Statistical mechanics of fluids confined by polytopes: The hidden geometry of the cluster integrals

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Abstract

This paper, about a fluid-like system of spatially confined particles, reveals the analytic structure for both, the canonical and grand canonical partition functions. The studied system is inhomogeneously distributed in a region whose boundary is made by planar faces without any particular symmetry. This type of geometrical body in the $d$-dimensional space is a polytope. The presented result in the case of $d = 3$ gives the conditions under which the partition function is a polynomial in the volume, surface area, and edges length of the confinement vessel. Equivalent results for the cases $d = 1, 2$ are also obtained. Expressions for the coefficients of each monomial are explicitly given using the cluster integral theory. Furthermore, the consequences of the polynomial shape of the partition function on the thermodynamic properties of the system, away from the so-called thermodynamic limit, is studied. Some results are generalized to the $d$-dimensional case. The theoretical tools utilized to analyze the structure of the partition functions are largely based on integral geometry.

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I. INTRODUCTION

Thermodynamic properties of fluids are relevant to biology, chemistry, physics and engineering. In most cases of interest the fluid system is inhomogeneously distributed in the space, confined to a region of finite size and constituted by a bounded number of molecules. A typical example of this kind of systems is that of fluids confined in pores. They constitute a prototypical inhomogeneous system which occupies a small region of the space and may involve a small number of particles. It is well known that the spatial distribution of a fluid confined in a small pore may follow or not the symmetry of the cavity [1, 2], and that its properties may be strongly influenced by the geometry of the container. To study the thermodynamic properties of these systems it is customary to introduce several strong assumptions or approximations that simplify the analysis. An usual approach is to treat the system as it were homogeneous (which necessarily implies that the system completely fills the space, and thus, involves infinitely many particles). A second usual approach assumes that the inhomogeneous fluid is spatially distributed in several regions, each one with homogeneous properties, while the inhomogeneous nature of the system is concentrated in regions with vanishing size (surfaces, lines and points). Frequently, this scenario is complemented with the assumption that the spatial distribution of the fluid involves continuous translational and/or rotational symmetries. Finally, a third approach only assumes that the inhomogeneous fluid takes spatial configurations with those symmetries. In general, the assumed symmetric distribution of the fluid could be attained spontaneously (as in the case of free drops or bubbles) or could be induced by an external potential as it is the case of confined system that are constrained to regions with simple symmetry: a semi-space, a slit, an infinite cylinder, or a sphere (for example in wetting and capillary condensation, phenomena). Anyway, the continuous symmetries (translations and/or rotations) play an important role providing the bases to identify the extensive and intensive magnitudes which enable the development of thermodynamic theory [3].

Moreover, thermodynamics only provides an incomplete set of relations between intensive and extensive magnitudes which must be complemented with other sources of information to obtain the thermodynamic properties of a given fluid system. In any case, these sources, that may be experimental, theoretical, or based on numerical simulation, also involve assumptions or approximations related to the existence of continuous symmetries. In this sense,
our statistical mechanical and thermodynamical approach to the study of inhomogeneous fluids appears to be intrinsically entangled with some hypothesis about the constitution and behavior of the system under study [24]. Particularly, I refer to three hypothesis concerning the fluid system: the symmetry of its spatial distribution, the large volume occupied and the large (and unbounded) number of particles involved. Of course, one may ask about if those hypothesis are or not a central part of the theories. What happens with inhomogeneous fluid-like systems which do not necessary attain spatial distribution with simple symmetry and/or occupy small regions of the space and/or are constituted by a small number of particles? Can we apply statistical mechanics and thermodynamics to study their equilibrium properties? How can we do that? The analysis presented below attempts to advance in the understanding of these questions. From a complementary point of view, this work also deals with the long standing objective of finding fluid-like systems that are exactly solvable, i.e., its partition function integral can be integrated and thus transformed into an analytic expression. Each of these systems provides the unique opportunity of testing some of the fundamental hypothesis of the theoretical framework.

This paper is devoted to analyze, using an exact framework, few- and many-body fluid like systems confined in cavities without continuous symmetry. In particular, we focus on their partition function and thermodynamic magnitudes as functions of the spatial set that defines the region in which particles are allowed to move. In fact, it is shown that under certain conditions the partition function of the fluid-like system is a polynomial function of certain geometric measures of the confining cavity, like its volume and surface area. The adopted approach is theoretical and exact, being our core results largely based on integral geometry. The rest of the manuscript is organized as follows: In Section II it is presented the general statistical mechanics approach to canonical and grand canonical ensemble with two modifications: the cutoff in the maximum number of particles which enables the analysis of few-body open systems and the generalization of cluster integrals to inhomogeneous fluids. Sections III and IV are devoted to study the structure of cluster integrals with particular emphasis in the case of a polytope-type confinement. There, two theorems and their corollaries are demonstrated, which constitute the main result of the present work (PW). Extensions to other type of confinements are discussed in Section V while the consequences of the cluster integral behavior in the thermodynamical properties of the system are studied in Sec. VI. The final discussion is given in Section VII.
II. PARTITION FUNCTION OF AN INHOMOGENEOUS SYSTEM

In this work we consider an open system of at most \( M \) particles that evolves at constant temperature in a restricted region \( \mathcal{A} \) of the \( d \)-dimensional euclidean space \( \mathbb{R}^d \). The region \( \mathcal{A} \) is the set of points where the center of each particle is free to move and has a boundary \( \partial \mathcal{A} \). From here on the system will be shortly referred to as the fluid while \( \mathcal{A} \) will be referred to as the region or set where the fluid is confined. In fact, the system is an inhomogeneous fluid due to the existence of \( \partial \mathcal{A} \). The restricted grand canonical partition function of the fluid is

\[
\Xi_M = \sum_{j=0}^{M} x^j Q_j ,
\]

where \( M \) is the maximum number of particles that are accepted in \( \mathcal{A} \). The absolute activity is \( x = \exp(\beta \mu) \), being \( \mu \) the chemical potential while \( \beta = 1/k_B T \), \( k_B \) and \( T \) are the inverse temperature, Boltzmann constant and temperature, respectively. \( \Xi_M \) is a \( M \)-degree polynomial in \( x \) and its \( j \)-th coefficient is the canonical partition function of the closed system with exactly \( j \) particles confined in \( \mathcal{A} \). The grand canonical partition function of the fluid without the cutoff in the maximum number of particles can be obtained from \( \lim_{M \to \infty} \Xi_M \).

On the other hand, the canonical partition function of the system with \( j \) particles is

\[
Q_j = I_j \Lambda^{-d j} Z_j ,
\]

where \( I_j = 1/j! \) is the indistinguishably factor, \( \Lambda = h/(2\pi m k_B T)^{1/2} \) is the thermal de Broglie wavelength, \( m \) is the mass of each particle and \( h \) is the Planck’s constant. Therefore, we can transform Eq. (1) into

\[
\Xi_M = \sum_{j=0}^{M} I_j z^j Z_j ,
\]

where the activity is \( z = \exp(\beta \mu) / \Lambda^d \). Finally, the configuration integral (CI) of a system with \( j \) particles is

\[
Z_j = \int \ldots \int \prod_{k=1}^{j} e_k \prod_{l<n} e_{ln} d^d r ,
\]

being \( Z_0 = 1 \) [alternative dimensionless definitions for \( z \) and \( Z_j \) may be obtained by introducing the volume of the system or the characteristic volume of a particle in Eq. (3)]. Here, \( e_{ln} = \exp[-\beta \phi(r_{ln})] \) is the Boltzmann factor related to the spherically symmetric pair potential \( \phi \) between the \( l \) and \( n \) particles, which are separated by a distance \( r_{ln} \). It will be
assumed that $\phi$ has a finite range $\xi$, being $\phi(r_{ln}) = 0$ and $e_{ln} = 1$ if $r_{ln} > \xi$. This assumption is not very restrictive because any pair interaction potential can be approximated by truncation at a finite range, e.g. it is frequent to study the Lennard Jones fluid cut and shifted at $r = 2.5\sigma$ \cite{4,5}. The indicator function

$$e_k = e(r_k) = \begin{cases} 
1 & \text{if } r_k \in A, \\
0 & \text{if } r_k \notin A,
\end{cases} \quad (5)$$

is the Boltzmann factor corresponding to the external potential produced by a hard wall confinement. Note that, the integration domain in Eq. (4) is the complete space due to the spatial confinement of the particles in $A$ is considered through $e_k$. The CI is a function of the set $A$ and a functional of $\phi$. $Z_i$ itself is given in its full generality by \cite{6}

$$Z_j = j! \sum_{m} \prod_{i=1}^{j} \frac{1}{m_i!} \left( \frac{\tau_i}{i!} \right)^{m_i}, \quad (6)$$

where the sum is over all sets of positive integers or zero $m = \{m_1, m_2, \ldots \}$ such that $\sum_{i=1}^{j} i m_i = j$. Eq. (6) shows that $Z_j$ is a polynomial in $\tau_1, \ldots, \tau_j$ which are essentially the (reducible) Mayer cluster integrals for inhomogeneous systems. This equation is obtained through the following procedure: replace in Eq. (4) each $e_{ln}$ using the identity $e_{ln} = 1 + f_{ln}$ (this Eq. defines $f_{ln}$), distribute the products, and collect all terms of the integrand which consist of groups of particles that conform a cluster, in the sense that they are at least simply connected between them by $f$-functions. Note that our assumption about $e_{ln} = 1$ for $r_{ln} > \xi$ implies $f_{ln} = 0$ if $r_{ln} > \xi$ showing the spatial meaning of the cluster term. The procedure gives Eq. (5) with

$$\tau_i = \int_{A} \cdots \int_{A} S_{1,2,\ldots,i} \prod_{k=1}^{i} e_k d^d r, \quad (7)$$

$$S_{1,2,\ldots,i} = \sum_{\text{cluster } <l,n>} \prod_{f_{ln}}, \quad (8)$$

where $S_{1,2,\ldots,i}$ is a sum of products of $f_{ln}$ functions with $1 \leq l, n \leq i$ that involves all the products of $f$ functions, which can be represented as a connected diagrams (clusters) with $i$ nodes and $f_{ln}$ bonds. Clearly, $\tau_i$ depends on $T, \phi$ and $A$. If one assume that $A$ is very large the usual homogeneous system approximation gives $\tau_i \rightarrow i! V b_i$, where $V$ is the volume of $A$ and $b_i$s are the Mayer cluster integrals which depend on $T$ and $\phi$. 

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The inversion of Eq. (6) gives the following expression for the dependence of \( \tau_i \) with the CIs (Eq. (23.44) in Ref. [6])

\[
\tau_i = i! \sum_n (-1)^{\sum_j n_j - 1} \left( \sum_j n_j - 1 \right)! \left[ \prod_{j=1}^{n_j} \frac{1}{n_j!} \left( \frac{Z_j}{j!} \right)^{n_j} \right],
\]

(9)

where the first sum is over all sets \( n = \{n_1, n_2, \ldots \} \) with \( n_j \) non-negative integers such that \( \sum_j j n_j = i \) and \( \tau_1 = Z_1 b_1 \) with \( b_1 = 1 \). From Eq. (9) it is apparent that \( \tau_i \) depends on \( Z_j \) with \( j = 1, \ldots, i \), and thus, the \( \tau_i \)s with \( i = 1, \ldots, k \) and the \( Z_j \)s with \( j = 1, \ldots, k \) involve the same physical information. On the other hand, one can return to the Eqs. (1) - (4) to observe that they can be re-written in this alternative form: replace \( M \to \infty \) in Eq. (1) but assume \( Z_{M+k} = 0 \) with \( k = 1, \ldots, \infty \). In this context Eq. (9) shows that cluster integrals \( \tau_i \) with \( i = 1, \ldots, M \) are not affected by the restriction \( j \leq M \), being \( \tau_{M+1} \) the first affected \( \tau \) (because it depends on \( Z_{M+1} \), which is zero).

Before ending this section we wish to focus on a relevant characteristic of \( \Xi_M, Z_j \) and \( \tau_i \) functions. Let us define \( S = \{A/A \subseteq \mathbb{R}^d\} \) (the set of all the subsets of \( \mathbb{R}^d \)), for fixed \( T, \phi \) and \( z \) one can write \( \Xi_M(A) : S \to \mathbb{R} \) which implies that \( \Xi_M(A) \) may depend on the shape of \( A \). Clearly, the same argument applies to \( Z_j \) and \( \tau_i \) which may also depend on the shape of \( A \). Here we anticipate the principal result of PW, related with this non-trivial shape dependence, that will be demonstrated in the Secs. III and IV. Thus, we turn the attention to a fluid confined by a polytope \( A \). For simplicity we focus in the three dimensional case, i.e. a fluid confined by a polyhedron. If a system of particles that interact via a pair potential of finite range \( \xi \) is confined in a polyhedron \( A \) such that its characteristic length \( \mathcal{L}(A) \) [see Eq. (25)] is greater than \( k\xi + C \) (being \( C \) a constant) for some integer \( k \geq 1 \). Then the \( i \)-th cluster integral \( \tau_i \) with \( 1 \leq i \leq k \) is a linear function in the variables \( V, A \) and \( \{L_1, L_2, \ldots\} \) (the length of the edges of \( A \)). In fact

\[
\tau_i/i! = V b_i - A a_i + \sum_{\text{edges}} L_n c_{i,n}^\xi + \sum_{\text{vertex}} c_{i,n}^\gamma,
\]

where the coefficients \( b_i \) and \( a_i \) are independent of the shape of \( A \) while \( c_{i,n}^\xi \) and \( c_{i,n}^\gamma \) are functions of the dihedral angles involved. Besides, all the coefficients depend on the pair interaction potential and temperature. Expressions similar to Eq. (10) are also found for the euclidean space with dimension 2 and 1, while they are conjectured for dimension larger than 3. Two non-trivial consequences derive from the Eq. (10). On one hand it implies
that, if the system of particles confined by $\mathcal{A}$ involves $N$ particles and $\mathfrak{L}(\mathcal{A}) > N\xi + C$, then $Z_N$ is polynomial on $V$, $A$ and \{\$L_1, L_2, \ldots\$. On the other hand it implies that, if the system of particles confined by $\mathcal{A}$ is open, involves at most $M$ particles and $\mathfrak{L}(\mathcal{A}) > M\xi + C$, then $\Xi_M$ is a polynomial in $z$, $V$, $A$ and \{\$L_1, L_2, \ldots\$.

