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Exact Moments of Curvature Measures in the Boolean Model

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Curvature measures are important for the characterization of spatial structures since many physical phenomena depend essentially on the geometry of spatial configurations. Curvature-weighted correlation functions can be defined and calculated explicitly within the Boolean model. This standard model in statistical physics generates random geometries by overlapping grains (spheres, sticks) each with arbitrary location and orientation. A general decomposition relation for characteristic functions of submanifolds based on Chern's differential kinematic formula is used to obtain exact expressions for mean values and second order moments of curvature integrals, i.e., of Minkowski functionals. An exact relation for the canonical and grand-canonical second order moments of the morphological Minkowski measures can be derived based only on thermodynamic arguments. The results are applied on the morphological thermodynamics of complex fluids where specific heats are expressed in terms of curvature moments.

KEY WORDS: Random sets; integral geometry; Minkowski functionals; Euler characteristic; Boolean model.

1. INTRODUCTION: SPATIAL PATTERNS IN STATISTICAL PHYSICS

The spatial structure of systems becomes more and more important in statistical physics. For instance, transport properties in porous media depend on the shape and statistical distribution of the pores shown in Fig. 1.[1, 2] If the volume fraction of pores (black) increases above a threshold, an infinite cluster of connected pores may span through the whole system which enables the transport of fluids. The knowledge of the dependence of this percolation threshold on the shape and distribution of the

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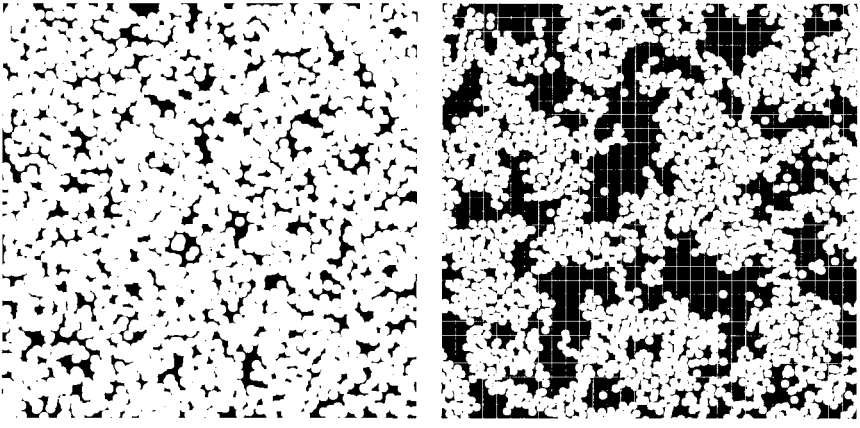

Fig. 1. (a) Porous media (left) can be described by the Boolean model, i.e., by overlapping grains such as spheres and discs distributed in space. (b) Inhomogeneous domains of thermodynamic stable phases of complex fluids (right) may also be described by overlapping grains. Such configurations resemble, for instance, the structure of microemulsions. The stochastic geometry of the black domains can be described by mean values and second order moments of curvature integrals, so-called Minkowski functionals, i.e., of area, boundary length, and Euler characteristic of the black region.

grains is essential for many applications in physics. It was argued that close to the threshold the averaged Gaussian curvature vanishes which may provide an estimate for the percolation density.[3] In order to improve this estimate it may be relevant to consider second order moments of curvatures in addition to averages.

Also the interest in microemulsions and colloidal suspensions rests primarily on the complex spatial structures of mesophases, e.g., the bicontinuous phases on a mesoscopic scale of an emulsion of oil and water stabilized by amphiphiles.[4] The spatial structure of complex fluids can be resembled by configurations of overlapping spheres shown in Fig. 1. The free energy of the homogeneous oil phase in a microemulsion may be then given by a bulk term (volume energy), a surface term (surface tension), and curvature terms (bending energies) of the white region, for instance. Thus, the spatial structure of the phases, i.e., the morphology of the white regions determines the configurational energy which determines itself the spatial structure due to the Boltzmann factor in the partition function of a canonical ensemble.[5–7] In order to perform high-temperature expansions of such a morphological model for complex fluids and to derive expressions for specific heats, for instance, it is mandatory to know mean values and second order moments of volume, surface area, and curvatures of overlapping spheres. Moreover, in order to understand scattering experiments with

neutrons or X-rays, one needs to calculate two-point structure functions of homogeneous domains which is a necessary first step in determining second order moments of curvatures.

Further examples where second order moments of curvatures play an important role are the modeling and reconstructing of disordered microstructures such as soils and porous media[8] and the statistical analysis of point patterns:[9] in order to apply curvature measures to point patterns each point is decorated by a d-dimensional sphere. The scale-dependent morphological features of this coverage may then be explored by varying the radius of the spheres. Calculating the curvatures for a given covering a quantitative characterization is obtained for the scale-dependent morphology of the underlying spatial point process, which generalizes the spherical contact probability—a standard technique in spatial statistics.[10] Second order moments of curvatures are needed to estimate the robustness of the method, i.e., to estimate the errors and reliability of model assumptions.

The spatial structures shown in Fig. 1 are configurations of the Boolean model, a standard model of stochastic geometry.[10] This stochastic model generates spatial structures by overlapping grains K of arbitrary shape and size. For convenience, spheres or discs of fixed radius are often used. Although a number of lattice models have been defined and extensive computer simulations have been performed for percolation phenomena and the study of complex fluids, not many continuum models have been studied. Here, we consider for the first time the distribution of curvatures in this continuum standard model.

In order to describe spatial structures one has to define suitable morphological measures. Integral geometry furnishes a whole family of descriptors, known as Minkowski functionals M_ν, which are related to curvature integrals and do not only characterize connectivity (topology) but also content and shape (geometry) of patterns.[9, 11, 12] In the three-dimensional Euclidean space the family of Minkowski functionals M_ν consists of the volume $V = M_0$, the surface area $S = 8M_1$ of the pattern, its integral mean curvature $H = 2\pi^2 M_2$ and integral of Gaussian curvature, i.e., the Euler characteristic $\chi = (4\pi/3)\, M_3$.[12] Besides the definition of morphological measures integral geometry provide theorems, formulae, and elegant calculus in order to derive exact results, in particular, for the Boolean model.[9, 11, 12]

Although analytic expressions for mean values of Minkowski functionals are known for the Boolean model since many years,[3] second order moments have never been exactly calculated except for special cases.[5] But variances of Minkowski functionals are essential for the understanding of the statistical physics of spatial patterns, i.e., of fluctuations and structure functions in the Boolean model, for high temperature expansions of the

partition sum in a morphological model for complex fluids, and for determining percolation thresholds in porous media. In order to derive exact expressions for second order moments, the global functional M_ν is decomposed into a sum of local functionals M_ν^λ. The latter can be expressed as an integral over a characteristic function $\chi^\lambda(\mathbf{x})$, $\mathbf{x} \in \mathbb{R}^d$, so that averages of products $S^{\lambda_1\lambda_2}(\mathbf{x}_1, \mathbf{x}_2) \sim \langle \chi^{\lambda_1}(\mathbf{x}_1)\, \chi^{\lambda_2}(\mathbf{x}_2) \rangle$ can be used to calculate averages of products of Minkowski functionals $m_{\nu\mu} \sim \langle M_\nu M_\mu \rangle$.

