuous lines between p and a particle (the e_i-bond). This sign convention determines the positiveness or negativeness of each graph which are also monotonous functions of $R \geq 0$. In order to solve the integrals involved in the irreducible graphs with four nodes they are expressed in terms of the overlap volume between two spheres with different radii.[2,6] We obtain

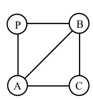


$$= \begin{cases} \frac{64\pi^3}{2835}\left(10-81\,R^2+105\,R^3\right), & \text{if } R \geq 1 \\ \frac{64\pi^3}{2835} R^6\left(105-81\,R+10\,R^3\right), & \text{if } 0 \leq R < 1, \end{cases} \tag{A1}$$



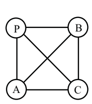
$$= \begin{cases} \frac{\pi^3}{11340}(2120+2835\,R-25488\,R^2+26880\,R^3), & \text{if } R \geq 1 \\ \frac{\pi^3}{11340}\left(-440+2835\,R-4752\,R^2 \right. \\ \qquad \left. +26880\,R^6-20736\,R^7+2560\,R^9\right), & \text{if } \frac{1}{2} \leq R < 1 \\ \frac{64\pi^3}{27} R^9, & \text{if } 0 \leq R < \frac{1}{2}, \end{cases} \tag{A2}$$

where the last row comes from a reduction of the graph to Z_1^3, and



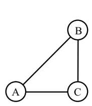
$$= \begin{cases} -\frac{\pi^3}{11340}(335-6588\,R^2+12600\,R^3), & \text{if } R \geq \frac{1}{2} \\ -\frac{64\pi^3}{2835} R^6(105-81\,R+10\,R^3), & \text{if } 0 \leq R < \frac{1}{2}, \end{cases} \tag{A3}$$

which for $0 \leq R < 1/2$ reduce to Eq. (A1) with an overall factor -1. For the special case of the four-vertex star-graph it was obtained using Eqs. (9) and (17),

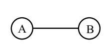


$$= \begin{cases} \frac{\pi^3}{3780}(440-2835R+4752R^2+840R^3-15120R^5 \\ \qquad +20736R^7-11520R^9)+h\,\Theta(R-1/\sqrt{3}), & \text{if } R \geq \frac{1}{2} \\ -\frac{64\pi^3}{27} R^9, & \text{if } 0 \leq \mathrm{R} < \frac{1}{2}. \end{cases} \tag{A4}$$

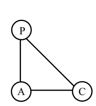
We observe that for $0 \leq R < 1/2$ the star-graph reduces to $-Z_1^3$, which determines that $B_4^{[1]} = Z_1^3/4$ for the same range in R [see Eq. (10)]. The following expressions show several three and two nodes irreducible cluster integrals of different kind



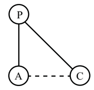
$$= -3B_3 = -\frac{5\pi^2}{6}, \tag{A5}$$



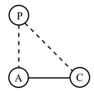
$$= 2b_2(\infty) = -2B_2 = -\frac{4\pi}{3}, \tag{A6}$$



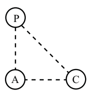
$$= \tau_2 = \begin{cases} \pi^2\left(-\frac{16}{9}R^3+R^2-\frac{1}{18}\right), & \text{if } R \geq \frac{1}{2} \\ -\frac{16\pi^2}{9} R^6, & \text{if } 0 \leq R < \frac{1}{2}, \end{cases} \tag{A7}$$



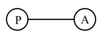
$$= Z_2 = \begin{cases} \pi^2\left(\frac{16}{9}R^6 - \frac{16}{9}R^3 + R^2 - \frac{1}{18}\right), & \text{if } R \geq \frac{1}{2} \\ 0, & \text{if } 0 \leq R < \frac{1}{2}, \end{cases} \tag{A8}$$



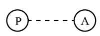
$$= \tilde{\tau}_2 = \begin{cases} -\frac{4\pi}{3}V_\infty + \pi^2\left(\frac{16}{9}R^3 + R^2 - \frac{1}{18}\right), & \text{if } R \geq \frac{1}{2} \\ -\frac{4\pi}{3}V_\infty + \pi^2\left(-\frac{16}{9}R^6 + \frac{32}{9}R^3\right), & \text{if } 0 \leq R < \frac{1}{2}, \end{cases} \tag{A9}$$



$$= \tilde{Z}_2 = \left(V_\infty - \frac{8\pi}{3}R^3\right)\left(V_\infty - \frac{4\pi}{3}\right) + Z_2, \tag{A10}$$



$$= \tau_1 = Z_1 = \frac{4\pi}{3}R^3, \tag{A11}$$



$$= -\tilde{Z}_1 = -\left(V_\infty - Z_1\right), \tag{A12}$$

where B_i is the i-th virial coefficient for the bulk HS fluid. The expressions for τ_2 and $\tilde{\tau}_2$ are taken from[2] for $R \geq 1/2$. For $0 < R < 1/2$ two particles do not fit into the pore and therefore $Z_2 = 0$. This condition provides $\tau_2 = -Z_1^2$ for $0 < R < 1/2$. Note that $b_1(p) = b_1 = 1$.

[1] M. Uranagase and T. Munakata, Phys. Rev. E **74**, 066101 (2006).
[2] I. Urrutia, J. Stat. Phys. **131**, 597 (2008).
[3] I. Urrutia, J. Chem. Phys. **133**, 104503 (2010).
[4] I. Urrutia and G. Castelletti, J. Chem. Phys. **134**, 064508 (2011).
[5] T. L. Hill, *Statistical Mechanics* (Dover, New York, 1956).
[6] R. Blaak, Mol. Phys. **95**, 695 (1998).
[7] S. Labík and J. Kolafa, Phys. Rev. E **80**, 051122 (2009).

[8] We note a cuple of minor misprints in Ref. 7. In Eq. (32) of that work, where P_{10} is piece-wise deffined, the value $s = 2^{1/4}$ in which the domain of the P_{10} function is break should be replaced with $s = 2^{1/4} - 1$. In addition, Eqs. (A9) and (A11) are only valid for $s > 1$.

[9] I. Urrutia and L. Szybisz, J. Math. Phys. **51**, 033303 (2010).
[10] L. Boruvka and A. W. Neumann, J. Chem. Phys. **66**, 5464 (1977).
[11] S. M. Oversteegen, P. A. Barneveld, J. van Male, F. A. M. Leermakers, and J. Lyklema, Phys. Chem. Chem. Phys. **1**, 4987 (1999).

[12] The complete study of the 4-HS system is beyond the scope of the current work and is not presented here.

[13] A. Bellemans, Physica **28**, 493 (1962).
[14] J. Stecki and S. Sokołowski, Phys. Rev. A **18**, 2361 (1978).
[15] J. R. Henderson and F. van Swol, Mol. Phys. **51**, 991 (1984).
[16] J. R. Henderson, Mol. Phys. **50**, 741 (1983).
[17] J. R. Henderson, in *Fluid interfacial phenomena*, edited by C. A. Croxton (Wiley, New York, 1986), pp. 555–605.
[18] J. R. Henderson, J. Chem. Phys. **116**, 5039 (2002).
[19] M. C. Stewart and R. Evans, Phys. Rev. E **71**, 011602 (2005).