III. THE PROPERTIES OF SOME FUNCTIONS RELATED TO $\tau_i$

In this section we analyze the properties of some many-body functions related to the partial integration of the cluster integral $\tau_i$ [Eqs. (7) and (8)]. This analysis will be complemented in the next section where we will reveal the linear behavior of $\tau_i$. In the following paragraphs several definitions are introduced and two different proofs of the locality and rigid invariance of functions related to the partial integration of $\tau_i$ are presented. Both proofs are necessary for clarity. In the first approach the mentioned properties of those functions are demonstrated and it is found a cutoff for its finite range, while in the second approach (which is more complex than the first one) the properties are proved and a better bound of the finite range is obtained.

We define, $G(\mathcal{A}, \mathbf{r}) : \mathbb{S} \times \mathbb{R}^d \rightarrow \mathbb{R}$ is a local function in $\mathbf{r}$ over $\mathcal{A}$ with range $\lambda$ (from hereon local with range $\lambda$) if its value is entirely determined by the set $U(\mathbf{r}, \lambda) \cap \mathcal{A}$ that is $G(\mathcal{A}, \mathbf{r}) = G(U(\mathbf{r}, \lambda)\cap \mathcal{A})$ where $U(\mathbf{r}, \lambda)$ is the ball centered at $\mathbf{r}$ with radius $\lambda$. This definition can be generalized to functions of several variables in the following way: $G(\mathcal{A}, \mathbf{r}_1, \ldots, \mathbf{r}_n) : \mathbb{S} \times \mathbb{R}^{d\mathfrak{m}} \rightarrow \mathbb{R}$ is said to be a local function in $\mathbf{r}_i$ over $\mathcal{A}$ with range $\lambda$ if $G(\mathcal{A}, \mathbf{r}_1, \ldots, \mathbf{r}_n) = G(U(\mathbf{r}_i, \lambda) \cap \mathcal{A}, \mathbf{r}_1, \ldots, \mathbf{r}_{i-1}, \mathbf{r}_{i+1}, \ldots, \mathbf{r}_n)$ for $\{\mathbf{r}_1, \ldots, \mathbf{r}_{i-1}, \mathbf{r}_{i+1}, \ldots, \mathbf{r}_n\} \subset U(\mathbf{r}_i, \lambda) \cap \mathcal{A}$ and $G(\mathcal{A}, \mathbf{r}_1, \ldots, \mathbf{r}_n) = 0$ when exist $\mathbf{r}_j \neq \mathbf{r}_i \notin U(\mathbf{r}_i, \lambda) \cap \mathcal{A}$.

Let $G(\mathcal{A}, \mathbf{r})$ be a local function with range $\lambda$. We say that $G(\mathcal{A}, \mathbf{r})$ is invariant under rigid transformations (the elements of the euclidean group, i.e., any composition of translations, rotations, inversions and reflections) if $\forall$ rigid transformation $R$, $R[U(\mathbf{r}, \lambda)\cap \mathcal{A}] = U(\mathbf{r}', \lambda)\cap \mathcal{A}'$ with $\mathbf{r}' = R\mathbf{r}$ implies $G[U(\mathbf{r}, \lambda)\cap \mathcal{A}] = G[U(\mathbf{r}', \lambda)\cap \mathcal{A}]$. The generalization to functions with many variables is: let $G(\mathcal{A}, \mathbf{r}_1, \ldots, \mathbf{r}_n) : \mathbb{S} \times \mathbb{R}^{d\mathfrak{m}} \rightarrow \mathbb{R}$ be a local function in $\mathbf{r}_i$ with range $\lambda$, we say that $G(\mathcal{A}, \mathbf{r}_1, \ldots, \mathbf{r}_n)$ is invariant under rigid transformations if $\forall$ rigid transformation $R$, $R[U(\mathbf{r}_i, \lambda)\cap \mathcal{A}] = U(\mathbf{r}_i, \lambda)\cap \mathcal{A}'$ implies $G[U(\mathbf{r}_i, \lambda)\cap \mathcal{A}, \mathbf{r}_1, \ldots] = G[U(\mathbf{r}', \lambda)\cap \mathcal{A}', \mathbf{r}_1, \ldots]$, with $\mathbf{r}_j = R\mathbf{r}_j$. A direct consequence of the locality with range $\lambda$ and rigid transformation invariance of a bounded function $G(\mathcal{A}, \mathbf{r})$ is that it attains a constant value for all $\mathbf{r} \in \mathcal{A}$.
such that \( U(r, \lambda) \cap \partial A \).

**Theorem 1:** Let \( e_k(r) \) and \( S_{1,2,\ldots,i} \) be the Boltzmann factor and cluster integrand introduced in Eqs. (5) to (8), and \( A \in \mathbb{S} \) a set in \( \mathbb{R}^d \) for which the integral in Eq. (11) is finite. Then

\[
E_1(A, r_1) \equiv \int \cdots \int S_{1,2,\ldots,i} \prod_{k=2}^i e_k dr_2 \cdots dr_i
\]  

(11)

is a local function with finite range invariant under rigid transformations.

**First Proof:** Consider the following \( i \)-body function

\[
E_i(r_1, y_2, \ldots, y_i) = S_{1,2,\ldots,i},
\]

(12)

with \( r_1 \) the position of an arbitrarily chosen particle, and the rule to obtain the \( (n-1) \)-body function from the \( n \)-body one given by

\[
E_{n-1}(A, r_1, y_2, \ldots, y_{n-1}) \equiv \int E_n(A, r_1, y_2, \ldots, y_n) e_n dy_n,
\]

(13)

where \( 2 \leq n \leq i \) and \( y_j = r_j - r_1 \) is the coordinate of particle \( j \) with respect to particle 1. \( S_{1,2,\ldots,i} \) has range

\[
\varsigma = (i - 1) \xi,
\]

(14)

being \( S_{1,2,\ldots,i} = 0 \) if \( r_{ab} = |r_a - r_b| > (i - 1) \xi \) for at least one pair of particles \( a \) and \( b \) in the cluster. This property derives from the fact that \( S_{1,2,\ldots,i} \) contains the open simple-chain cluster term \( S' = f_{12} f_{23} \cdots f_{i-1,i} \) that enables that two particles reach the maximum possible separation \( (i - 1) \xi \) of all the cluster terms in \( S_{1,2,\ldots,i} \) (there are \( i! / 2 \) terms of this type). Even more, one can show that \( S_{1,2,\ldots,i} \) is local with range \( \varsigma \). Naturally, Eq. (12) shows that \( E_i(r_1, y_2, \ldots, y_i) \) is also local with range \( \varsigma \). The integration in Eq. (13) applied to \( E_i(r_1, y_2, \ldots, y_i) \) implies that \( E_{i-1}(A, r_1, y_2, \ldots, y_{i-1}) \) is local in \( r_1 \) with range \( \varsigma \). We proceed by induction. Let us assume that for some \( n < i \), \( E_n(A, r_1, y_2, \ldots, y_n) \) is local with range \( \varsigma \), then by Eq. (13) \( E_{n-1}(A, r_1, y_2, \ldots, y_{n-1}) \) is also local with the same range. The procedure continue until the function \( E_1(A, r_1) \) is reached. Therefore, we find that the \( E_n(A, r_1, y_2, \ldots, y_n) \) functions with \( 1 \leq n < i \) are local in \( r_1 \) with range \( \varsigma \) [even more, we have obtained that \( E_n(A, r_1, \ldots, r_n) \) are local in \( r_j \) with range \( \varsigma \), for any \( 1 \leq j \leq n \)].

Taking into account that \( E_i(r_1, y_2, \ldots, y_i) \) has range \( \varsigma \) and that \( e_i = e_i(A, r_i) \) [see Eq. (5)] the right hand side of Eq. (13) for \( n = i \) can be written as

\[
\int_{U(r_1, \varsigma) \cap A} E_i(r_1, y_2, \ldots, y_i) dy_i.
\]

(15)
It is convenient to express the coordinates \((r_1, y_2, \ldots, y_i)\) in terms of the rigid transformed coordinates \((r'_1, y'_2, \ldots, y'_i)\) (related each other by \(r_j = R^{-1}r'_j\) and \(y_j = R^{-1}y'_j = R^{-1}r'_j - R^{-1}r'_1\) with \(R^{-1}\) the inverse of \(R\)) and to change the integration variable to \(y'_i\) (note that the Jacobian is one). Thus we find

\[
\int_{R[U(r_1, \varsigma) \cap A]} E_i(R^{-1}r'_1, R^{-1}y'_2, \ldots, R^{-1}y'_i) \, dy'_i, \tag{16}
\]

where the integration domain is equal to \(U(r'_1, \varsigma) \cap A'\) by hypothesis. Given that \(E_i\) is invariant under any rigid transformation applied to the coordinate of the particles one can drop each \(R^{-1}\) in Eq. (16) and return to the original form introducing \(e_i = e_i(A', r'_i)\)

\[
\int E_i(r'_1, y'_2, \ldots, y'_i) \, e_i \, dy'_i, \tag{17}
\]

which is the definition of \(E_{i-1}(A', r'_1, y'_2, \ldots, y'_{i-1})\). This shows that \(E_{i-1}(A, r_1, y_2, \ldots, y_{i-1})\) is invariant under rigid transformations. Again, we proceed by induction. Let us assume that \(E_n(A, r_1, y_2, \ldots, y_n)\), a local function in \(r_1\) over \(A\) with range \(\varsigma\), is invariant under rigid transformations. Taking into account that \(e_n = e_n(A, r_n)\) for the right hand side of Eq. (15) we can write an expression similar to Eq. (15) but replacing \(E_i(r_1, y_2, \ldots, y_i)\) by \(E_n(U(r_1, \varsigma) \cap A, y_2, \ldots, y_n)\) and \(i\) by \(n\). Turning to transformed coordinates we find

\[
\int_{R[U(r_1, \varsigma) \cap A]} E_n(R^{-1}[U(r'_1, \varsigma) \cap A'], R^{-1}y'_2, \ldots, R^{-1}y'_n) \, dy'_n, \tag{18}
\]

where the integration domain is equal to \(U(r'_1, \varsigma) \cap A'\) and we used that \(U(r_1, \varsigma) \cap A = R^{-1}[U(r'_1, \varsigma) \cap A']\). Given that \(E_n\) is invariant under rigid transformations we can drop each \(R^{-1}\) in the arguments of \(E_n\) in Eq. (18), use the finite range of \(E_n\) to split the argument \(U(r'_1, \varsigma) \cap A'\) into \((A', r'_1)\) and introduce \(e_n(A', r'_n)\) to obtain

\[
\int E_n(A', r'_1, y'_2, \ldots, y'_n) \, e_n \, dy'_n, \tag{19}
\]

which is the definition of \(E_{n-1}(A', r'_1, y'_2, \ldots, y'_{n-1})\). Therefore, \(E_{n-1}(A, r_1, y_2, \ldots, y_{n-1})\) is local of range \(\varsigma\) and rigid transformation invariant. The procedure continue until the function \(E_1\) is reached. Therefore, returning to the original coordinates, we obtain that \(E_n(A, r_1, \ldots, r_n)\) with \(1 \leq n \leq i\) is local in any \(r_j\) \((1 \leq j \leq n)\) with range \(\varsigma\) and rigid transformation invariant. In particular, for \(n = 1\) it implies that \(E_1(A, r_1)\) is local in \(r_1\) with range \(\varsigma\) and rigid transformation invariant.
Second Proof: This second proof is based on a more subtle consideration about the particle labeled as $r_1$ in the first proof. We introduce the coordinate of the central particle of the cluster, $r_c$, and the relative coordinates $y_j = r_j - r_c$ of the particle $j$ with respect to $r_c$. Again, consider the cluster integral $\tau_i$ and its simple open-chain cluster $S'$ term. For $S'$ we take $r_c = r_l$ with $l = \text{IntegerPart}[i/2 + 1]$ (if $i$ is an odd number $r_c = r_{(i+1)/2}$ is the position of the middle-chain particle while if $i$ is an even number $r_c = r_{i/2+1}$ is the position of one of the pair of particles that are at the middle of the chain). We note that $S'_{1,2,...,i}$ is zero if $|r_a - r_c| > (l - 1) \xi$ for at least one particle $a$ in the cluster. The procedure to obtain $r_c$ for all the other terms in $S_{1,2,...,i}$ is as follows: for a given cluster $S''$ of $i$ particles take iteratively each pair of particles, separate them to find the maximum possible elongation distance under the condition $S'' \neq 0$. Let the more stretchable chain of particles (that could be non-unique) be a chain of $k$ particles with end-particles $a$ and $b$. Thus, $|r_a - r_b| < (k - 1) \xi$ with $2 \leq k < i$ and for this cluster we can define $r_c = r_l$ with $l = \text{IntegerPart}[k/2 + 1]$. By using this second approach we find that $S_{1,2,...,i}$ has finite range

$$\varsigma = (i - 1) \xi / 2 \text{ if } i \text{ is odd, } \varsigma = i\xi / 2 \text{ if } i \text{ is even.} \quad (20)$$

Once $r_c$ is identified for each cluster term in $S_{1,2,...,i}$ we can rename $r_c$ as $r_1$ and follow the procedure developed in the first proof of the theorem. 

Based on Eq. (20) along with the assumption that the range of $E(r)$ must be a unique function of the maximum elongation length of $S_{1,2,...,i}$ independently of the parity of $i$ we have the following guess

$$\varsigma = (i - 1) \xi / 2 \forall i \in \mathbb{N}. \quad (21)$$

We may mention that Eq. (21) can be demonstrated for the case of $\mathcal{A}$ being a convex body [by virtue of Eq. (20) one must focus on the case of even $i$]. The demonstration follows a procedure similar to that used to obtain the Eq. (20), but for the case of even $i$ one define $r_c = (r_{i/2} + r_{(i/2+1)}) / 2$. The development made in this section enable to write Eq. (7) as

$$\tau_i = \int E(r_1)e_1 dr_1, \quad (22)$$

with two different definitions for $E(r_1)$. Both definitions and any other possible approach must give mathematically equivalent expressions for $\tau_i$. 