In Section 2 the basic facts from integral geometry are introduced, in particular, characteristic functions for curvatures and local Minkowski functionals. In Section 3 curvature-weighted structure functions are calculated for the Boolean model which are used in Section 4 to derive explicit expressions for second order moments. The difference of canonical and grand-canonical ensembles are discussed and illustrated for sticks and discs. As a first application of the main results a morphological thermodynamic model based on curvature integrals is introduced in the last Section 5 and thermodynamical quantities such as specific heats are related to mean values and second order moments of curvatures in the Boolean model.

2. INTEGRAL GEOMETRY

Let us first recall in this section the main results and theorems of integral geometry, the definition of Minkowski functionals M_ν (Section 2.1) and the Boolean model (Section 2.2). The definition of characteristic functions $\chi^\lambda(\mathbf{x})$ in Section 2.3 and of local Minkowski functionals M_ν^λ in Section 2.4 extends the standard reign of integral geometry and can be used to derive explicit expression for structure functions $S^{\lambda_1\lambda_2}$ (Section 3) and second order moments $m_{\nu\mu}$ (Section 4) of Minkowski functionals in the Boolean model.

2.1. Minkowski Functionals

Minkowski functionals (or intrinsic volumes, quermass integrals, curvature integrals) may be introduced as integrals of curvatures using differential geometry of smooth surfaces. Let A be a compact domain in $\mathbb{R}^d$ with regular boundary $\partial A \in \mathscr{C}^2$ and $d-1$ principal radii of curvature R_i $(i = 1,..., d-1)$. The functionals $W_\nu(A)$, with $\nu \geqslant 1$, can be defined by surface integrals[11]

$$W_{\nu+1}(A) = \frac{1}{(\nu+1)\binom{d}{\nu+1}} \int_{\partial A} S_\nu\left(\frac{1}{R_1},..., \frac{1}{R_{d-1}}\right) d\mathscr{S} \tag{1}$$

where S_ν denotes the νth elementary symmetric function and $d\mathscr{S}$ the $(d-1)$-dimensional surface element. In three dimensions one obtains $W_1 = \frac{1}{3}\int d\mathscr{S}$, $W_2 = \frac{1}{3}\int H\, d\mathscr{S}$, and $W_3 = \frac{1}{3}\int G\, d\mathscr{S}$ with the Gaussian $G = 1/R_1 R_2$ and the mean curvature $H = \frac{1}{2}((1/R_1) + (1/R_2))$. Although the Minkowski functionals are introduced as curvature integrals, they are well-defined at singular edges occurring, for instance, at the intersection of two grains clearly visible in Fig. 1. It is convenient to normalize the functionals

$$M_\nu(A) = \frac{\omega_{d-\nu}}{\omega_\nu \omega_d} W_\nu(A), \qquad \nu = 0,..., d \tag{2}$$

using the volume ω_d of a d-dimensional unit sphere $\omega_d = \pi^{d/2}/\Gamma(1 + d/2)$, namely $\omega_1 = 2$, $\omega_2 = \pi$, and $\omega_3 = 4\pi/3$. In three dimensions the family of Minkowski functionals consists of the volume $V = M_0$, the surface area $S = 8M_1$ of the coverage, its integral mean curvature $H = 2\pi^2 M_2$, and the Euler characteristic $\chi = (4\pi/3)\, M_3$.

The most important property of Minkowski functionals is additivity, i.e., the functional of the union $A \cup B$ of two domains A and B is the sum of the functional of the single domains subtracted by the intersection

$$\mathscr{M}_\nu(A \cup B) = \mathscr{M}_\nu(A) + \mathscr{M}_\nu(B) - \mathscr{M}_\nu(A \cap B) \tag{3}$$

This relation generalizes the common rule for the addition of the volume of two domains to the case of a general morphological measure, i.e., the measure of the double-counted intersection has to be subtracted.

A remarkable theorem is the "completeness" of the Minkowski functionals proven 1957 by H. Hadwiger. This characterization theorem asserts that any additive, motion-invariant and conditionally continuous functional $\mathscr{M}$ is a linear combination of the $d+1$ Minkowski functionals M_ν,

$$\mathscr{M}(A) = \sum_{\nu=0}^{d} c_\nu M_\nu(A) \tag{4}$$

with real coefficients c_ν independent of A.[13] Motion-invariance of the functional means that the functional $\mathscr{M}$ does not dependent on the location and orientation of the grain A. Since quite often the assumption of a homogeneous and isotropic system is made in physics, motion-invariance is not a very restrictive constraint on the functional. An important consequence of the additivity and the characterization theorem (4) is the possibility to calculate analytically certain integrals of Minkowski functionals. For instance, the kinematic fundamental formula[11]

$$\int_{\mathscr{G}} M_\nu(A \cap gB)\, dg = \sum_{\mu=0}^{\nu} \binom{\nu}{\mu} M_{\nu-\mu}(B)\, M_\mu(A) \tag{5}$$

describe the factorization of the Minkowski functionals of the intersection $A \cap B$ of two grains A and B if one integrates over the motions $g = (\mathbf{x}, \mathbf{r})$, i.e., translations $\mathbf{x}$ and rotations $\mathbf{r}$ of B. The integration $\int d\mathbf{g} = \int d\mathbf{x} \times \int d\mathbf{r}$ is the direct product of the integrations over all translations and orientations.

2.2. Boolean Model of Overlapping Grains

To be as rigorous as possible and desirable let us recapitulate definitions and notations of the Boolean model. We consider N convex grains K_i, $i = 1,..., N$ and assume that their Minkowski functionals $m_\nu(K_i)$ are finite. At a given point $\mathbf{x} \in A_i$ of each grain (the center) we fix a d-frame to determine the orientation $\mathbf{r}_i$ of the grain K_i. These so marked penetrable grains are placed independently at N random sites in a d-dimensional cube Ω with random isotropic orientation of their d-frames. To avoid edge effects we use periodic boundary conditions on $\partial\Omega$. Thus, a random configuration of grains gives rise to a set

$$\mathscr{A}_N = \bigcup_{i=0}^{N} g_i K_i \tag{6}$$

Our aim is to compute the mean values and second order moments of $M(\mathscr{A}_N)$, where the configurational average is done with the product density element

$$d\mu(g_1,..., g_N) = \frac{1}{|\Omega|^N} \prod_{i=1}^{N} dg_i \tag{7}$$

$\int dg_i = |\Omega| = \mathrm{vol}(\Omega)$. The integration over translations is restricted to Ω, i.e., the translated grains should have a nonempty intersection with Ω.