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IV. INTEGRATION OVER A POLYTOPE-SHAPED DOMAIN

In order to analyze the implications of the domain’s shape on certain type of integrals it is necessary to introduce some notions about sets $B, C \subseteq \mathbb{R}^d$. They are summarized in this and the next paragraphs. The closure of $B$ is $\text{cl}(B) = B \cup \partial B$. It is said that $B$ is a closed set if $B = \text{cl}(B)$. Besides, the interior of $B$ is $\text{int}(B) = B \setminus \partial B$. It is said that $B$ is an open set if $B = \text{int}(B)$. There are sets that are neither closed nor open. \{$B_1, \ldots, B_n$\} is a partition of the non-empty set $B$ if $B = \bigcup_{k=1}^n B_k$ and, for all $i, j \in \mathbb{N}_{\leq n}$ with $i \neq j$, $B_i \neq \emptyset$ and $B_i \cap B_j = \emptyset$. A set in $\mathbb{R}^d$ is connected if it cannot be partitioned in two non-empty sets $B$ and $C$ such that $\text{cl}(B) \cap C = B \cap \text{cl}(C) = \emptyset$, otherwise it is disconnected. We also introduce the concept of connectedness-based partition of a set; a partition \{$B_1, \ldots, B_n$\} of $B$ is the connectedness-based partition of $B$ if, for all $i, j \in \mathbb{N}_{\leq n}$ with $i \neq j$, $B_i$ is connected and $B_i \cup B_j$ is disconnected. The following notions of distances are adopted: the distance between the point $r \in \mathbb{R}^d$ and the set $B$ is $d(r, B) = \min(|r - b|, b \in B)$ with $|r - b|$ the usual Euclidean distance between points, while the distance between the sets $B$ and $C$ is $d(B, C) = \min(|b - c|, b \in B \text{ and } c \in C)$. Finally, a set $B$ is said to be convex if every pair of points $x$ and $y$ in $B$ are the endpoints of a line segment lying inside $B$.

An affine $k$-subspace is a linear variety of rank $k$ in $\mathbb{R}^d$, whether it contains the origin or not. For example, the $(d - 1)$-dimensional affine subspace is a hyperplane. The affine hull of a set $B \subseteq \mathbb{R}^d$, $\text{aff}(B)$, is the affine subspace with the smallest rank in which every point of $B$ is contained. Given that $d$ is a fixed parameter from hereon we will refer to the rank of $\text{aff}(B)$ as the dimension of the affine space of $B$, denoted $\dim[\text{aff}(B)]$ or simply $\dim(B)$. For $B \subseteq \mathbb{R}^d$, the sets $\text{relcl}(B)$, $\text{relint}(B)$ and $\text{rel}\partial(B)$ are the relative closure, the relative interior and the relative boundary of $B$, i.e., the closure, interior and boundary of $B$ within its affine hull, respectively [7].

Even though a polytope is essentially a mathematical entity, in the current work it also has a physical meaning because it serves to characterize the shape of the vessel where particles are confined. This duality makes difficult to start with a simple and satisfactory geometrical description of the kind of polytopes that are relevant for our purposes. We begin a somewhat indirect approach that ends in the definition of the set of polytopes that have simple boundary (a well behaved one), in the sense that the boundary can be dissected in its elements or faces. To make further progress it is convenient to introduce the convex
polytopes which, from a geometrical point of view, are simpler than the general polytopes. A convex polytope in \( \mathbb{R}^d \) is any set with non-null volume given by the intersection of finitely many half-spaces \( [7] \) (this definition includes unbounded, closed and non-closed polytopes). On the other hand, a connected and closed (CC) polytope \( A \) is the connected union of finitely many closed convex polytopes. We define, the CC polytope \( A \subseteq \mathbb{R}^d \) is a simple-boundary (SB) polytope if for each \( r \in \partial A \) \( \exists \varepsilon \in \mathbb{R}_{>0} \) such that \( \forall \lambda 0 < \lambda < \varepsilon \), both sets \( \text{int} [U (r, \lambda) \cap A] \) and \( \text{int} [U (r, \lambda) \cap A^c] \) are topologically equivalent (homeomorphic) to an open ball. It is clear that a closed convex polytope is also a CC SB polytope. In this sense, we say that the boundary of a CC SB polytope and the boundary of a convex polytope are locally equivalent. The SB condition excludes some degenerate or pathological cases e.g. a polytope with two vertex or two edges, in contact. On the other hand, the definition of SB polytopes includes bounded and unbounded polytopes, non-convex polytopes, polytopes with holes or cavities and many kind of faceted knots embedded in \( \mathbb{R}^d \). Let \( \mathbb{P}^d \) be the class of CC SB polytopes in \( \mathbb{R}^d \).

For a given polytope we focus on the partition of its boundary based on its faces. As before, we treat first the convex polytope case. Let \( B \in \mathbb{P}^d \) be a convex polytope and \( H \) a hyperplane. If \( H \cap \partial B \neq \emptyset \), \( H \cap \text{int} (B) = \emptyset \) and \( k = \dim (H \cap \partial B) \) with \( 0 \leq k \leq d - 1 \), then we say that \( H \cap \partial B \) is a closed \( k \)-face of \( B \) \([8]\). One can demonstrate that the set whose elements are all the closed \( 0 \)-faces and relopen \( k \)-faces with \( 0 < k \leq d - 1 \), of \( B \) is a partition of \( \partial B \). Other polytopes, non-necessarily convex, may admit a similar face-decomposition of its boundary. Given a polytope \( A \) with face-decomposable boundary, we introduce the notation \( \partial A_{m,n} \) \((1 \leq m < d)\) for the \( n \)-th \((d - m)\)-dimensional relopen face of \( A \) (from here on an open \((d - m)\)-face), while \( \partial A_{d,n} \) is the \( n \)-th closed 0-face. The closed 0-faces are the vertex of the polytope. The face-based partition of \( \partial A \) is \( \{ \partial A_{1,1}, \ldots, \partial A_{m,n}, \ldots, \partial A_{d,n'}, \ldots \} \) with \( \partial A_{m,i} \cap \partial A_{m',j} = \emptyset \) for every \( m, i \neq m', j \). Note that \( \partial A_{m,n} \) is \( [\partial A]_{m,n} \), i.e., the \((m, n)\)-element of \( \partial A \). Besides, we define

\[
\partial A_m \equiv \bigcup_n \partial A_{m,n},
\]

as the set of points in \( \partial A \) that lies in some of the \((d - m)\)-faces of \( A \), with \( \{ \partial A_{m,1}, \ldots, \partial A_{m,n}, \ldots \} \) a partition of \( \partial A_m \). Furthermore,

\[
\partial A = \bigcup_m \partial A_m,
\]

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with \( m \) going from 1 to \( d \), where \( \{ \partial A_1, \ldots, \partial A_d \} \) is a partition of \( \partial A \). Given any open face, the corresponding closed face is its closure. Furthermore, given any closed \( k \)-face with \( k > 0 \), its relint is the corresponding open \( k \)-face (an open face relative to its affine hull). Some \( k \)-faces are designed by their names: a 3-face is a cell (polyhedron), a 2-face is a facet (polygon) and a 1-face is an edge (line).

The next step is to demonstrate that every CC SB polytope is face-decomposable. To find the \((d - 1)\)-faces of a CC SB polytope one can exploit that locally they are equal to the \((d - 1)\)-faces of a convex polytope. Let \( A \subseteq \mathbb{P}^d \), \( r \in \partial A \) belongs to an open \((d - 1)\)-face of \( A \) if no matter how small is \( \lambda \) with \( \lambda \in \mathbb{R}_{>0} \) the set \( \text{int} [U (r, \lambda) \cap A] \) is the interior of a half-ball (a ball cut by a hyperplane through its center). In this case, relint \( [U (r, \lambda) \cap \partial A] \subset \partial A_1 \) belongs to a given open \((d - 1)\)-face and we introduce the tangent affine space \( \text{aff} (r, \partial A) = \text{aff} [U (r, \lambda) \cap \partial A] \) of this face. Let \( r, s \in \partial A_1 \) with \( \text{aff} (r, \partial A) = \text{aff} (s, \partial A) \) and assume that exist a path \( C (r, s) \subset \partial A_1 \) that connects \( r \) and \( s \) such that for every \( x \in C (r, s) \) \( \text{aff} (x, \partial A) = \text{aff} (r, \partial A) \), then \( r, s \) and \( C (r, s) \) are in the same open \((d - 1)\)-face of \( A \). Furthermore, the connectedness-based partition of \( \partial A_1 \) is the set of open \((d - 1)\)-faces of \( A \), i.e. \( \{ \partial A_{1,1}, \cdots, \partial A_{1,n}, \cdots \} \). Given that \( \partial A = \cup_n \text{cl} (\partial A_{1,n}) \), thus every \( r \in \partial A \setminus \partial A_1 \) belongs to the relative boundary of two \((d - 1)\)-faces (may be more than two). Let \( \partial A_{1,i} \) and \( \partial A_{1,j} \) be two different open \((d - 1)\)-faces of \( A \) with \( \text{cl} (\partial A_{1,i}) \cap \text{cl} (\partial A_{1,j}) \neq \emptyset \), then \( \text{cl} (\partial A_{1,i}) \cap \text{cl} (\partial A_{1,j}) \) is a closed \( m \)-face of \( A \) with \( m = \dim [\text{cl} (\partial A_{1,i}) \cap \text{cl} (\partial A_{1,j})] \). By analyzing each pair of mutually intersecting closed \((d - 1)\)-faces one find each of the remaining \( \partial A_{m,n} \) and \( \partial A_m \) elements with \( 1 < m \leq d \). Now, given \( A \in \mathbb{P}^d \) we can obtain a non-closed SB polytope by removing from \( A \) one or several of its faces. However, for PW purposes the polytope represents the integration domain of a well behaved function. Given that the value of the integral is not modified by removing one or several faces, we will only consider the case of closed \( A \).

Let \( A \in \mathbb{P}^d \), we say that the two elements \( \partial A_{m,i} \) and \( \partial A_{m',j} \) of \( \partial A \) are neighbors if \( \partial A_{m,i} \subseteq \text{cl} (\partial A_{m',j}) \) or \( \partial A_{m',j} \subseteq \text{cl} (\partial A_{m,i}) \), for \( m, i \neq m', j \). On the other hand, they are adjacent if \( \text{cl} (\partial A_{m,i}) \cap \text{cl} (\partial A_{m',j}) \neq \emptyset \). It is simple to verify that if two elements are neighbors they are adjacent, and the distance between two adjacent elements is zero. We define the characteristic length of the polytope \( A \) as

\[
\mathcal{L} (A) = \min \{ d \left[ \partial A_{m,i}, \partial A_{m',j} \right] \neq 0 \}, \tag{25}
\]
i.e. the minimum distance between two non-adjacent elements of $\partial A$. It is clear that if $A \in \mathbb{P}^d$, then $\exists \varepsilon \in \mathbb{R}_{>0}$ such that $\mathcal{L}(A) > \varepsilon$.

In the following lines we state the general proposition for positive integer values of $d$. The cases of $d = 1, 2, 3$ are demonstrated each one in a separated proof. The remaining cases that concern every positive integer value $d \geq 4$ are not demonstrated here and thus, the proposition is for these cases a conjecture. We note that Theorem 2 and its the conjectured generalization to $\mathbb{R}^d$ given in the following Eq. (26) strongly resemble the combination of Hadwiger’s characterization theorem and the general kinematic formula (see Theorems 9.1.1 and 10.3.1 in pp. 118 and 153 of [9], respectively) and transpires analogies with several results of integral geometry. These points will be discussed at the end of Sec. VII.

General conjecture (cases $d \geq 1$): Consider $A \in \mathbb{P}^d$ and let $G(A, r) : \mathbb{P}^d \times \mathbb{R}^d \to \mathbb{R}$ be a well behaved function in $r \in \text{cl} (A)$ (with fixed $A$), and a local function with range $\varsigma \in \mathbb{R}_{>0}$ invariant under rigid transformations with $2\varsigma < \mathcal{L}(A)$ [for fixed $A \in \mathbb{P}^d$ function $G(r, A)$ is simply $G(r) : A \to \mathbb{R}$]. Then

$$
t = \hat{A} G(r) dr = \chi_d c_0 + \chi_{d-1} c_1 + \sum_{m=2}^{d} \sum_{m\text{-elem}} \chi_{d-m,n} c_{m,n}, \quad (26)
$$

where $\chi_d$ is the $d$-dimensional measure (Lebesgue measure) of $A$ (i.e. its volume $V$), $\chi_{d-1}$ is the $(d - 1)$-dimensional measure of $\partial A$, and $\chi_{m,n}$ is the $m$-dimensional measure of the $n$-th $m$-element of $\partial A$ (in particular $\chi_{0,n} = 1$). Besides, $c_0$ and $c_1$ are constant coefficients which are independent of the size and shape of $A$, while $c_{m,n}$ is a function of the angles that define the geometry of $A$ near its $n$-th $m$-element $\partial A_{d-m,n}$ far away from its relative boundary.

Theorem 2 (case $d=3$): For the case $d = 3$ the Eq. (26) is

$$
t = \int_{A} G(r) dr = V c_0 + A c_1 + \sum_{n \text{ edges}} L_n c_{2,n} + \sum_{n \text{ vertex}} c_{3,n}, \quad (27)
$$

where $V$ is the volume of $A$, $A$ is the surface area of $\partial A$, and $L_n$ is the length of the $n$-th edge. Besides, $c_0$ and $c_1$ are constant coefficients which are independent of the size and shape of $A$, while $c_{2,n}$ is a function of the dihedral angle in the $n$-th edge, and $c_{3,n}$ is a function of the set of dihedral angles between the adjacent planes that converge to the $n$-th vertex.
Figure 1: Picture describing the partition for \( \mathcal{A} \) in its principal and skin parts, \( \mathcal{A}_o \) and \( \mathcal{A}_{sk} \), respectively.

Proof (case \( d=3 \)): Consider the set \( \mathcal{A} \in \mathbb{P} \) and introduce a partition of \( \mathcal{A} \) given by \( \{\mathcal{A}_o, \mathcal{A}_{sk}\} \) with the principal part \( \mathcal{A}_o = \{r \in \mathcal{A} \mid d(r, \partial \mathcal{A}) \geq \varsigma\} \) (the inner parallel body of \( \mathcal{A} \)) and the boundary or skin part \( \mathcal{A}_{sk} = \mathcal{A} \setminus \mathcal{A}_o \) characterized by a thickness \( \varsigma \). We have

\[
\mathcal{A} = \mathcal{A}_o \cup \mathcal{A}_{sk}.
\] (28)

Here \( \mathcal{A}_o \) is the region where \( G(r) \) takes a constant value. This partition may be obtained by wrapping \( \partial \mathcal{A} \) through sliding the center of a ball of radius \( \varsigma \) on \( \partial \mathcal{A} \). Let \( w(\partial \mathcal{A}, \varsigma) \) be the set of points that are inside of any of these balls, then \( \mathcal{A}_o = \mathcal{A} \setminus w(\partial \mathcal{A}, \varsigma) \). Besides, it may also be obtained in terms of a Minkowski sum. Let \( U \) be the unit ball centered at the origin, then the Minkowski sum \( \mathcal{A}^c + \varsigma U \) is the outer parallel body of \( \mathcal{A}^c \) and \( \mathcal{A}_o = \mathcal{A} \setminus (\mathcal{A}^c + \varsigma U) \). In Fig. 1 a picture representing this partition for \( \mathcal{A} \) is shown. There, one can observe \( \partial \mathcal{A} \) on continuous line and several balls of radius \( \varsigma \) (in dotted lines) corresponding to the wrapping procedure. For the case of \( \mathcal{A} \) being the shaded region (both the darker and brighter ones), the darker shaded region represents \( \mathcal{A}_o \) while the brighter shaded one corresponds to \( \mathcal{A}_{sk} \). On the contrary, if \( \mathcal{A} \) is the non-shaded or white region then \( \mathcal{A}_{sk} \) corresponds to the white region between \( \partial \mathcal{A} \) and the dashed line while the rest of the white region represents \( \mathcal{A}_o \). For both cases a dashed line separates regions \( \mathcal{A}_o \) and \( \mathcal{A}_{sk} \). The integral in Eq. (27) gives

\[
\int_{\mathcal{A}} G(r) dr = Vc_0 + \int_{\mathcal{A}_{sk}} g(r) dr,
\] (29)

with \( g(r) = G(r) - c_0 \) and \( c_0 = G(r) \) for all \( r \in \mathcal{A}_o \). Naturally, \( g(r) : \mathcal{A} \to \mathbb{R} \) is a bounded and local function with range \( \varsigma \) invariant under rigid transformations which implies that \( g(r) = g(U(r, \varsigma) \cap \mathcal{A}) \) and its value is independent of the position and orientation that the set \( U(r, \varsigma) \cap \mathcal{A} \) takes on the space, \( g(r) \) only depends on the shape of \( U(r, \varsigma) \cap \mathcal{A} \). Besides if \( r \notin \mathcal{A}_{sk} \) then \( g(r) = 0 \).
Note that in the context of \( d = 3 \) a planar face is simply a face. Consider the set \( \mathcal{A}_{sk} \) partitioned in terms of \( \{ \mathcal{A}_1, \mathcal{A}_2, \mathcal{A}_3 \} \),

\[
\mathcal{A}_{sk} = \mathcal{A}_1 \cup \mathcal{A}_2 \cup \mathcal{A}_3 .
\]

Here, \( \mathcal{A}_1 \) is the surface-type region \( \mathcal{A}_1 = \{ r \in \mathcal{A}_{sk}/U(r, \varsigma) \cap \partial \mathcal{A}_{1,n} \neq \emptyset \text{ for only one value of } n \text{ face} \} \) where each \( r \in \mathcal{A}_1 \) is related to a unique face. Let us define \( \mathcal{A}_{1,n} = \{ r \in \mathcal{A}_1/U(r, \varsigma) \cap \partial \mathcal{A}_{1,n} \neq \emptyset \text{ for the } n\text{-th face} \} \) thus \( \{ \mathcal{A}_{1,1}, \ldots, \mathcal{A}_{1,n}, \ldots \} \) is a partition of \( \mathcal{A}_1 \). Since \( r \in \mathcal{A}_1 \) then \( r \in \mathcal{A}_{1,n} \) for some \( n \) face. Hence, the shape of \( U(r, \varsigma) \cap \mathcal{A} \) is determined by the one dimensional position variable \( r^{(1)} = d(r, \partial \mathcal{A}_{1,n}) = z \), and then, \( g(r) = g_1(r) = g_1(r^{(1)}) = g_1(z) \). In Eq. (30), \( \mathcal{A}_2 \) is the edges-type region \( \mathcal{A}_2 = \{ r \in \mathcal{A}_{sk}/U(r, \varsigma) \cap \partial \mathcal{A}_{1,m} \neq \emptyset \text{ for two and only two values of } m \text{ faces} \} \) where each \( r \in \mathcal{A}_2 \) is related to a unique pair of faces. Let \( r \in \mathcal{A}_2 \) and \( m_1, m_2 \) be such that \( U(r, \varsigma) \cap \partial \mathcal{A}_{1,m_1} \neq \emptyset \) and \( U(r, \varsigma) \cap \partial \mathcal{A}_{1,m_2} \neq \emptyset \), given that \( 0 < 2\varsigma < \mathcal{L}(\mathcal{A}) \) the pair of faces \( m_1, m_2 \) converge to a common edge. Let us define \( \mathcal{A}_{2,n} = \{ r \in \mathcal{A}_2/U(r, \varsigma) \cap \partial \mathcal{A}_{1,m} \neq \emptyset \text{ for the two values of } m \text{ faces that join in the } n\text{-th edge} \} \) thus \( \{ \mathcal{A}_{2,1}, \ldots, \mathcal{A}_{2,n}, \ldots \} \) is a partition of \( \mathcal{A}_2 \). Since \( r \in \mathcal{A}_2 \) then \( r \in \mathcal{A}_{2,n} \) for only one edge (the \( n\)-th). Hence, the shape of \( U(r, \varsigma) \cap \mathcal{A} \) is determined by both, the dihedral angle and the two-dimensional vector \( r^{(2)} \) that lies in a plane orthogonal to \( \partial \mathcal{A}_{2,n} \) and goes from \( \partial \mathcal{A}_{2,n} \) to \( r \), and thus, \( g(r) = g_2(r) = g_2(r^{(2)}) \). \( \mathcal{A}_3 \) is the vertex-type region \( \mathcal{A}_3 = \{ r \in \mathcal{A}_{sk}/U(r, \varsigma) \cap \partial \mathcal{A}_{1,m} \neq \emptyset \text{ for three or more values of } m \text{ face} \} \) where each \( r \) is related to a unique set of faces. Let \( r \in \mathcal{A}_3 \) and \( \{ m_1, m_2, m_3, \ldots \} \) be such that \( U(r, \varsigma) \cap \partial \mathcal{A}_{1,m_1} \neq \emptyset \), \( U(r, \varsigma) \cap \partial \mathcal{A}_{1,m_2} \neq \emptyset \), \( U(r, \varsigma) \cap \partial \mathcal{A}_{1,m_3} \neq \emptyset \), ... , given that \( 0 < 2\varsigma < \mathcal{L}(\mathcal{A}) \) the set of faces \( \{ m_1, m_2, m_3, \ldots \} \) converge to one vertex. Let us define \( \mathcal{A}_{3,n} = \{ r \in \mathcal{A}_3/U(r, \varsigma) \cap \partial \mathcal{A}_{1,m} \neq \emptyset \text{ for the } i \text{ values (with } i \geq 3 \text{) of } m \text{ faces that join in the } n \text{ vertex} \} \) thus \( \{ \mathcal{A}_{3,1}, \ldots, \mathcal{A}_{3,n}, \ldots \} \) is a partition of \( \mathcal{A}_3 \). Since \( r \in \mathcal{A}_3 \) then \( r \in \mathcal{A}_{3,n} \) for some \( n \) vertex. Hence, the shape of \( U(r, \varsigma) \cap \mathcal{A} \) is determined by the three-dimensional vector \( r^{(3)} \) that goes from \( \partial \mathcal{A}_{3,n} \) to \( r \) (and the angles that define the geometry of the vertex). Naturally, \( g(r) = g_3(r) = g_3(r^{(3)}) \). Care must be taken about \( \partial \mathcal{A}_{m,n} \) [the \((m, n)\) element of \( \partial \mathcal{A} \)] that should not be confused with \( \partial (\mathcal{A}_{m,n}) \) [the boundary of the \((m, n)\) element of the partition of \( \mathcal{A} \)] an irrelevant magnitude in PW.
Using the partition introduced for $A_1$, $A_2$, $A_3$ and the properties of $g(r)$ we obtain

$$
\int_{A_{sk}} g(r)dr = \sum_{n \text{ faces}} \int_{A_{1,n}} g_1(r)dr + \sum_{n \text{ edges}} \int_{A_{2,n}} g_2(r)dr + \sum_{n \text{ vertex}} \int_{A_{3,n}} g_3(r)dr,
$$

where the right hand side term is a contribution to each vertex similar to that appearing in Eq. (27). Each of the edge’s terms

$$
\int_{A_{2,n}} g_2(r)dr,
$$

can be treated separately. Let us consider the family of orthogonal planes to the direction of the $n$-th edge which intersects $\partial A_{2,n}$. Each of these planes cuts $A_{2,n}$ producing a slice or orthogonal cross section of $A_{2,n}$. Let $A^\perp_{2,n}$ be the cross section defined by one of such planes that intersects $A_{2,n}$ in a region where both endpoints of the $n$-th edge are away to ensure that the shape of $A^\perp_{2,n}$ does not depend on any arbitrary choice. One can define $B_{2,n}$ as the righted version of $A_{2,n}$, which is the right (generalized) cylinder obtained by translate $A^\perp_{2,n}$ along $\partial A_{2,n}$, and extend the domain of $g_2(r)$ to $B_{2,n}$. The set $B_{2,n} \setminus A_{2,n}$ contains two disconnected regions one around each endpoint of $\partial A_{2,n}$ (related to a given vertex). Each of these regions is $(B_{2,n} \setminus A_{2,n})_{n'}$ with $n'$ running over the vertex of $A$ and $(B_{2,n} \setminus A_{2,n})_{n'} = \emptyset$ if edge $n$ and vertex $n'$ are not neighbors. Therefore

$$
\int_{A_{2,n}} g_2(r)dr = \int_{B_{2,n}} g_2(r)dr - \sum_{n' \text{ vertex}} \int_{(B_{2,n} \setminus A_{2,n})_{n'}} g_2(r)dr,
$$

with

$$
\int_{B_{2,n}} g_2(r)dr = L_n \int_{A^\perp_{2,n}} g_2(r^{(2)})dr^{(2)},
$$

where $r^{(2)}$ is the two-dimensional coordinate of a point in $A^\perp_{2,n}$ and the last integral is a function of the dihedral angle at the $n$-th edge. Hence, for the central term in the right-hand side of Eq. (31) we found

$$
\sum_{n \text{ edges}} \int_{A_{2,n}} g_2(r)dr = \sum_{n \text{ edges}} L_n \int_{A^\perp_{2,n}} g_2(r^{(2)})dr^{(2)} - \sum_{n' \text{ vertex}} \sum_{n \text{ edge}} \int_{(B_{2,n} \setminus A_{2,n})_{n'}} g_2(r^{(2)})dr^{(3)}.
$$

Now, to analyze each of the face terms in Eq. (31)

$$
\int_{A_{1,n}} g_1(r)dr,
$$

let us define $B_{1,n}$ as the righted version of $A_{1,n}$, which is the right (generalized) cylinder obtained by translate the face $\partial A_{1,n}$ along $\hat{z}_n$ being $\hat{z}_n$ the inner (to $A$) normal unit vector,
note that $A_{1,n} \subset B_{1,n}$. One can extend the domain of $g_1(r)$ to all the semi-space that contains $B_{1,n}$ and includes $\partial A_{1,n}$ in its boundary plane to obtain

$$
\int_{A_{1,n}} g_1(r)dr = \int_{B_{1,n}} g_1(r)dr - \int_{B_{1,n}\setminus A_{1,n}} g_1(r)dr,
$$

with

$$
\int_{B_{1,n}} g_1(r)dr = A_n \int_0^{\infty} g_1(z)dz,
$$

where the last integral is independent of the involved face. Besides, $B_{1,n} \setminus A_{1,n}$ is a set of points distributed in the neighborhood of the relative boundary of $A_{1,n}$ i.e. $\partial A_{1,n} = \cup_{n'} \partial A_{2,n'} \cup_{n''} \partial A_{3,n''}$ with $n'$ ($n''$) running over the edges (vertex) that are neighbors of $\partial A_{1,n}$. We make a partition of $B_{1,n} \setminus A_{1,n}$ in regions corresponding to edges and vertex

$$
\hat{\cdots}, B'_{2,nn'}, B'_{3,nn''}, \ldots
$$

therefore

$$
\int_{B_{1,n}\setminus A_{1,n}} g_1(r)dr = \sum_{n'\text{edges}} \int_{B'_{2,nn'}} g_1(r)dr + \sum_{n''\text{vertex}} \int_{B'_{3,nn''}} g_1(r)dr,
$$

where again $n'$ ($n''$) runs over the edges (vertex) that are neighbors of the $n$ face. This partition is a simple extension of $A_{2,n'}$ and $A_{3,n''}$, and it is warranted because the boundaries between $A_{1,n}$ $A_{2,n'}$ and $A_{3,n''}$ are built by pieces of planes, cylinders and spheres that can be trivially extended to such regions $B_{1,n} \setminus A_{1,n} \not\subset A$. For the $n'$-th edge we consider the family of orthogonal planes that cut $B'_{2,nn'}$ each plane producing a slice or orthogonal cross section. Let $(B_{1,n} \setminus A_{1,n})_{n'}^{-}$ be one of such cross section that cut $\partial A_{2,n'}$ in a region where both endpoints of the $n'$ edge are away to ensure that the cross section does not depend on any arbitrary choice. For each $n'$ edge we define $B''_{2,nn'}$ as the right (generalized) cylinder obtained by moving $(B_{1,n} \setminus A_{1,n})_{n'}^{-}$ along $\partial A_{2,n'}$. We note that $B''_{2,nn'} \setminus B'_{2,nn'}$ contains two disjoint parts one around each endpoint of $\partial A_{2,n'}$ which we assign to the corresponding vertex. Each of these contributions is $(B''_{2,nn'} \setminus B'_{2,nn'})_{n''}$ with $n'$ running over the vertex and $(B''_{2,nn'} \setminus B'_{2,nn'})_{n''} = \emptyset$ if face $n$, edge $n'$ and vertex $n''$ are not all neighbors (taken in pairs). Therefore, for a given $n$ face and $n'$ edge we have

$$
\int_{B''_{2,nn'}} g_1(r)dr = \int_{B''_{2,nn'}} g_1(r)dr - \sum_{n''\text{vertex}} \int_{(B''_{2,nn'} \setminus B'_{2,nn'})_{n''}} g_1(r)dr,
$$
with
\[
\int_{\mathcal{B}_{2,n}^{(2),n'}} g_1(\mathbf{r}) d\mathbf{r} = L_n' \int_{(\mathcal{B}_{1,n} \cup \mathcal{A}_{1,n})_{n'}} g_1(z) dz .
\] (42)