The kinematic formula (5) is extremely useful to calculate mean values of the additive Minkowski functionals for random distributions of grains. Following the method in ref. 3 one obtains for the mean values of the Minkowski measures per unit volume the explicit expression $m_0(\rho) = 1 - e^{-\rho m_0(K)}$ and for $\nu \geqslant 1$

$$\begin{aligned} m_\nu(\rho) &= -\frac{\partial^\nu}{\partial t^\nu} \exp\left\{ -\rho \sum_{\alpha=0}^{d} m_\alpha(K) \frac{t^\alpha}{\alpha!} \right\}\Bigg|_{t=0} \\ &= -e^{-\rho m_0(K)} \sum_{\mu=1}^{\nu} \frac{(-\rho)^\mu}{\mu!} \bar{I}_\nu^\mu(K) \end{aligned} \tag{8}$$

with coefficients $\bar{I}_\nu^\mu$ which do not depend on the density ρ but solely on the shape of the grains K_i. In particular, one finds $m_1(\rho) = \rho m_1(K)\, e^{-\rho m_0(K)}$, $m_2(\rho) = (\rho m_2(K) - m_1(K)^2\, \rho^2)\, e^{-\rho m_0(K)}$, and $m_3(\rho) = (\rho m_3(K) - 3m_1(K)\, m_2(K)\, \rho^2 + m_1(K)^3\, \rho^3)\, e^{-\rho m_0(K)}$ where $m_\nu(K)$ are the Minkowski functionals for an arbitrary single shape K.

Remark. Since the squared functionals $M_\nu^2(\mathscr{A}_N)$ are not additive the kinematic formula (5) does not help to calculate second order moments. Therefore, local functionals and characteristic structure functions has to be defined first (Sections 2.3–2.4) in order to decompose the squared functionals into local contributions for which averages can be calculated within the Boolean model (Section 4).

2.3. Characteristic Functions

In Section 2.1 Minkowski functionals are introduced as global measures $M_\nu(\mathscr{A}_N)$ of configurations $\mathscr{A}_N$ in order to describe the morphology of the stochastic spatial structures emerging in the Boolean grain model. It was emphasized that these measures can be written as surface integrals of curvatures. An important generalization of the concept of morphological characterization is the definition of local curvature measures.

In the Boolean grain model the surface $\partial\mathscr{A}_N$ of a configuration $\mathscr{A}_N = \bigcup_{i=1}^N K_i$ of N overlapping grains K_i can be decomposed into $d-\nu$-dimensional parts resulting from the intersection of surfaces ∂K_i of ν different single grains K_i. The $d-\nu$-dimensional surface is defined by

$$\mathscr{A}^{(\nu)} := \partial^\nu \mathscr{A} = \left\{ \mathbf{x} \in \partial\mathscr{A} \;\middle|\; \exists K_i \text{ with } \mathbf{x} \in \bigcap_{i=1}^{\nu} \partial K_i \right\} \tag{9}$$

and $\mathscr{A}^{(0)} := \partial^0 \mathscr{A} := \mathscr{A}$. The set $\mathscr{A}^{(\nu)}$ is closed with $M_\lambda(\mathscr{A}^{(\nu)}) = 0$ for $\lambda < \nu$. Analogous to the characteristic function

$$\chi^0(\mathscr{A}, \mathbf{x}) = \chi(\mathscr{A} \cap \mathbf{x}) = \begin{cases} 1 & \mathbf{x} \in \mathscr{A} \\ 0 & \mathbf{x} \notin \mathscr{A} \end{cases} \tag{10}$$

i.e., to the Euler characteristic $\chi = \omega_d M_d$ which indicates whether the point $\mathbf{x} \in \Omega$ belongs to $\mathscr{A}$, one may define local characteristic functions of submanifolds $\mathscr{A}^{(\nu)}$ by

$$\chi^\nu(\mathscr{A}, \mathbf{x}) = \int_{\mathbf{y} \in \partial^\nu \mathscr{A}} d\mathscr{S}^{(\nu)}\mathbf{y}\; \delta(\mathbf{y} - \mathbf{x}) \tag{11}$$

and $\chi^0(\mathscr{A}, \mathbf{x}) := \chi(\mathscr{A} \cap \mathbf{x})$, where $d\mathscr{S}^{(v)}\mathbf{y}$ denotes the infinitesimal volume element of $\partial^v\mathscr{A}$ at the point $\mathbf{y} \in \mathscr{A}^{(v)}$. The function $\chi^v(\mathscr{A}, \mathbf{x})$ $(v > 0)$ is strictly speaking a distribution defined as functional which maps functions $f(\mathbf{x})$ to $\mathbb{R}$. They are zero for points $\mathbf{x} \notin \mathscr{A}^{(v)}$ whereas the integral over $\mathbb{R}^d$

$$M_0^v(\mathscr{A}) = \int_{\mathbb{R}^d} \chi^v(\mathscr{A}, \mathbf{x})\, d\mathbf{x} \tag{12}$$

yields the $(d-v)$-dimensional volume M_0^v of $\mathscr{A}^{(v)}$, for example, the $d-1$-dimensional surface area $M_0^1(\mathscr{A}) = d\, W_1(\mathscr{A})$. In addition to the not covered surface area of the grains $(v = 1)$ one obtains in three dimensions the boundary length $M_0^2(\mathscr{A})$ of the intersection of two grains $(v = 2)$ and the number $M_0^3(\mathscr{A})$ of triple intersections of three grains $(v = 3)$. Because of $M_0^v(\mathscr{A}) = M_0^v(\partial\mathscr{A})$ one obtains for the union of v grains $(v \neq 0)$ the relations

$$\begin{aligned}
\chi^v\left(\bigcup_{i=1}^{v} K_i, \mathbf{x}\right) &= \chi^v\left(\partial \bigcup_{i=1}^{v} K_i, \mathbf{x}\right) = \chi^v\left(\bigcup_{i=1}^{v} \partial K_i, \mathbf{x}\right) \\
&= \chi^v\left(\bigcap_{i=1}^{v} \partial K_i, \mathbf{x}\right) = \chi^v\left(\bigcap_{i=1}^{v} K_i, \mathbf{x}\right) \\
M_0^v\left(\bigcup_{i=1}^{v} K_i\right) &= M_0^v\left(\partial \bigcup_{i=1}^{v} K_i\right) = M_0^v\left(\bigcup_{i=1}^{v} \partial K_i\right) \\
&= M_0^v\left(\bigcap_{i=1}^{v} \partial K_i\right) = M_0^v\left(\bigcap_{i=1}^{v} K_i\right)
\end{aligned} \tag{13}$$

Instead of the decomposition

$$\chi(\mathscr{A} \cap \mathbf{x}) = 1 - \prod_{i=1}^{N} (1 - \chi(K_i \cap \mathbf{x})) \tag{14}$$

of the characteristic function $\chi(\mathscr{A} \cap \mathbf{x})$ one obtains for $v > 0$ the decomposition of $\chi^v(\mathscr{A}, \mathbf{x})$ into characteristic functions of single grains K_i

$$\chi^v(\mathscr{A}, \mathbf{x}) = \sum_{\{C_v^N\}} \chi^v\left(\bigcup_{j \in C_v^N} K_j, \mathbf{x}\right) \prod_{j \notin C_v^N} (1 - \chi(K_j \cap \mathbf{x})) \tag{15}$$

where C_v^N denotes a combination of v numbers out of N. The decomposition (15) of the characteristic functions separates the combinatorial features of N overlapping grains $\mathscr{A} = \bigcup_{i=1}^{N} K_i$ from the local geometric measure χ^v. An important property of χ^v is the symmetry relation

$$\chi^v(K_\mathbf{y}, \mathbf{x}) = \chi^v(\hat{K}_\mathbf{x}, \mathbf{y}) \tag{16}$$

where $\hat{K}_{\mathbf{x}} = \{\mathbf{y} \in \mathbb{R}^d \mid -(\mathbf{y}-\mathbf{x}) \in K_{\mathbf{x}}\}$ denotes the inverted grain where $\mathbf{x}$ is the center of mass of K. In the decompositions (14) and (15) the multiplication rule

$$\chi(K \cap \mathbf{x}) \cdot \chi(K' \cap \mathbf{x}) = \chi(K \cap K' \cap \mathbf{x}) \tag{17}$$

of two characteristic functions at the same point $\mathbf{x}$ has been used. Analogously, one finds the general relation

$$\Delta_{\nu\mu}^{(d)}(r_{\mathbf{x}})\, \chi^{\nu}\left(\bigcap_{i=1}^{\nu} K_i, \mathbf{x}\right) \chi^{\mu}\left(\bigcap_{j=1}^{\mu} K_j, \mathbf{x}\right) = \chi^{\nu+\mu}\left(\bigcap_{i=1}^{\nu+\mu} K_i, \mathbf{x}\right) \tag{18}$$

for $\nu, \mu \neq 0$ and $\nu + \mu \leqslant d$. It should be noted that the product vanishes for $\nu + \mu \geqslant d$. The factor $\Delta_{\nu\mu}^{(d)}(r_{\mathbf{x}})$ does not depend on the position $\mathbf{x}$ at the intersection of the boundaries ∂K_i but on the relative orientation $r_{\mathbf{x}}$ of the grains $K = \bigcap_{i=1}^{\nu} K_i$ and $K' = \bigcap_{j=1}^{\mu} K_j$ at $\mathbf{x}$. It is given as functional determinant in the differential kinematic formula[14, 15] (compare Eq. (15.9) in ref. 11)

$$d\mathscr{S}^{(\nu+\mu)}(K' \cap K) \wedge dK = \Delta_{\nu\mu}^{(d)}(K_{[\mathbf{x}]})\, dK_{[\mathbf{x}]} \wedge d\mathscr{S}^{(\mu)}(K') \wedge d\mathscr{S}^{(\nu)}(K) \tag{19}$$

which describes the decomposition of the kinematic density dK of the group of motions, i.e., translations and orientations of the $(d-\nu)$-dimensional grain K with respect to the fixed $(d-\mu)$-dimensional grain K'. Here, $dK_{[\mathbf{x}]}$ is the kinematic density of the group of special rotations of K about $\mathbf{x}$ which is isomorphic to $SO(d)$. The integration measure $d\mathscr{S}^{(\nu)}$ denotes the $(d-\nu)$-dimensional volume element of K which has been used already in Eq. (11) and Eq. (1) for $\nu = 1$. Details of the derivation of the factor $\Delta_{\nu\mu}^{(d)}(K_{[\mathbf{x}]})$ can be found in [11, Chap. 15]. Let us consider the $(r+q-d)$-dimensional intersection $S^{r+q-d} = M^r \cap N^q$ of a r-dimensional manifold M^r and a fixed q-dimensional manifold N^q. At each point $\mathbf{x} \in S^{r+q-d}$ orthonormal vectors $\mathbf{e}_i$, $i = 1,..., r+q-d$ can be found which span the tangent plane of S^{r+q-d} at $\mathbf{x}$. Let e_i, $i = r+q-d,..., r$ be orthonormal vectors which are perpendicular to S^{r+q-d} but tangent to M^r. Accordingly, let $\mathbf{b}_i$, $i = 1,..., d-r$ be orthonormal vectors which are perpendicular to S^{r+q-d} but tangent to N^q. Obviously $\mathbf{b}_i$ do not be necessarily perpendicular to M^r so that the $(d-r) \times (d-r)$ determinant $(i, j = 1,..., d-r)$

$$\Delta_{rq}^{(d)} := |(\mathbf{b}_i \cdot \mathbf{e}_{r+j})| \tag{20}$$

is not equal unity due to non-rectangular angles between tangent vectors $\mathbf{b}_i$ at N^q and $\mathbf{e}_{r+i}$ at M^r. Thus, the decomposition Eq. (18) of the characteristic functions $\chi^{\nu}(\mathbf{x})$ of $(d-\nu)$-dimensional submanifolds of $\mathscr{A} = \bigcup_i K_i$

(see Eq. (11)) requires a volume element defined by the tangent vectors, i.e., normals $\mathbf{n}_i$ of K_i at $\mathbf{x}$.

Example 2.1. In two dimensions, for instance, the determinant

$$\Delta_{11}^{(2)}(\phi) = |\mathbf{n}_1 \cdot \mathbf{n}_2| = \left|\cos\left(\frac{\pi}{2} - \phi\right)\right| = \sin\phi(\mathbf{n}_1\mathbf{n}_2) \tag{21}$$

at an intersection point $\mathbf{x} \in \partial K_1 \cap \partial K_2$ of the two one-dimensional manifolds ∂K_i is given by the angle $\phi(\mathbf{n}_1\mathbf{n}_2)$ $(0 \leqslant \phi \leqslant \pi)$ between the two normal vectors $\mathbf{n}_i$ at K_i, respectively. Generally, one finds for two $(d-1)$-dimensional manifolds ∂K_i in d dimensions the factor $\Delta_{11}^{(d)} = |\sin(\phi)|$ where ϕ denotes the angle between the two normal vectors of ∂K_i at $\mathbf{x} \in \partial K_1 \cap \partial K_2$.

Example 2.2. Accordingly, one finds in three dimensions for the intersection of three grain boundaries ∂K_i with $N^1 = \partial K_1 \cap \partial K_2$ and $M^2 = \partial K_3$ the determinant

$$\Delta_{21}^{(3)} = |\mathbf{b}_1 \cdot \mathbf{e}_3| = |\cos(\phi((\mathbf{n}_1 \times \mathbf{n}_2)\,\mathbf{n}_3))| = \frac{|(\mathbf{n}_1 \times \mathbf{n}_2)\,\mathbf{n}_3)|}{|\sin\phi(\mathbf{n}_1\mathbf{n}_2)|} \tag{22}$$

where the tangent $\mathbf{b}_1 = \mathbf{n}_1 \times \mathbf{n}_2 / |\mathbf{n}_1 \times \mathbf{n}_2|$ of N^1 at $\mathbf{x}$ is given by the normal vectors $\mathbf{n}_i$ of K_i at $\mathbf{x}$ and $\phi(\mathbf{eb})$ denotes the angle between two vectors $\mathbf{e}$ and $\mathbf{b}$, in particular, between $\mathbf{e}_3 = \mathbf{n}_3$ and $\mathbf{b}_1$. It should be noted that $\Delta_{21}^{(3)}(\mathbf{n}_1, \mathbf{n}_2; \mathbf{n}_3)$ is not symmetric in the normals $\mathbf{n}_i$ since the position of K_1 and K_2 is fixed in Eq. (22) whereas K_3 denotes a moving grain.