One can verify that the edge contribution in Eq. (42) for each of the two faces that meet at the \(n'\)-th edge is the same. By adding the contribution of all the faces, i.e. joining results from Eq. (37) to Eq. (42), one found
\[
\sum_{n \text{ faces}} \int_{\mathcal{A}_{1,n}} g_1(\mathbf{r}) d\mathbf{r} = A \int_0^c g_1(z) dz - 2 \sum_{n' \text{ edges}} L_{n'} \int_{(\mathcal{B}_{1,n} \cup \mathcal{A}_{1,n})_{n'}} g_1(z) dz
\]
\[
+ \sum_{n' \text{ vert}} \sum_{n \text{ face}} \left[ \sum_{n' \text{ edge}} \int_{(\mathcal{B}_{2,n}^{(2),n} \cup \mathcal{B}_{2,n}^{(2),n'})_{n'}} g_1(z) dz - \int_{\mathcal{B}_{3,n}^{(3),n'}} g_1(z) dz \right] ,
\] (43)

where the \(m\) label (which is not an index) corresponds to any of both faces that meet at the \(n'\) edge. Putting all together, one obtain
\[
t = V c_0 + A c_1 + \sum_{n \text{ edges}} L_n c_2,n + \sum_{n \text{ vertex}} c_3,n ,
\] (44)

with the coefficients
\[
c_0 = G(\mathbf{r}) \text{ for all } \mathbf{r} \in \mathcal{A}_0 ,
\] (45)
\[
c_1 = \int_0^c g_1(z) dz ,
\] (46)
\[
c_2,n = \int_{\mathcal{A}_{2,n}} g_2(\mathbf{r}^{(2)}) d\mathbf{r}^{(2)} - 2 \int_{(\mathcal{B}_{1,n} \cup \mathcal{A}_{1,n})_{n'}} g_1(z) dz ,
\] (47)
\[
c_3,n = \int_{\mathcal{A}_{1,n}} g_3(\mathbf{r}^{(3)}) d\mathbf{r}^{(3)} - \sum_{n' \text{ edges}} \int_{(\mathcal{B}_{2,n}^{(3),n} \cup \mathcal{B}_{2,n}^{(3),n'})_{n'}} g_2(\mathbf{r}^{(2)}) d\mathbf{r}^{(2)}
\]
\[
+ \sum_{n' \text{ faces}} \left[ \sum_{n' \text{ edges}} \int_{(\mathcal{B}_{2,n}^{(3),n} \cup \mathcal{B}_{2,n}^{(3),n'})_{n'}} g_1(z) dz - \int_{\mathcal{B}_{3,n'}^{(3),n'}} g_1(z) dz \right] ,
\] (48)

and \(g(\mathbf{r}) = G(\mathbf{r}) - c_0\).

Theorem 2 (case \(d=2\)): For the case \(d = 2\) Eq. (26) reads
\[
t = \int_{\mathcal{A}} G(\mathbf{r}) d\mathbf{r}
\]
\[
= A c_0 + L c_1 + \sum_{n \text{ vertex}} c_2,n ,
\] (49)

where \(A\) is the surface area of \(\mathcal{A}\) and \(L\) is the length of its perimeter \(\partial \mathcal{A}\). Besides, \(c_0\) and \(c_1\) are constant coefficients which are independent of the size and shape of \(\mathcal{A}\), while \(c_2,n\) is a function of the angle in the \(n\)-th vertex.
Proof (case d=2): For brevity, we only present such parts of the demonstration that differs from the case $d = 3$. Introduce a partition of $A$ given by $\{A_o, A_{sk}\}$ to obtain
\[
\int_A G(r)dr = A_0 + \int_{A_{sk}} g(r)dr. 
\] (50)
Consider the set $A_{sk}$ partitioned in terms of $\{A_1, A_2\}$,
\[
A_{sk} = A_1 \cup A_2. 
\] (51)
$A_1$ is the line-type region $A_1 = \{r \in A_{sk}/U(r, \varsigma) \cap \partial A_{1,n} = \emptyset \text{ for only one } n \text{ side}\}$ where each $r \in A_1$ is related to a unique side. Let us define $A_{1,n} = \{r \in A_1/U(r, \varsigma) \cap \partial A_{1,n} = \emptyset \text{ for the } n\text{-th side}\}$ thus $\{A_{1,1}, \ldots, A_{1,n}, \ldots\}$ is a partition of $A_1$. Since $r \in A_1$ then $r \in A_{1,n}$ for only one side (the $n$-th). Hence, the shape of $U(r, \varsigma) \cap A$ is determined by the one dimensional position variable $r^{(1)} = d(r, \partial A_{1,n}) = z$, and then, $g(r) = g_1(r) = g_1(r^{(1)}) = g_1(z)$. $A_2$ is the vertex-type region $A_2 = \{r \in A_{sk}/U(r, \varsigma) \cap \partial A_{1,m} = \emptyset \text{ for two and only two values of } m \text{ side}\}$ where each $r \in A_2$ is related to a unique pair of sides. Let $r \in A_2$ and $m_1, m_2$ be such that $U(r, \varsigma) \cap \partial A_{1,m_1} = \emptyset$ and $U(r, \varsigma) \cap \partial A_{1,m_2} = \emptyset$, given that $0 < 2\varsigma < L(A)$ the pair of sides $m_1, m_2$ converge to a common vertex. Let us define $A_{2,n} = \{r \in A_2/U(r, \varsigma) \cap \partial A_{1,m} = \emptyset \text{ for the two values of } m \text{ sides that join in the } n\text{-th vertex}\}$ thus $\{A_{2,1}, \ldots, A_{2,n}, \ldots\}$ is a partition of $A_2$. Since $r \in A_2$ then $r \in A_{2,n}$ for only one vertex (the $n$-th). Hence, the shape of $U(r, \varsigma) \cap A$ is determined by both, the vertex angle and the vector $r^{(2)}$ that goes from $\partial A_{2,n}$ to $r$, and thus, $g(r) = g_2(r) = g_2(r^{(2)})$.

Using the partition introduced for $A_1, A_2$ and the properties of $g(r)$ one obtain
\[
\int_{A_{sk}} g(r)dr = \sum_{n \text{ sides}} \int_{A_{1,n}} g_1(r)dr + \sum_{n \text{ vertex}} \int_{A_{2,n}} g_2(r)dr, 
\] (52)
where the right hand side integral is part of the $n$-th vertex contribution to $t$, similar to that appearing in Eq. (49). To analyze each of the side terms in Eq. (51)
\[
\int_{A_{1,n}} g_1(r)dr, 
\] (53)
it is convenient to define $B_{1,n}$ as the righted version of $A_{1,n}$, which is the rectangle obtained by translate the side $\partial A_{1,n}$ along $\varsigma \hat{z}_n$ being $\hat{z}_n$ the inner (to $A$) normal unit vector, note that $A_{1,n} \subset B_{1,n}$. Let us consider the domain of $g_1(r)$ extended to all the semi-plane that includes $\partial A_{1,n}$ and contains $B_{1,n}$. In terms of $B_{1,n}$ the Eq. (53) can be written as
\[
\int_{A_{1,n}} g_1(r)dr = \int_{B_{1,n}} g_1(r)dr - \int_{B_{1,n} \setminus A_{1,n}} g_1(r)dr, 
\] (54)
with
\[ \int_{B_{1,n}} g_1(r)dr = L_n \int_0^\infty g_1(z)dz , \] \hfill (55)
where \( L_n \) is the length of the \( n \)-th side and the right hand side integral is independent of the involved side. Furthermore, \( B_{1,n} \setminus A_{1,n} \) contains two disjoint parts one around each endpoint of \( \partial A_{1,n} \) which one assign to the corresponding vertex. Each of these contributions is \( (B_{1,n} \setminus A_{1,n})_{n'} \) with \( n' \) running over the vertex and \( (B_{1,n} \setminus A_{1,n})_{n'} = \emptyset \) if side \( n \) and vertex \( n' \) are not neighbors. Adding the contribution of all the sides, joining results from Eq. (54) to Eq. (55) and taking into account that each vertex contributes (with identical contribution) to a pair of sides it is found
\[ \sum_{n \text{ sides}} \int_{A_{1,n}} g_1(r)dr = L \int_0^\infty g_1(z)dz - 2 \sum_{n' \text{ vertex}} \int_{(B_{1,m} \setminus A_{1,m})_{n'}} g_1(z)dr^{(2)} \] \hfill (56)
where the \( m \) label corresponds to any of both sides that meet at the \( n' \) vertex (and each side must be considered once). Putting all together, one obtain
\[ t = Ac_0 + Lc_1 + \sum_{n \text{ vertex}} c_{2,n} , \] \hfill (57)
with the coefficients
\[ c_0 = G(r) \text{ for all } r \in A_0 , \] \hfill (58)
\[ c_1 = \int_0^\infty g_1(z)dz , \] \hfill (59)
\[ c_{2,n} = \int_{A_{2,n}} g_2(r^{(2)})dr^{(2)} - 2 \int_{(B_{1,m} \setminus A_{1,m})_{n}} g_1(z)dr^{(2)} . \] \hfill (60)

Theorem 2 (case \( d=1 \)): For the case \( d = 1 \) the Eq. (26) reads
\[ t = \int_A G(r)dr \]
\[ = Lc_0 + 2c_1 , \] \hfill (61)
where \( L \) is the length of \( A \) while \( \partial A \) is composed by two separated points. Besides, \( c_0 \) and \( c_1 \) are both constant coefficients which are independent of the size \( A \). Note that, being \( A \) a straight line its shape is unique. Furthermore, in this case \( L = L(A) \).

Proof (case \( d=1 \)): Again, we present such parts of the demonstration that differs from the cases \( d = 2, 3 \). Introduce a partition of \( A \) given by \( \{ A_o, A_{sk} \} \) to obtain
\[
\int_A G(r)dr = Lc_0 + \int_{A_{sk}} g(r)dr.
\] (62)

with \( g(r) = G(r) - c_0 \) and \( c_0 = G(r) \) for all \( r \in A_o \). Now, \( A_{sk} = A_1 = \{ \{A_{1,1}, A_{1,2}\} \} \) is a pure vertex-type region. Here, \( A_{1,1} \) and \( A_{1,2} \) are disjoint regions and each one corresponds to a given vertex or point, being \( \partial A_{1,n} \subset A_{1,n} \). Since both vertex have the same shape and the shape of \( U(r, \varsigma) \cap A_{1,n} \) is determined by the one dimensional position variable \( r^{(1)} = d(r, \partial A_{1,n}) = z \), then \( g(r) = g_1(r) = g_1(r^{(1)}) = g_1(z) \). Thus, one find

\[
\int_{A_{sk}} g(r)dr = 2c_1 = 2 \int_0^\varsigma g_1(z)dz.
\] (63)

The Eqs. (62, 63) can be re-arranged to obtain

\[
t = Lc_0 + 2c_1,
\] (64)

with

\[
c_0 = G(r) \text{ for all } r \in A_o,
\] (65)

\[
c_1 = \int_0^\varsigma g_1(z)dz.
\] (66)

Finally we can broaden the field of application of Theorem 2 from \( \mathbb{P}^d \) to \( \mathbb{P}_\infty^d \supset \mathbb{P}^d \). We define \( \mathcal{A} \in \mathbb{P}_\infty^d \) if \( \mathcal{A} \subseteq \mathbb{R}^d \), and \( \mathcal{A} \) is the connected union of countably many closed convex polytopes, and \( \exists \varepsilon \in \mathbb{R}_{>0} \) such that \( \forall \lambda \in (0, \varepsilon) \) and for every \( r \in \mathcal{A} \) the set int \( \{U(r, \lambda) \cap \mathcal{A}\} \) is connected. In this case it is sufficient to consider the extension of Eqs. (27) and (49) to the case of sums over countable many faces. Note that even when \( \mathcal{A} \in \mathbb{P}_\infty^d \) the theorem produce useful results only if \( \mathcal{L}(\mathcal{A}) \) is positive definite.

A. Application of both theorems to confined fluids

Now we turn the attention to a fluid confined by a polytope \( \mathcal{A} \in \mathbb{P} \) (the fluid was described in Sec. III) and analyze the functions \( \tau_i : \mathbb{P} \to \mathbb{R} \), \( Z_i : \mathbb{P} \to \mathbb{R} \) and \( \Xi_M : \mathbb{P} \to \mathbb{R} \). In particular, to analyze \( \tau_i \), one must first consider the Theorem 1 and thus apply Theorem 2 to solve the integral in Eq. (22). We have obtained the following corollaries of the Theorems 1 and 2 that apply to a confined fluid (relations are written for the case \( d = 3 \) but other values of \( d \) are easily included in our approach):
1. If a system of particles that interact via a pair potential of finite range $\xi$ is confined in a polytope $A \in \mathbb{P}^3$ such that $\mathcal{L}(A) > 2 \varsigma$ with $\varsigma$ taken from Eq. (20) for some positive integer $i > 1$ then, the $i$-th cluster integral $\tau_i : \mathbb{P}^3 \rightarrow \mathbb{R}$ is a linear function in the variables $V, A$ and $\{L_1, L_2, \ldots\}$ (the length of the edges of $A$). It follows by replacing in Eq. (27) the magnitudes $t, G$ with $\tau_i, E_1$ and in Eqs. (44) to (48) the magnitudes $t, G, c_0, c_1, c_2, n$ and $c_3, n$ with $\tau_i, E_1, i!b_i, -i!a_i, ilc_{i,n}^e$ and $ilc_{i,n}^v$, respectively. Then, $g(r) = E_1(r) - c_0$ (being $c_0 = E_1(r)$ with $r \in A_o$) and the expression of the $i$-th cluster integral is

$$\tau_i/i! = V b_i - A a_i + \sum_{\text{nedges}} L_n c_{i,n}^e + \sum_{\text{vertex}} c_{i,n}^v,$$ 

(67)

where the coefficients of $b_i$ and $a_i$ are independent of the shape of $A$ while $c_{i,n}^e$ is a function of the dihedral angle in the $n$-th edge and $c_{i,n}^v$ is a function of the dihedral angles involved in the $n$-th vertex. Besides, all the coefficients depends on the pair interaction potential, the temperature and $i$. Finally, Eq. (9) shows that $b_1 = 1$ and $a_1 = c_{1,n}^e = c_{1,n}^v = 0$.