2.4. Local Minkowski Functionals

In Section 2.1 curvature integrals are defined over the total surface $\partial\mathscr{A}$ of a configuration $\mathscr{A}$. Restricting the range of integration one may define *local* curvature measures[16–18]

$$W_\nu(A, B) = \frac{1}{\nu\binom{d}{\nu}} \int_{\mathbf{x} \in B \cap \partial A} S_{\nu-1}(\mathbf{x})\, d\mathscr{S} \tag{23}$$

by integrating the curvature functions S_ν, i.e., the symmetric combination of the local curvatures R_i^{-1} only over a part $B \cap \partial A \subset \partial A$ of the surface ∂A. These "local Minkowski functionals" are continuous, additive, homogeneous of order $d-\nu$, and motion invariant, $W_\nu(gA, gB) = W_\nu(A, B)$, if B is moved

according to A. Choosing the special case of a point $B = \mathbf{x} \in \partial A$ on the surface one obtains the νth elementary symmetric function of the curvatures at $\mathbf{x}$,

$$W_\nu(A, \mathbf{x}) = \frac{1}{\nu\binom{d}{\nu}} S_{\nu-1}(\mathbf{x}) \tag{24}$$

if the boundary ∂A is smooth. At singular points $\mathbf{x} \subset \bigcap_{i=1}^n K_i$ where, for instance, boundaries of convex bodies intersect the local curvature $W_\nu(A, \mathbf{x})$ is given by the derivative of the parallel volume[13]

$$W_\nu\left(\bigcup_{i=1}^n K_i, \mathbf{x}\right) = (-1)^{n+1} \frac{(d-\nu)!}{d!} \left(\frac{\partial}{\partial \varepsilon}\right)^\nu V(B_\varepsilon^d(\mathbf{x}))\Big|_{\varepsilon=0} \tag{25}$$

where $B_\varepsilon^d(\mathbf{x})$ denotes the set of points with distance less than ε to $\mathbf{x}$ and V its volume.

Example 2.3. One finds in d dimensions for spheres $B_R^d(\mathbf{x}_i)$ of radius R and center $\mathbf{x}_i$ at the intersection $S^{(2)} = \partial B_R^d(\mathbf{x}_1) \cap \partial B_R^d(\mathbf{x}_2)$ ($|\mathbf{x}_1 - \mathbf{x}_2| < 2R$) the local Minkowski functionals

$$W_2(B_R^d(\mathbf{x}_1) \cap B_R^d(\mathbf{x}_2), S^{(2)}) = \frac{2}{d}\omega_{d-1}\left(R^2 - \frac{|\mathbf{x}_1 - \mathbf{x}_2|^2}{4}\right)^{(d-2)/2} \arcsin\left(\frac{|\mathbf{x}_1 - \mathbf{x}_2|}{2R}\right) \tag{26}$$

and, particularly, for $d = 3$ the local Euler characteristic $W_3(B_R^d(\mathbf{x}_1) \cap B_R^d(\mathbf{x}_2), S^{(2)}) = \omega_3 |\mathbf{x}_1 - \mathbf{x}_2|/(2R)$.

Example 2.4. At the intersection $S^{(3)} = \partial B_R^d(\mathbf{x}_1) \cap \partial B_R^d(\mathbf{x}_2) \cap \partial B_R^d(\mathbf{x}_3)$ of three spheres in three dimensions one obtains the local Euler characteristic

$$W_3(B_R^d(\mathbf{x}_1 \cap B_R^d(\mathbf{x}_2 \cap B_R^d(\mathbf{x}_3), S^{(3)}) = \tfrac{2}{3}\Delta(\alpha_1, \alpha_2, \alpha_3) \tag{27}$$

with $|\mathbf{x}_i - \mathbf{x}_j| < 2R$ $(i \neq j)$ and the spherical excess $\Delta(\alpha_1, \alpha_2, \alpha_3)$ given by l'Huiliersche formula

$$\tan^2\frac{\Delta}{4} = \tan\frac{\alpha_1+\alpha_2+\alpha_3}{4} \tan\frac{\alpha_1+\alpha_2-\alpha_3}{4} \tan\frac{\alpha_1-\alpha_2+\alpha_3}{4} \times \tan\frac{-\alpha_1+\alpha_2+\alpha_3}{4} \tag{28}$$

The factor $|\Delta|/3$ denotes the Gaussian curvature at $\mathbf{x} \in S^{(3)}$ where boundaries of three spheres intersect. It equals the area of a spherical triangle

with edges $\alpha_i = 2 \arcsin(|\mathbf{y}_j - \mathbf{y}_k|/2R)$ $(i \neq j \neq k)$ where $\mathbf{y}_i = \mathbf{x}_i - \mathbf{x}$ denotes the distance of the intersection point $\mathbf{x}$ to the centers $\mathbf{x}_i$ of the spheres.

Applying the normalization (2) and using the characteristic functions χ^ν of the intersection sets $\mathscr{A}^{(\nu)}$ of grains given by Eq. (11) one can define analogously to the volume integrals $M_0^\nu(\mathscr{A})$ the local Minkowski functionals $(\nu \geqslant \lambda \geqslant 1)$

$$M_\nu^\lambda(\mathscr{A}) = \int M_\nu(\mathscr{A}, \mathbf{x})\, \chi^\lambda(\mathscr{A}, \mathbf{x})\, d\mathbf{x} \tag{29}$$

of a configuration $\mathscr{A}$ of the Boolean model (see Eq. (6)). The decomposition

$$M_\nu(\mathscr{A}) = \sum_{\lambda=1}^{\nu} M_\nu^\lambda(\mathscr{A}) \tag{30}$$

of the global Minkowski functional into contributions located on the $(d-\lambda)$-dimensional intersection $\mathscr{A}^{(\lambda)}$ of λ grain boundaries ∂K_i (see Eq. (9) is the main result of this section. It should be noted that $M_\nu^\lambda(\mathscr{A}) \neq M_\nu(\mathscr{A}, \partial^\lambda \mathscr{A}) = \sum_{\mu=\lambda}^{\nu} M_\nu^\mu(\mathscr{A})$ since $\partial^\lambda \mathscr{A}$ contains lower dimensional parts $\partial^\mu \mathscr{A}$ $(\mu \geqslant \lambda)$ of the surface. Equation (30) describes the separation of the curvature measures $M_\nu(\mathscr{A}, \mathbf{x})$ and its geometric support $\chi^\lambda(\mathscr{A}, \mathbf{x})$ which can be used in Section 4 to determine exact second order moments of $M_\nu(\mathscr{A})$ in terms of structure functions of $\mathscr{A}^{(\lambda)}$. The characteristic functions $\chi^\nu(\mathscr{A}, \mathbf{x})$ and the local Minkowski functionals $M_\lambda(\mathscr{A}, \mathbf{x}) = S_{\lambda-1}/(\lambda \binom{d}{\lambda})$ are two complement quantities describing the morphology at a point $\mathbf{x}$ of the boundary of a spatial structure. Whereas χ focuses on the partition of the surface into inter-sectional parts, the functionals W_λ describe the geometry in terms of local curvatures.

Let us discuss some examples and elementary properties of the local Minkowski functionals $M_\nu^\lambda(\mathscr{A})$. For d-dimensional polyhedra P, for instance, one finds $M_\nu^\lambda(P) = M_\nu(P)\, \delta_{\lambda\nu}$, i.e., the functional M_ν is completely located at the $(d-\nu)$-dimensional edges of P. In particular, the Euler characteristic equals the sum of all 0-dimensional corner contributions. Since $M_\nu^\lambda(\mathscr{A})$ is located at the $(d-\lambda)$-dimensional intersection of boundaries one finds according to Eq. (13) for the union of λ grains K_i the relations $(\lambda > 0)$

$$\begin{aligned} M_\nu^\lambda\left(\bigcup_{i=1}^{\lambda} K_i\right) &= (-1)^{\lambda+1} M_\nu^\lambda\left(\bigcap_{i=1}^{\lambda} K_i\right) \\ M_\nu^\lambda\left(\bigcup_{i=1}^{\lambda} K_i\right) &= M_\nu\left(\bigcup_{i=1}^{\lambda} K_i, \bigcap_{i=1}^{\lambda} \partial K_i\right) = (-1)^{\lambda+1} M_\nu\left(\bigcap_{i=1}^{\lambda} K_i, \bigcap_{i=1}^{\lambda} \partial K_i\right) \end{aligned} \tag{31}$$

where the sign $(-1)^{\lambda+1}$ follows from the additivity relation (3). Using the kinematic formula (5), for instance, the integrals over the group of motions $\mathscr{G}$ yields for $\lambda = \nu$ and $\lambda = \nu - 1$

$$\begin{aligned} \prod_{i=2}^{\nu} \int_{\mathscr{G}} dg_i \, M_\nu^\nu \left(\bigcap_{i=1}^{\nu} g_i K \right) &= \nu! \, M_1(K)^\nu \\ \prod_{i=2}^{\nu} \int_{\mathscr{G}} dg_i \, M_{\nu+1}^\nu \left(\bigcap_{i=1}^{\nu} g_i K \right) &= \binom{\nu+1}{2} \nu! \, M_2(K) \, M_1(K)^{\nu-1} \end{aligned} \tag{32}$$

Finally, mean values of the local Minkowski functionals M_ν^λ can be discussed in the Boolean model of overlapping grains. Using the decomposition (30) as well as the definitions (29) and Eq. (31) one obtains immediately the coefficients

$$\bar{I}_\nu^\lambda = \prod_{i=2}^{\lambda} \int_{\mathscr{G}} dg_i \, M_\nu \left(\bigcap_{i=1}^{\lambda} g_i K, \bigcap_{i=1}^{\lambda} g_i \, \partial K \right) = \prod_{i=2}^{\lambda} \int dg_i \, M_\nu^\lambda \left(K \bigcap_{i=2}^{\lambda} g_i K \right) \tag{33}$$

for the mean values (8) of the Minkowski functionals with

$$\bar{I}_\nu^\lambda = \frac{\partial^\nu}{\partial t^\nu} \left(\sum_{\alpha=0}^{d} M_\alpha(K, \partial K) \frac{t^\alpha}{\alpha!} \right)^\lambda \Bigg|_{t=0} = \underbrace{\sum_{\nu_1, \ldots, \nu_\lambda = 1}^{\nu-\lambda+1}}_{\sum_{i=1}^{\lambda} \nu_i = \nu} \frac{\nu!}{\nu_1! \cdots \nu_\lambda!} \prod_{i=1}^{\lambda} m_{\nu_i}(K) \tag{34}$$

where the sum is restricted to values of ν_i which obey the sum rule $\sum_{i=1}^{\lambda} \nu_i = \nu$.

Example 2.5. In particular, one finds $\bar{I}_0^0 = 1$, $\bar{I}_\nu^1 = m_\nu$, $\bar{I}_2^2 = 2(m_1)^2$, $\bar{I}_3^2 = 6 m_1 m_2$, $\bar{I}_3^3 = 6(m_1)^3$. Thus, integrals of local Minkowski functionals given in Eq. (33) can be evaluated by using the kinematical formula (5) where terms containing $M_0(K, \partial K) = 0$ vanish. Therefore, the coefficient $\bar{I}_\nu^\lambda$ in the polynomial (8) equals the local Minkowski functional of the boundary where λ grains K_i intersect, averaged over translations and rotations of K_i.

Remark. The coefficients for non-spherical convex grains K are always larger than the coefficients for a d-dimensional sphere $B^{(d)}$ of equal volume $m_0(K)$, i.e.,

$$\bar{I}_\nu^\mu(K) / \bar{I}_\nu^\mu(B^{(d)}) \geqslant (m_0(K)/m_0(B^{(d)}))^{\lambda - \nu/d} \tag{35}$$

This relation is directly related to the well-known isoperimetric inequalities[13]

$$\left(\frac{M_0(K)}{M_0(B^{(d)})}\right)^{d-\nu} \leqslant \left(\frac{M_\nu(K)}{M_\nu(B^{(d)})}\right)^{d}, \qquad \frac{M_\nu(K)}{M_\nu(B^{(d)})} \leqslant \frac{M_{d-1}(K)}{M_{d-1}(B^{(d)})} \tag{36}$$

for the Minkowski functionals of arbitrary convex grains K in d dimensions. Such inequalities causes a liquid drop to relax into a spherical shape which minimizes its free energy because of its minimal surface area.