2. If a system with $N$ particles that interact via a pair potential of finite range $\xi$ is confined in a polytope $A \in \mathbb{P}^3$ such that $\mathcal{L}(A) > 2 \varsigma$ with $\varsigma$ taken from Eq. (20) and $i$ replaced by $N$, then its canonical partition function is polynomial on $V, A$ and $\{L_1, L_2, \ldots\}$. It follows from the previous corollary, Eqs. (2) and (6). From them the polynomials $Z_N$ and $Q$ can be explicitly obtained.

3. If a system with at most $M$ particles that interact via a pair potential of finite range $\xi$ is confined in a polytope $A \in \mathbb{P}^3$ such that $\mathcal{L}(A) > 2 \varsigma$ with $\varsigma$ taken from Eq. (20) and $i$ replaced by $M$ then, its (restricted) grand canonical partition function is polynomial on $z, V, A$ and $\{L_1, L_2, \ldots\}$. This follows from the second corollary and Eqs. (1)-(3). From them the polynomial $\Xi_M$ can be explicitly obtained.

For practical purposes one introduce the mean value for the edge and vertex coefficients $c_{i,n}^e = L_e^{-1} \sum_{\text{nedges}} L_n c_{i,n}^e$ and $c_{i,n}^v = N_v^{-1} \sum_{\text{vertex}} c_{i,n}^v$, respectively (with $L_e = \sum_{\text{nedges}} L_n$ and $N_v$ the quantity of vertex in $A$). Using this mean values the Eq. (68) is re-written as

$$\tau_i/i! = V b_i - A a_i + L_e c_{i}^e + N_v c_{i}^v,$$ 

(68)

with $a_1 = c_{1}^e = c_{1}^v = 0$. 

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As a closing remark we can mention that for \( d = 1 \) it is easy to demonstrate that the conjectured relation (21) is true. Therefore, one found that \( \tau_i/i! = b_iL - 2a_i \) apply to any \( i < i_{\text{max}} \) with \( i_{\text{max}} = \text{IntegerPart}(L/\varsigma) + 1 \) [see Eq. (61)].

B. Classification of \( g \)

The three corollaries of Theorems 1 and 2 fix the structure of \( \tau_i, Z_N \) and \( \Xi \), and provide explicit expressions that enables to obtain the coefficients of \( \tau_i \). To make a further step in this direction we analyze the different scenarios for \( E_1(r) \) and \( g(r) \). At fixed \( r \in \mathcal{A} \) both functions depend on the set \( U(r, \varsigma) \cap \mathcal{A} \) throw the shape of \( U(r, \varsigma) \cap \partial \mathcal{A} \). Once again, we mainly concentrate in the case \( d = 3 \). In terms of the partition for \( \mathcal{A} \) introduced in Eqs. (28) and (30) \( r \in \mathcal{A} \Rightarrow r \in \mathcal{A}_k \) (for some \( k = 0,1,2,3 \)) and then \( g(r) = g_k(r) \). We have considered all the possible polyhedrons \( \mathcal{A} \) with \( \mathfrak{L}(\mathcal{A}) > 2\varsigma \) and observed that there exist countable many different cases for the geometry of \( U(r, \varsigma) \cap \mathcal{A} \) and in each of this geometries \( g(r) \) must be a smooth function of \( r \) and the angles that describe the local shape of \( \partial \mathcal{A} \). In Table I we present such a classification for \( d = 3 \) and the case where at most three faces join in each vertex. There, the increasing complexity of the scenario with increasing \( k \) is apparent, there are only one case for \( k = 0,1 \), three cases for \( k = 2 \) and nine cases for \( k = 3 \). This behavior is a consequence of the number of independent parameters involved, which are \( 0,1,3,5 \) (none; \( z \); \( r^{(2)} \) and \( \beta \); and \( r^{(3)} \) and two -of the three- angles \( \alpha \)) for \( k = 0,1,2,3 \), respectively. This table shows e.g. that for a given \( \tau_i \) we must know three different expressions for \( g_2 = g_2(r^{(2)}, \alpha) \) if we expect to obtain the function \( c^\ell_i(\alpha) \) which enable to describe all the possible \( c^\ell_{i,n} \). Finally, Table I also apply for \( d = 1,2 \). For \( d = 2 \) we must restrict to \( 0 \leq f \leq 2 \) and drop column \( v \). On the other hand, the columns \( f \) and \( e \) should be renamed as: \( s \) (sides) and \( v \) (vertex), respectively. For \( d = 1 \) we must restrict to \( 0 \leq f \leq 1 \), drop the columns \( e \) and \( v \), and rename column \( f \) as \( v \) (vertex).

V. EXTENSIONS TO NON POLYTOPE SHAPE OF THE CONFINEMENT

Once we have demonstrated the theorems and corollaries that reveal the shape of \( \tau(\mathcal{A}) \) (and other magnitudes) for \( \mathcal{A} \in \mathbb{P} \) with a characteristic length \( \mathfrak{L}(\mathcal{A}) > 2\varsigma \), we are ready to relax some of the constraints on the geometry of \( \mathcal{A} \). In a first step we analyze the case of
Table I: Classification for the different shapes of \( U(r, \varsigma) \cap \mathcal{A} \) (dark region of the draws, blue online). The \( k \) index means that \( r \in \mathcal{A}_k \) and \( g(r) = g_k(r^{(k)}) \) with \( g_0(r) = E_1(r) \), the \( j \) index is introduced to enumerate the different scenarios for the shape of \( U(r, \varsigma) \cap \mathcal{A} \) at a given \( k \). Columns \( f, e \) and \( v \) count the number of faces, edges and vertex, respectively, that intersects the ball centered at \( r \) with radii \( \varsigma \).

curved faces. Focusing on \( \mathbb{R}^3 \), if one of the planar faces is replaced with a curved surface with constant and small curvature along it (cylindrical or spherical surfaces), what can we expect to obtain for the behavior of \( \tau(\mathcal{A}) \)? On the basis of the locality and translational invariance of \( E_1(r) \), the Eqs. (22) and (67), and the ideas developed in the proof of Theorem 2 (case d=3), we expect that the coefficients corresponding to the curved face, their vertex and edges transform to functions of the principal radii of curvature of the curved face \( R_I, R_{II} \) (and the involved dihedral angles). This functions of curvature radii could be expressed in powers of its curvatures \( R_I^{-1} \) and \( R_{II}^{-1} \), being the independent term of each series that corresponds to the planar case given in Eq. (67). For several faces with small constant curvature one follow the same argument, in this case the edges (vertex) coefficients will depend on the curvatures of the faces that meet in the edge (vertex) and also on the involved dihedral angles. Related to this curvature dependence, in the case of a hard spheres (HS) fluid the cluster integrals \( \tau_2 \) and \( \tau_3 \) were obtained for a system confined by spherical walls [10–12], while \( \tau_2 \) was also evaluated for HS confined by cylindrical and planar walls [10, 13]. In addition, the analysis of the HS fluid confined in the \( d \)-dimensional space have provided explicit expressions of \( \tau_2 \) in the cases of spherical and slit, confinement [14, 15]. Furthermore, in the case of square-
well particles $\tau_2$ was evaluated for a spherical wall confinement \cite{16}. In all these cases the obtained expressions coincide with the above discussed general picture.

A second generalization of the theorem corresponds to the periodic boundary conditions which are frequently used in molecular dynamic and montecarlo simulations. We consider a set of three non-coplanar vectors $\{v_1, v_2, v_3\}$ that define the cell $C = \{r/ r = x_1 v_1 + x_2 v_2 + x_3 v_3, \forall 0 \leq x_i < 1\}$, a parallelepiped, and the corresponding vectors of the Bravais lattice $v = m_1 v_1 + m_2 v_2 + m_3 v_3$ with $m_i$ running over all the integers. The translation of the cell over all the Bravais lattice vectors $v$ tiles $\mathbb{R}^3$. Note that systems with discrete translational symmetry in only two or one or zero directions (the last case corresponds to the absence of discrete translational symmetry) can be obtained in two ways; by fixing $m_i = 0$ in the definition of the Bravais lattice vectors for one or two or three of the integer numbers $\{m_1, m_2, m_3\}$ (which reduce the lattice dimension), or alternatively, by taking the large cell limit in one or two or three of the lengths $\{v_1, v_2, v_3\}$ with $v_i = |v_i|$. We will take the second point of view to analyze the periodic polyhedron problem in the framework of the three dimensional Bravais lattice. Let us define the periodic polyhedron $A$ by giving, a set of lattice vectors $\{v_1, v_2, v_3\}$ that define $C$ and $v$, a polyhedron $B \subset C$ and the periodic array of polyhedrons formed by all the copies of $B$ over the lattice, $B_{lat}$. Furthermore, we assume that $B_{lat}$ belongs to a kind of generalized $\mathbb{P}$ space where the possibility of certain types of union of infinite convex sets (that consistent with a Bravais lattice) are allowed. We have strong evidence that shows that theorems 1 and 2 and their corollaries can be extended to include the case of a periodic polytope $A$. In this case the characteristic length $\mathcal{L}(A)$ should be redefined. On one side, one should consider the characteristic length of the normal boundary of $A$, $\mathcal{L}'(A) = \mathcal{L}(B_{lat})$, given by Eq. \cite {25}, that can be measured on a subset of $B_{lat}$ given by the cell and its $3^3 - 1$ neighbors. On the other side, one should take into account the second characteristic length of $A$ which concerns the geometry of the periodic cell, given by $\mathcal{L}''(A) = \min (v_1, v_2, v_3)$. The minimum between both lengths $\mathcal{L}'(A)$ and $\mathcal{L}''(A)$ is the characteristic length of the periodic polytope $\mathcal{L}(A)$. Due to at present, we have not a full demonstration of this generalization to periodic polytopes, it must be considered a conjecture.

Other interesting extensions that should be analyzed in the future are: multi-component systems, system with non-spherical interaction potential, and external potentials that include other non-hard wall-particle interactions.
VI. THERMODYNAMIC PROPERTIES

In Secs. III and IV it were derived new exact results on the statistical mechanics of confined fluids inhomogeneously distributed in the space without any particular spatial symmetry that applies both, to systems composed of few particles, as well as to systems composed by many particles. Recently, a thermodynamic approach that enables to study in a unified way both types of systems was formulated \[13, 17\]. We apply here this thermodynamic approach to study the properties of a fluid confined in a polytope in the framework of both, canonical and grand canonical ensembles. This approach rest in two basic assumptions made about the system: (1) it can be assigned to the system a free energy, this can be done through the usual free-energy ↔ partition-function relation which is a well established link between statistical mechanics and thermodynamics, (2) under general ergodic conditions there exist an identity between: the mean temporal value of the properties of the system, those obtained from a thermodynamic approach, and those found from mean ensemble value (the ensemble that mimics the real constraints on the system must be considered). In the rest of this section we will find and discuss the thermodynamic relations, the equations of state (EOS), the relations between different EOS, and their meaning.

For a system with a fixed number of particles, \( N \), and temperature, \( T \), one must adopt the canonical ensemble. In this framework, the connection between statistical mechanics and thermodynamics is

\[
F = -\beta^{-1} \ln Q ,
\]

where \( F \) is the Helmholtz free energy of the system. Besides, the thermodynamic fundamental relations for \( F \) that follows from the first and second laws of thermodynamic through a Legendre transformation are

\[
F = U - TS ,
\]

\[
dF = -S dT - dW_r .
\]
\( \mathcal{A} \to \mathcal{A}(\lambda), dV \to d\lambda dV/d\lambda \) and the first EOS of the system

\[
P_W = - \frac{\partial F}{\partial \lambda} \bigg|_{T,N} \left( \frac{dV}{d\lambda} \right)^{-1}.
\]

(72)

It is interesting to note that once the expression for \( F(T, \lambda) \) and \( P_W \) are known an apparently thorough description of the thermodynamic magnitudes involved in Eqs. (70)(71) is obtained. On the other hand, given that the system under study is an inhomogeneous one \( P_W \) is not the pressure in the fluid, in fact, this simple observation shows that the obtained description of the system in terms of \( P_W \) alone is unsatisfactory because it said almost nothing about the properties of the fluid itself.

To make further progress toward a more satisfactory thermodynamic description of the system properties, we assume that \( \mathcal{A} \in \mathbb{P}^3 \) is a SB polyhedron and the confined fluid is such that the Corollaries 1 and 2 in Sec. IV A apply. Thus, based on Eq. (67) we adopt the continuous measures \( X = \{ V, A, L, \alpha \} \) where bold symbols \( L \) and \( \alpha \) are short notations for the set of edges length and dihedral angles, \( \alpha \). Naturally, these measures can also be parametrized with \( \lambda \) when it becomes convenient. Besides, from Corollary 2 and Eqs. (70), (71), we obtain the explicit form of \( F, S, U \) (from the statistical mechanical mean value recipe \( U = \partial \beta F/\partial \beta \big|_{N,A} \)) and \( P_W \) in terms of \( X \). We also found the following EOS

\[
P = - \frac{\partial F}{\partial V} \bigg|_{T,N,X-V}, \quad \gamma = \frac{\partial F}{\partial A} \bigg|_{T,N,X-A},
\]

(73)

\[
T_n = \frac{\partial F}{\partial L_n} \bigg|_{T,N,X-L_n}, \quad \omega_n = \frac{\partial F}{\partial \alpha_n} \bigg|_{T,N,X-\alpha_n},
\]

(74)

where the partial derivatives can be interpreted as the response of \( F \) to an small change of \( V \) \( (A, L_n, \alpha_n) \) while the other measures are kept constant. The Eqs. (73, 74) may be seen simply as definitions for \( P, \gamma, T_n \) and \( \omega_n \). In this context, each of these magnitudes is related to certain type of work, for example \( P \) is the work needed to change the volume of the system from \( V \) to \( V + dV \) (at constant \( A, L, \) and \( \alpha \)) and \( \omega_n \) is the work necessary to change the dihedral angle \( \alpha_n \) in \( d\alpha_n \) (at all the measures \( X \) but \( \alpha_n \) constants, which affect both the edge and their vertex). However, the Eqs. (73, 74) also suggest the meaning of \( P, \gamma \) and \( T_n \); hence, \( P \) should be the pressure in the fluid, \( \gamma \) its wall-fluid surface tension and \( T_n \) the line tension corresponding to the \( n \)-th edge. In favor of this interpretation one observe that when the fluid develops a region with homogeneous density the pressure \( P \) from Eq. (73) is the pressure of the fluid in this region. This fact can be demonstrated using
Theorems 1 and 2 and an approach similar to that developed in Ref. [13]. Thermodynamic magnitudes \( P, \gamma, T_n \) and \( \omega_n \) depend on the adopted measures \( X \) but are independent of the adopted transformation. An equilibrium equation relates the different EOS,

\[
P - P_W = q_\gamma \gamma + \langle q_T T \rangle + \langle q_\omega \omega \rangle,
\]

where the \( q \) coefficients are of geometrical nature \( q_\gamma = \frac{dA}{dX} (\frac{dV}{dX})^{-1} \), \( \langle q_T T \rangle = \sum_{\text{edges}} q_{T,n} T_n \), \( \langle q_\omega \omega \rangle = \sum_{\text{vertex}} q_{\omega,n} \omega_n \), with \( q_{T,n} = (\frac{dV}{dX})^{-1} \frac{dL_n}{dX} \) and \( q_{\omega,n} = (\frac{dV}{dX})^{-1} \frac{d\omega_n}{dX} \). The Eq. (75) is very similar to the Laplace Equation for a drop that express the equilibrium between the inner pressure (in the liquid phase), the outer pressure (in the vapor phase) and the liquid-vapor surface tension. Hence, we say that Eq. (75) is a Laplace-like relation. For the case of \( \frac{dV}{dX} = 0 \) where Eqs. (72) and (75) have none sense one may define \( dW = -\gamma_W dA \), \( \gamma_W = \frac{\partial E}{\partial X} \bigg|_T (\frac{dA}{dX})^{-1} \) and the Laplace-like relation gives

\[
\gamma_W - \gamma = \langle r_T T \rangle + \langle r_\omega \omega \rangle,
\]

where \( \langle r_T T \rangle = \sum_{\text{edges}} r_{T,n} T_n \langle r_\omega \omega \rangle = \sum_{\text{vertex}} r_{\omega,n} \omega_n \), with \( r_{T,n} = (\frac{dA}{dX})^{-1} \frac{dr_n}{dX} \) and \( r_{\omega,n} = (\frac{dA}{dX})^{-1} \frac{d\omega_n}{dX} \). Eq. (76) makes explicit that the usual approach to the surface tension which consist in measure the reversible work of doing a transformation at constant volume does not give the thermodynamic surface tension \( \gamma \), even it measure \( \gamma_W \) for this adopted transformation. Now we focus on the case of some simpler shapes for \( \mathcal{A} \) to obtain more explicit expressions of Eq. (75). For a convex polyhedron \( \mathcal{A} \) which is also regular all its edges and vertex are equivalent (equal dihedral angles and edges length), one can make a re-scaling transformation (at fixed angles) by multiplying the vectors that fix the position of each vertex by a parameter \( \kappa \approx 1 \). In this case, for an initial state \( X = \{V_o, A_o, L_o\} \) we found \( V' = 3\kappa^2 V_o, A' = 2\kappa A_o, L'_n = L_{n,o}, q_\gamma = \frac{2A_o}{3\kappa V_o}, \langle q_T T \rangle = T \frac{L_{e,o}}{3\kappa^2 V_o} \) (with \( T = T_n \) for any \( n \)-edge) and \( \langle q_\omega \omega \rangle = 0 \). On the other hand, for the case of polyhedron \( \mathcal{A} \) such that its complement \( \mathcal{A}^c \) is convex and regular (if \( \mathcal{A}^c \) is convex we say that \( \mathcal{A} \) is com-convex), starting with an initial state \( X = \{V = V_\infty - V_o, A_o, L_o\} \), we obtain \( V' = -3\kappa^2 V_o, A' = 2\kappa A_o, L'_n = L_{n,o} \), which produce a minus sign in \( q_\gamma = -\frac{2A_o}{3\kappa V_o} \) and \( \langle q_T T \rangle = -T \frac{L_{e,o}}{3\kappa^2 V_o} \). By fixing \( \kappa = 1 \) the Eq. (75) for both, the convex and com-convex regular cases, reduce to

\[
(P - P_W) \times \text{sg} = \gamma \frac{2A_o}{3V_o} + T \frac{L_{e,o}}{3V_o},
\]

where \( \text{sg} \) gives the sign of \( \frac{dV(k)}{dk} \) (which is 1 or \(-1\) for the convex and com-convex cases, respectively). This equation applies not only to a cuboidal confinement, both for the fluid
in the cuboid and for the fluid surrounding it, but also, for the tetrahedron and other platonic solids (octahedron, dodecahedron and icosahedron), evenmore it also applies to the cuboctahedron and the icosidodecahedron confinements (see [25] for geometrical details). It is interesting to note that for the above analyzed cases, where Eq. (77) apply, \( P_W \) reduce to the mean pressure at the wall (wall-pressure) related with the mean density on the wall \( \rho_w \) through the contact theorem

\[
P_W = \beta^{-1} \rho_w .
\]  

(78)

Open systems with inasmuch \( M \) particles and \( T, \mu \)-or \( z \)- and \( A \) fixed must be analyzed in the framework of the grand canonical ensemble. In this ensemble the connection between statistical mechanics and thermodynamics is

\[
\Omega = -\beta^{-1} \ln \Xi ,
\]

(79)

while the thermodynamic fundamental relations that follow from the first and second laws are

\[
\Omega = U - TS - \mu N ,
\]

(80)

\[
d\Omega = -S dT - dW_r - N d\mu .
\]

(81)

By introducing a parametrization for the cavity transformation one find

\[
P_W = -\frac{\partial \Omega}{\partial \lambda} \bigg|_{T,z} \left( \frac{dV}{d\lambda} \right)^{-1} .
\]

(82)

For the case of \( A \in \mathbb{P}^3 \) a SB polyhedron and a fluid such that the Corollaries [1 to 3] apply, we use the same measures \( X \) adopted above. Besides, from Corollary [3] and using Eqs. (1) to (7) we obtain the explicit form of \( \Omega \) and \( P_W \) in terms of \( X \). The expressions for \( S \), \( U \) and the EOS in this GCE are easily found by replacing \( F \) with \( \Omega \) in Eqs. (72) to (74). For the other EOS we obtain

\[
P = -\frac{\partial \Omega}{\partial V} \bigg|_{T,z,X-V} , \quad \gamma = \frac{\partial \Omega}{\partial A} \bigg|_{T,z,X-A} ,
\]

(83)

\[
T_n = \frac{\partial \Omega}{\partial L_n} \bigg|_{T,z,X-L_n} , \quad \omega_n = \frac{\partial \Omega}{\partial \alpha_n} \bigg|_{T,z,X-\alpha_n} .
\]

(84)

As can be seen, several results are similar to that found for the canonical ensemble case and thus we only draw about some features of this GCE study. For example, from the EOS one obtain the equilibrium relation

\[
P - P_W = q_T \gamma + \langle q_T T \rangle + \langle q_\omega \omega \rangle ,
\]

(85)
this Laplace-like relation is the same that Eq. (75) and again $P$ is the pressure in the fluid, which coincides with the pressure in a region with homogeneous density [see details in Eq. (75) or Eqs. (77, 78) for the specific case of regular polygons]. Other usual thermodynamic and statistical mechanical relations that are valid even for the case of inhomogeneous systems with a finite $M$ value are

$$ N \equiv \langle N \rangle = -z \left. \frac{\partial \beta \Omega}{\partial z} \right|_{T, A}, \tag{86} $$

$$ \sigma_N^2 \equiv \langle N^2 \rangle - N^2 = z \left. \frac{\partial N}{\partial z} \right|_{T, A}, \tag{87} $$

where $\sigma_N$, the standard deviation in the mean number of particles $N$, quantifies its spontaneous fluctuation. Note that derivatives with respect to $z$ are taken with the fluid in a fixed region $A$ (all the $X$ measures fixed).

A. The low $z$ expansion

To study the thermodynamic behavior of the confined open fluid in the low $z$ regime one express Eq. (79) as a power series in $z$ [see also Eq. (3)]. We introduce the vector of coefficients $b_i = (b_i, a_i, c_{i,1}^e, \cdots, c_{i,1}^v, \cdots)$ which depends on $\alpha$, and the vector of extensive-like magnitudes $Y = \{V, A, L, 1_v\}$ with $1_v$ the vector of $N_v$ components all of them equal to one being $N_v$ the number of vertex. Hence

$$ \frac{\tau_i}{i!} = Y \cdot b_i, \tag{88} $$

an expression equivalent to Eqs. (67) and (68). Using Eq. (9) we can write

$$ \beta \Omega = - \sum_{i \geq 1} \frac{\tau_i}{i!} z^i = - \sum_{i=1}^M z^i Y \cdot b_i + O_{M+1} (z), \tag{89} $$

which is exact to order $M$. Notably, Eq. (89) shows that to this order $\Omega$ is linear in the extensive-like magnitudes in $Y$, on the other hand, Eq. (68) shows that to this order $\Omega$ is also linear in $V, A, L_e$ and $N_v$. To the same order we found

$$ N \approx \sum_{i=1}^M iz^i Y \cdot b_i, \tag{90} $$

$$ \sigma_N^2 \approx \sum_{i=1}^M i^2 z^i Y \cdot b_i. \tag{91} $$
Therefore, in Eqs. (89)-(91) and to order $M$ one can separate each component. For example the Eq. (89) is

$$\Omega = \Omega_b + \Omega_s + \Omega_l + \Omega_p,$$

(92)

with the volumetric part of the grand-potential $\Omega_b$, and the grand potential of surface, line and points $\Omega_s$, $\Omega_l$ and $\Omega_p$, respectively. Each of they correspond to the sum of terms proportional to $V$, $A$, $L$, $N_v$; and is trivially related with a grand potential density (per unit volume, area, etc.)

$$P_b = -\frac{\Omega_b}{V} = -\frac{\partial \Omega}{\partial V}|_{z,T,X-V} \doteq \beta^{-1} \sum_{i=1}^{M} z^i b_i,$$

(93)

$$\gamma_{\infty} = \frac{\Omega_s}{A} = \frac{\partial \Omega}{\partial A}|_{z,T,X-A} \doteq \beta^{-1} \sum_{i=2}^{M} z^i a_i,$$

(94)

$$T_{\infty} = \frac{\Omega_l}{L_e} \doteq -\beta^{-1} \sum_{i=2}^{M} z^i c^e_i,$$

(95)

$$\nu = \frac{\Omega_p}{N_v} \doteq -\beta^{-1} \sum_{i=2}^{M} z^i c^v_i.$$

(96)

Note that the right hand side equality in Eqs. (93) to (96) is up to order $M$ in $z$. Here, Eqs. (93) and (94) coincide with work terms definitions (83) while the Eqs. (95) and (96) may be understood as mean works. From the right hand side term of Eq. (93) one find that $P_b$ is the pressure of the bulk system (with the same $T$ and $z$). This series was studied by Mayer and others (see Ref. [18] and a more complete survey in [6, p.122]) in their approach to the virial equation of state for the bulk system. On the other hand, from the right hand side term in Eq. (94) one find that $\gamma_{\infty}$ is the (wall-fluid) surface tension for the bulk fluid in contact with an infinite planar wall. This series is consistent with that obtained by Sokolowski and Stecki [19], a question that will be briefly discussed at the end of this section. Furthermore, $P_b$ and $\gamma_{\infty}$ clearly corresponds to $P$ and $\gamma$ from Eq. (83) but also to the CE Eqs. (73), which validates our thermodynamical approach. The additional work terms, to order $M$ in $z$ are [from Eq. (84)]

$$T_n \doteq -\beta^{-1} \sum_{i=2}^{M} z^i c^e_{i,n},$$

(97)

$$\omega_n \doteq -\beta^{-1} \sum_{i=2}^{M} z^i \left( L_n \frac{\partial c^e_{i,n}}{\partial \alpha_n} + \frac{\partial c^v_{i,p}}{\partial \alpha_n} + \frac{\partial c^v_{i,q}}{\partial \alpha_n} \right)|_{z,T,X-\alpha_n},$$

(98)
where \( p \) and \( q \) are the vertex at the endpoints of the \( n \)-th edge. Eq. (97) corresponds to the line tension on the \( n \)-th edge. Thus, one can prove [using Eq. (68)] that \( T_\infty = \langle T_n \rangle = L_e^{-1} \sum_{\text{edges}} T_n L_n \), i.e., \( T_\infty \) is a mean-work term (the work needed to increase the edges length in \( dL_e \) of an edge with mean properties) it is the mean line tension. On the other hand,

\[
\omega_n = L_n \frac{\partial T_n}{\partial \alpha_n} \bigg|_{z,T,X-\alpha_n} + \frac{\partial (N_{v\nu})}{\partial \alpha_n} \bigg|_{z,T,X-\alpha_n}.
\]

(99)

In terms of the densities the Eq. (92) transforms to

\[
\Omega \doteq -VP_b + A\gamma_\infty + L_e T_\infty + N_{v\nu},
\]

(100)

which is a demonstration that the grand potential is a homogeneous function of the so-called extensive variables \( V, A, L_e \) and \( N_{v\nu} \) (at least to order \( M \) in powers of \( z \)). Note that this is a central assumption in the thermodynamic and statistical mechanics theories of macroscopic systems composed by many particles and spatially distributed following strong symmetries. On the opposite, here it is demonstrated for an inhomogeneous system, may be composed by few particles, without particular translational or rotational spatial symmetries. Naturally, explicit expression for several excess grand potential can also be obtained, for example the (over-bulk) surface excess grand-potential density is \( \tilde{\gamma} = (\Omega + VP_b)/A = \beta^{-1} \sum_{i=2}^M z^i (a_i - c_i^e L_e/A - c_{i\nu}^e N_{v\nu}/A) \) which is a rough estimate of the surface tension. Introducing the \( \lambda \) parametrization for a general vessel transformation we found the Laplace-like equilibrium relation

\[
P_b - P_W = q \gamma_\infty + \langle q T \rangle + \langle q \omega \rangle,
\]

(101)

equivalent to Eq. (85), but in this case we found the expression and meaning of each term to order \( M \) in \( z \). Again, for the particular cases analyzed below Eq. (76) we obtain

\[
(P_b - P_W) \times \text{sg} = \gamma_\infty \frac{2A}{3V_o} + T_\infty \frac{L_e}{3V_o},
\]

(102)

where \( T_\infty = T_n = T \) is a function of the dihedral angle [details are given below Eq. (77)]. This Eq. suggest the following procedure to obtain information about \( \gamma_\infty \) and \( T_\infty \). Consider \( \tilde{\gamma} \) defined below

\[
\tilde{\gamma} = \frac{3V_o}{2A} \text{sg} \times (P_b - P_W) = \gamma_\infty + T_\infty \frac{L_e}{2A},
\]

(103)

all the magnitudes between the equal signs are simple to measure in a molecular dynamic simulation of the open system. In particular Eq. (78), which remains valid in the GCE,
provides a simple way to evaluate $P_W$. Hence, one can fix the vessel shape, $T$ and a small $z$ value, and then do measures of $\bar{\gamma}$ along simulations for several different sizes of the vessel. Plotting $\bar{\gamma}$ vs. $\frac{L_e}{z}$ and fitting the points with a linear regression we obtain from the ordinate and the slope $\gamma_\infty$ and $T_\infty$, respectively. If we repeat the procedure for different values of $z$ we obtain a table of values for $\gamma_\infty(z)$ and $T_\infty(z)$ which enable to evaluate the coefficients $a_i$ and $c_\ell^\epsilon_i$ through a second fit in this case with a polynomial function.