For a finite number N of grains K_i in a box Ω with periodic boundary conditions and volume $|\Omega|$ one obtains the canonical mean values

$$\begin{aligned} m_0(N) &= 1 - \left(1 - \frac{V}{|\Omega|}\right)^N \\ m_\nu(N) &= \sum_{\lambda=1}^{\nu} (-1)^{\lambda+1} \binom{N}{\lambda} \left(1 - \frac{V}{|\Omega|}\right)^{N-\lambda} \frac{\bar{I}_\nu^\lambda}{|\Omega|^\lambda} \end{aligned} \tag{37}$$

Example 2.6. Using the additivity relation (3) and the kinematic formula (5) one obtains the mean values

$$\langle M_\nu(K_1 \cup K_2) \rangle = 2M_\nu - \frac{1}{|\Omega|} \sum_{\mu=0}^{\nu} \binom{\nu}{\mu} M_\mu M_{\nu-\mu} \tag{38}$$

of the Minkowski functionals for two grains K_i where the bracket denotes an integration over translations and rotations of K_i. Applying the Eqs. (34) and (37), $|\Omega|\, m_\nu(N=2) = 2(1 - V/|\Omega|)\, \bar{I}_\nu^1 - \bar{I}_\nu^2/|\Omega|$, one recovers the result (38) with $\bar{I}_\nu^1 = M_\nu(K)$ and $\bar{I}_\nu^2 = \sum_{\mu=1}^{\nu-1} \binom{\nu}{\mu} M_\mu M_{\nu-\mu}$.

Accordingly, using the decomposition (15) one obtains for the $(d-\lambda)$-dimensional volume of N grains the mean values

$$m_0^\lambda(N) = \langle \chi^\lambda(\mathscr{A}, \mathbf{x}) \rangle = \binom{N}{\lambda} \left(1 - \frac{V}{|\Omega|}\right)^{N-\lambda} \frac{\bar{I}_0^\lambda}{|\Omega|^\lambda} \tag{39}$$

in the Boolean model with $\bar{I}_0^0 = 1$ and the averaged volume of the intersection of λ boundaries

$$\begin{aligned} \bar{I}_0^\lambda &:= \prod_{i=1}^{\lambda} \int dg_i\, \chi^\lambda\left(\bigcup_{i=1}^{\lambda} g_i K, \mathbf{x}\right) = \prod_{i=2}^{\lambda} \int dg_i\, M_0^\lambda\left(K \bigcup_{i=2}^{\lambda} g_i K\right) \\ &= \frac{(d-\lambda+1)\,\omega_{d-\lambda+1}}{(d+1)\,\omega_{d+1}} \left(\frac{(d+1)\,\omega_{d+1}}{d\omega_d}\, M_0^1(K)\right)^\lambda \end{aligned} \tag{40}$$

For example, the $(d-1)$-dimensional surface area is $\bar{I}_0^1 = dW_1(K)$, the mean number of intersection points $\bar{I}_0^2(K) = (2/\pi)\ U(K)^2$ $(\bar{I}_0^3(K) = (\pi/8)\ S(K)^3)$ of two (three) grain boundaries in two (three) dimensions is given by the circumference $U(K)$ (surface area $S(K)$) of the grains, respectively, and in three dimensions the boundary length of two intersecting grains is $\bar{I}_0^2(K) = (\pi/2)\ S(K)^2$. Thus, one obtains for discs of radius R in two dimensions $\bar{I}_0^2(B_R) = 8\pi R^2$ and for spheres in three dimensions $\bar{I}_0^3(B_R) = 8\pi^4 R^6$. Of course, this explicit result could have been calculated directly by using the determinant (21) but using the kinematic formula (5) is much more convenient. In the thermodynamic limit $N,\ \Omega \to \infty,\ \rho = N/|\Omega|$ fixed one obtains the grand-canonical average

$$m_0^\lambda(\rho) = \langle M_0^\lambda \rangle_{gk} = \sum_{N=\lambda}^{\infty} \frac{(\rho\Omega)^N}{N!} e^{-\rho\Omega} m_0^\lambda(N, \omega) = \frac{\rho^\lambda}{\lambda!} e^{-\rho V} \bar{I}_0^\lambda \tag{41}$$

and for the mean values $m_\nu^\lambda(N) = \langle M_\nu^\lambda(\mathscr{A}, \mathbf{x}) \rangle$ of the local Minkowski functionals

$$m_\nu^\lambda(N) = (-1)^{1+\lambda} \binom{N}{\lambda} \left(1 - \frac{V}{|\Omega|}\right)^{N-\lambda} \frac{\bar{I}_\nu^\lambda}{|\Omega|^\lambda}$$

$$\to m_\nu^\lambda(\rho) = (-1)^{1+\lambda} \frac{\rho^\lambda}{\lambda!} e^{-\rho V(K)} \bar{I}_\nu^\lambda \tag{42}$$

in accordance with $m_\nu(\rho) = \sum_{\lambda=1}^{\nu} m_\nu^\lambda(\rho)$ given by Eq. (8).

3. STRUCTURE FUNCTIONS IN THE BOOLEAN MODEL

In the previous section local Minkowski functionals $M_\nu^\lambda(\mathscr{A})$ have been introduced in order to decompose the global functionals M_ν into terms located on the $(d-\lambda)$-dimensional intersection set $\mathscr{A}^{(\lambda)}$ of λ grain surfaces. In a last step structure functions $S^{\lambda_1\lambda_2}(\mathbf{x}_1, \mathbf{x}_2)$ are defined for these geometric locations so that second order moments of local functionals $M_\nu^\lambda(\mathscr{A})$ can be written as integrals over curvature-weighted structure functions $M_{\nu_1\nu_2}^{\lambda_1\lambda_2}(\mathbf{x}_1, \mathbf{x}_2)$ (Section 4).

The expectation value that a point $\mathbf{x}$ is covered by a configurations $\mathscr{A} = \bigcup_{i=1}^N K_i$ of the Boolean model is given by the density

$$S^0(\mathbf{x}) = \langle \chi(\mathscr{A} \cap \mathbf{x}) \rangle = m_0(N) \tag{43}$$

Analogously, one can define the centered n-point correlation function

$$\begin{aligned}
&\overbrace{S^{0\cdots 0}}^{n\text{-times}}(N; \mathbf{x}_1,..., \mathbf{x}_n) \\
&\quad = \left\langle \prod_{i=1}^{n} (\chi(\mathscr{A} \cap \mathbf{x}_i) - S^0(\mathbf{x}_i)) \right\rangle \\
&\quad = \sum_{l=0}^{n} (-1)^l \sum_{C_l^n} \left[\left(1 - \frac{V(K)}{|\Omega|}\right)^{n-l} \left(1 - \frac{V(\{\mathbf{x}_j\}_{j\in C_l^n})}{|\Omega|}\right)\right]^N
\end{aligned} \tag{44}$$

that simultaneously all points $\mathbf{x}_i$ are located in $\mathscr{A}$. Here, C_l^n denotes a combination of l numbers out of $\{1,..., n\}$ and

$$V(\{\mathbf{x}_j\}_{j=1,..., n}) = \int_{\mathscr{R}} dr\ V\left(\bigcup_{j=1}^{n} rK_{\mathbf{x}_j}\right) \tag{45}$$

is the covered volume of grains centered at $\mathbf{x}_j$ and averaged over all rotations r of the grains K_i where all of them have the same orientation. In the thermodynamic limit $N, \Omega \to \infty$ with fixed density $\rho = N/|\Omega|$ one obtains instead of the canonical function (44) the grand-canonical correlation function

$$S^{0\cdots 0}(\rho; \{\mathbf{x}_i\}) = \sum_{l=0}^{n} (-1)^l \sum_{C_l^n} e^{-(n-l)\rho V(K) - \rho V(\{\mathbf{x}_j\}_{j\in C_l^n})} \tag{46}$$