The splitting of $\Omega$ in terms of its components to order $M$ in $z$, given in Eqs. (92) and (100), can also be done for Eq. (90). It gives

$$\rho - \rho_b V = A\bar{\Gamma} = A\Gamma + L_e\Gamma_e + N_v\Gamma_v \doteq \sum_{i=2}^{M} i z^i (A - a_i A + L_e c_\ell^\epsilon_i + N_v c_\ell^\nu_i),$$

where $\rho = N/V$ is the mean number density, $\rho_b \doteq \sum_{i=1}^{M} i z^i b_i$ is bulk density, $\bar{\Gamma}$ is the total effective adsorption, while the area, edge and vertex adsorptions are $\Gamma$, $\Gamma_e$ and $\Gamma_v$, respectively. On the other hand, the same procedure applied to the fluctuation in Eq. (91) produce

$$\sigma_\rho^2 - \sigma_b^2 = A\bar{s} = A s + L_e s_e + N_v s_v \doteq \sum_{i=2}^{M} i z^i (A - a_i A + L_e c_\ell^\epsilon_i + N_v c_\ell^\nu_i),$$

with $\sigma_b^2 = V \sum_{i=1}^{M} i z^i b_i$ the fluctuation in the number of particles in the bulk, $\bar{s}$ an excess effective fluctuation per unit area while $s$, $s_e$, and $s_v$ are the components of surface-area, edges length and vertex of the number density fluctuation. Particular attention deserve such polytopes for which $L(A)$ is infinite. They are the unbounded polytopes with one face, or one edge, or one vertex. In this cases $M$ can take any positive integer value and thus it be made as larger as one wishes. Therefore all the series in powers of $z$ given between Eq. (89) and Eq. (105) are valid to any order. Besides, the linear decomposition of several functions in its basic extensive measures $Y(A)$ is also exact to any order. In particular, the grand potential becomes an homogeneous function of the extensive measures [see Eq. (100)].

The structure of Eqs. (92,96,100,104) and (105) show that the relations between the functions

$$\left(\beta P_b - z, \rho_b - z, \sigma_b^2 - z\right) \text{ and } b_{i>1},$$

(where $\beta P_b - z, \rho_b - z$ and $\sigma_b^2 - z$ are excess magnitudes with respect to the ideal gas system) is the same that the relation between the functions

$$\left(\beta \gamma, -\Gamma, -\bar{s}\right) \text{ and } a_i - c_\ell^\epsilon_i L_e A^{-1} - c_\ell^\nu_i N_v A^{-1},$$

34
while the same apply to these other sets of functions and coefficients

\begin{align}
(\beta \gamma_\infty, -\Gamma, -s) & \text{ and } a_i, \\
(-\beta \mathcal{T}_\infty, \Gamma_e, s_e) & \text{ and } c_i^e, \\
(-\beta \nu, \Gamma_v, s_v) & \text{ and } c_i^v.
\end{align}

These simple observations show for example that $-\beta \gamma_\infty(\Gamma)$ and the dependence of $\beta P_b - z$ on $\rho_b - z$ is the same except that $-a_i$ in the first case must be replaced by $b_i$ in the second case.

Trivial series manipulation (inversion and composition) enables to obtain explicit expressions for the power series (to order $M$) of $P_b(\rho)$, $P_b(\rho_b)$, $\gamma_\infty(\rho_b)$, $\gamma(\rho)$, $\gamma(s_e)$, $\Gamma(\rho_b)$, $\mathcal{T}_\infty(\rho)$, $\mathcal{T}_\infty(\rho_b)$ and others. Several examples of these series discussed in terms of the formal symmetries given in Eqs. (106) to (110) are explicitly evaluated in Appendix A. For fixed $M$ we have verified that the series for $P_b(\rho_b)$ (to order $M$) is the usual virial series (see for example Ref. [6]), while $\gamma_\infty(\rho_b)$ and $\Gamma(\rho_b)$ reproduce the approach of Bellemans [20] and subsequent improvements of Sokolowski and Stecki [19] which have developed a complete theory of virial expansion for surface thermodynamic properties for the case of a fluid in contact with a planar infinite wall. As far as we known the series representation of any other of the discussed functional relations were never analyzed before.

**VII. FINAL REMARKS**

The obtained polynomial structure of the CE and GCE partition functions of few- and many-body inhomogeneous fluid-like systems confined by polytopes is interesting in several ways. It shows that the statistical mechanical properties of many of these fluid-like systems with a fixed number of particles can be exactly described if the involved coefficients (which depend on $T$) are known. This consideration also applies to open systems if we conveniently restrict the maximum number of particles considered. The key point for these results was the analysis of the geometrical properties of the reducible cluster integrals for inhomogeneous systems. It is interesting to mention that from the decade of 1950 until present this integrals (introduced by Mayer and Mayer [21] for the study of homogeneous fluids) were not the focus of much interest and were almost ignored in the study of inhomogeneous fluids. On the other hand, given that our approach to Theorems 1, 2 and their corollaries is constructive we found
Figure 2: The size vs. number domain for the system of $N$ particles in a cube with side $L$. Below the dotted curve the Corollaries 2 and 3 do not apply and thus the exact structure of the partition functions is unknown.

explicit integral expressions for the coefficients. In a work in progress we evaluate some of the unknown lower order coefficients for a system of hard sphere particles.

The results for the partition functions were complemented with a statistical mechanical and thermodynamical recipe that, based on the linear decomposition of cluster integrals enable to find the exact properties of the confined inhomogeneous fluid (for both the open and closed systems). This fact is notable because the studied confined inhomogeneous systems, which are far away from the many particles in large volumes condition, have not any particular spatial symmetry and thus the very basic assumptions of the usual approach to thermodynamics theory are not satisfied. Furthermore, it was shown that in the low density (and low $z$) regime the obtained grand potential is a homogeneous function of the extensive variables, which is a consequence of the linear decomposition of the cluster integrals in their extensive components (for $d = 3$ they are volume, boundary surface area, edges length and vertex number). Even more, it was found a generalized version of virial series EOS, that provides expressions for pressures, wall-fluid surface tension, line tension, adsorption, etc.

All this findings strongly suggest that it is possible to build a wider scope formulation of both, statistical mechanics and thermodynamics, theories. These generalized formulations should concern to systems with or without symmetries, involving from few- to many-bodies, and constrained to regions of any size.

In Fig. 2 it is represented the domain where the CE (GCE) partition function is a polynomial for the case of $N$ particles (at most $N$ particles) confined in a cube with side $L$. Broad straight lines show this domain for $Z_N$ and $\Xi_N$ for different (fixed) number of
particles. Each line extends from the infinite dilution limit $L^{-1} \to 0$ to the maximum density for which the Corollaries given in Sec. IV A apply. This maximum density condition is given by $N^{-1} = (1 + L/\xi)^{-1}$ (in accord with Eq. (21) and Sec. IV A) and is drawn in dotted line. The large systems limit corresponds to $V \to \infty$, $N \to \infty$ and coincides with the origin. However, to analyze the thermodynamic limit one must reach large systems by following a constant density path, which correspond to a dependence $N^{-1} \propto L^{-3}$. In the figure it is plotted for a small value $\rho = 0.2 \xi^{-3}$ with a dashed line. It is clear that our results about CE are insufficient to analyze the thermodynamic limit because for large volumes (small abscissa values) the highest density under which the structure of the partition function is known gives a linear relation $N^{-1} \simeq L^{-1}$. On the basis of this result is the nature of Theorems 1 and 2 which show that the end of validity of Eq. (67) relates with the existence of a cluster configuration that is capable to percolate the cavity $A$.

An attempt to analyze the polytopes $A$ such that $2\zeta \gtrsim L(A)$ shows two folds. On one hand, that for some of these polytopes the Eq. (67) remains valid (as well as, apply the conclusions of Corollaries 2 and 3). In this case, appears a less restrictive condition $2\zeta' < L(A)$ with $\zeta' < \zeta$ that replace $2\zeta < L(A)$. On the other hand, that the end of applicability of Eq. (67) relates with the non-universal behavior of $\tau_N$ due to the existence of a non-analytic term [which is identically null for $2\zeta < L(A)$] that depends on the shape of $A$ in a more complex way. The study of this term for some simple confinements is interesting because it may enlighten how to describe the system properties in the thermodynamic limit.

The core of the formal result presented in this work relies on Theorems 1 and 2. As was mentioned, Theorem 2 for $d = 1, 2, 3$ and the conjectured generalization to $\mathbb{R}^d$ given in Eq. (26) strongly resemble well known results of integral geometry. In particular, the expressions given in Eqs. (26, 27, 49) and (61) look like the combination of Hadwiger’s characterization theorem and The general kinematic formula (Theorems 9.1.1 and 10.3.1 in pp. 118 and 153 of [9], respectively) as it were applied to a polytope and a ball. Even that, several differences can be underlined. On one hand, in PW it was not established if the functions $G(A, r)$ and $E_1(A, r)$ are valuations (also called additive functions) or not. On the other hand, the integration domain of the integral solved in PW is not the complete space. Furthermore, the question about the continuity or monotonic behavior of both functions on $\mathbb{P}$ (see p. 153 in Ref. [9] and pp. 211 and 253 in Ref. [1]) is open. Despite these differences, the connection of our results with various formulae from integral geometry and convex bodies, theories is
evident. For example, some parts of the presented formulation resemble to Steiner’s formula for the measure of the Minkowski sum of a convex polytope and a ball (see Theorem 9.2.3 in p.122 of [9]), while the solved integrals are similar to certain integrals over functions that depend on the distance between a point and the boundary of a convex set. (p.132 of [9] and p. 258 of [7]). These connections should deserve a deeper analysis.

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Appendix A: Series Expansions of the EOS

We present here the expressions for several series expansions of thermodynamic magnitudes. In the following Eqs. the series were truncated to the next order that were written. In the derivations we make intensive use of relations expressed in Eqs (106) to (110). From Eqs. (94) and (104), we found

\[ \beta \gamma_\infty (\rho_b) = a_2 \rho_b^2 + (a_3 - 4a_2b_2) \rho_b^3 + (a_4 - 6a_3b_2 + 20a_2b_2^2 - 6a_2b_3) \rho_b^4. \]  

(A1)

Besides, \(-\beta T_\infty (\rho_b)\) is identical to the right hand side of Eq. (A1) but with the replacement \(a_i \rightarrow c_i^e\). The same applies to \(\beta \nu (\rho_b)\) with the replacement \(a_i \rightarrow c_i^w\) and also to \(\beta \gamma (\rho_b)\) with \(a_i \rightarrow a_i - c_i^e L_e A^{-1} - c_i^w N_v A^{-1}\). From Eqs. (94) and (104), we found the relation between surface tension and adsorption

\[ \beta \gamma_\infty (\Gamma) = -\frac{1}{2} \Gamma + \frac{a_3}{4\sqrt{2}(-a_2)^{3/2}} \Gamma^{3/2} + \frac{(-9a_3^2 + 8a_2a_4) \Gamma^2}{32a_2^3} + \frac{3 (63a_3^3 - 96a_2a_3a_4 + 32a_2^2a_5) \Gamma^{5/2}}{256\sqrt{2}(-a_2)^{9/2}}, \]  

(A2)

which shows a non-analytic dependence between fluid-wall surface tension and the surface adsorption in \(\Gamma = 0\). Besides, \(-\beta T_\infty (\Gamma_e)\) is identical to the right hand side of Eq. (A2) but with the replacement \(a_i \rightarrow c_i^e\), while the same applies to \(-\beta \nu (\Gamma_v)\) with the replacement \(a_i \rightarrow c_i^w\) and also to \(\beta \gamma (\Gamma)\) with \(a_i \rightarrow a_i - c_i^e L_e A^{-1} - c_i^w N_v A^{-1}\). Furthermore, from Eqs. (94) and (105), we found

\[ \beta \gamma_\infty (s) = \frac{s}{2} - \frac{3 a_3}{16 a_2^{3/2}} s^{3/2} + \frac{(81a_3^2 - 64a_2a_4) s^2}{256a_2^3}. \]  

(A3)

The same general ideas applied above in relation with Eqs. (A1) and (A2) enable to obtain e.g. \(-\beta T_\infty (s_e)\) and \(-\beta \nu (s_v)\). Fluctuation and density in the bulk, taken from Eqs. (105) and (104), relates by

\[ \sigma_b^2 = V \rho_b [1 + 2b_2 \rho_b + (-8b_2^2 + 6b_3) \rho_b^2 + (40b_2^3 - 48b_2b_3 + 12b_4) \rho_b^3], \]  

(A4)

while to obtain \(\sigma_v^2\) we must replace \(\rho_b \rightarrow \rho\) and \(b_i \rightarrow b_i - a_i AV^{-1} + c_i^e L_e V^{-1} + c_i^w N_v V^{-1}\), in this case \(V \rho = N\). On the other hand, \(s(\rho_b)\) is

\[ s(\rho_b) = 4a_2 \rho_b^2 + (9a_3 - 16a_2b_2) \rho_b^3 + (16a_4 - 54a_3b_2 + 80a_2b_2^2 - 24a_2b_3) \rho_b^4, \]  

(A5)

while, \(s_e(\rho_b)\) can be obtained through the replacement \(a_i \rightarrow c_i^e\), while \(s_v(\rho_b)\) can be obtained through the replacement \(a_i \rightarrow c_i^w\). To obtain \(\bar{s}(\rho)\), we replace \(\rho_b \rightarrow \rho\) and \(a_i \rightarrow a_i - c_i^e L_e A^{-1} - c_i^w N_v A^{-1}\) in Eq. (A5).