Instead of Eq. (44) for the covered region $\mathscr{A}$ one can also define correlation functions for the $(d-\lambda)$-dimensional intersection sets $\mathscr{A}^{(\lambda)}$, namely

$$\begin{aligned}
S^{\lambda}(N; \mathbf{x}) &= \langle \chi^{\lambda}(\mathscr{A}, \mathbf{x}) \rangle = m_0^{\lambda}(N) \\
S^{\lambda_1\lambda_2\cdots\lambda_n}(N; \mathbf{x}_1,..., \mathbf{x}_n) &= \left\langle \prod_{i=1}^{n} [\chi^{\lambda_i}(\mathscr{A}, \mathbf{x}_i) - S^{\lambda_i}(N; \mathbf{x}_i)] \right\rangle
\end{aligned} \tag{47}$$

i.e., the expectation value that the points $\mathbf{x}_i$ are located on $\mathscr{A}^{(\lambda_i)}$, respectively.

In contrast to the structure functions for $\mathscr{A}$ given by Eq. (44) it is not possible to decompose the functions (47) for the intersection sets $\mathscr{A}^{(\lambda)}$ straightforwardly since the characteristic functions χ^{λ} do not obey the simple multiplication rule (14) but the decomposition (15). Applying Eq. (15) to the structure function (47) yields terms of the form

$$\chi^2(K_1 \cup K_2, \mathbf{x}_1) \cdot \chi^1(K_1, \mathbf{x}_2) \cdot (1 - \chi(K_2 \cap \mathbf{x}_2) \tag{48}$$

which have to be integrated over the motions of the grains K_i. Instead of the kinematic formula as for mean values one has to use the differential geometric factors (20) in combination with the symmetry relation (16), the multiplication rules (14)–(18), and combinatorial factors due to permutations of the equal shaped grains K_i in Eq. (48).

Then, for $\lambda_1 \geqslant \lambda_2 > 0$, $\lambda > 0$ the canonical correlation functions reads

$$\begin{aligned}
S^{00}(N; \mathbf{x}_1, \mathbf{x}_2) &= \left(1 - \frac{V(\mathbf{x}_1, \mathbf{x}_2)}{|\Omega|}\right)^N - \left(1 - \frac{V}{|\Omega|}\right)^{2N} \\
S^{\lambda 0}(N; \mathbf{x}_1, \mathbf{x}_2) &= \binom{N}{\lambda}\left(1 - \frac{V}{|\Omega|}\right)^{2N-\lambda} \frac{\bar{I}_0^{\lambda}}{|\Omega|^{\lambda}} \\
&\quad - \binom{N}{\lambda}\left(1 - \frac{V(\mathbf{x}_1, \mathbf{x}_2)}{|\Omega|}\right)^{N-\lambda} \frac{I_0^{\lambda}(\mathbf{x}_1, \mathbf{x}_2)}{|\Omega|^{\lambda}} \\
S^{\lambda_1\lambda_2}(N; \mathbf{x}_1, \mathbf{x}_2) &= -\binom{N}{\lambda_1}\binom{N}{\lambda_2} \frac{\bar{I}_0^{\lambda_1}\bar{I}_0^{\lambda_2}}{|\Omega|^{\lambda_1+\lambda_2}}\left(1 - \frac{V}{|\Omega|}\right)^{2N-\lambda_1-\lambda_2} \\
&\quad + \sum_{l=0}^{\lambda_2} \binom{N}{\lambda_1}\binom{\lambda_1}{l}\binom{N-\lambda_1}{\lambda_2-l} \frac{S_l^{\lambda_1\lambda_2}(\mathbf{x}_1, \mathbf{x}_2)}{|\Omega|^{\lambda_1+\lambda_2-l}} \\
&\quad \times \left(1 - \frac{V(\mathbf{x}_1, \mathbf{x}_2)}{|\Omega|}\right)^{N-\lambda_1-\lambda_2+l}
\end{aligned} \tag{49}$$

with the geometric amplitudes

$$\begin{aligned}
S_l^{\nu_1\nu_2}(\mathbf{x}_1, \mathbf{x}_2) &= \left(\prod_{j=1}^{\nu_1+\nu_2-l} \int dK_j\right) \chi^{\nu_1}\left(\bigcup_{j=1}^{\nu_1} K_j, \mathbf{x}_1\right) \chi^{\nu_2}\left(\bigcup_{j=\nu_1-l+1}^{\nu_1+\nu_2-l} K_j, \mathbf{x}_2\right) \\
&\quad \times \prod_{j=\nu_1+1}^{\nu_1+\nu_2-l} (1 - \chi(K_j \cap \mathbf{x}_1)) \prod_{j=1}^{\nu_1-l} (1 - \chi(K_j \cap \mathbf{x}_2))
\end{aligned} \tag{50}$$

i.e., the constrained structure functions that l grains out of $\nu_1 + \nu_2 - l$ are linked to $\mathbf{x}_1$ and $\mathbf{x}_2$. Equation (49) resembles the combinatorial features of the correlation functions whereas the coefficients $S_l^{\nu_1\nu_2}(\mathbf{x}_1, \mathbf{x}_2)$ given by Eq. (50) describe the geometric properties of local configurations $\bigcup_{j=1}^{\nu_1+\nu_2-l} K_j$ and do not depend on the density, i.e., the total number N of grains.

Remark. The structure function $S^{\lambda_1\lambda_2}(N; \mathbf{x}_1, \mathbf{x}_2) \neq 0$ is *not* zero for $|\mathbf{x}_1 - \mathbf{x}_2| > 2R$ because the difference between $(1 - (V/|\Omega|))^{2N}$ and $(1 - (2V/|\Omega|))^N$ vanishes only in the thermodynamic limit $N \to \infty$, $|\Omega| = N/\rho$. For convenience, the smallest distance $2R$ of two grains,

$$R := \tfrac{1}{2} \operatorname{Max}_{\{r, \mathbf{x}\}} \{ |\mathbf{x}| \text{ with } rK_{\mathbf{0}} \cap rK_{\mathbf{x}} \neq \varnothing \} \tag{51}$$

is introduced where an overlap is not possible for any orientation r. In case of spheres R equals the radius of the spheres. It is the largest distance where one can find an orientation of the grains so that they overlap.

If no grain is fixed to both points $\mathbf{x}_i$, i.e., for $l=0$ the geometric coefficients factorize,

$$S_0^{\lambda_1\lambda_2}(\mathbf{x}_1, \mathbf{x}_2) = I_0^{\lambda_1}(\mathbf{x}_1, \mathbf{x}_2)\, I_0^{\lambda_2}(\mathbf{x}_1, \mathbf{x}_2) \tag{52}$$

with $I_0^0(\mathbf{x}_1, \mathbf{x}_2) = 1$, $I_0^1 = \int_{\mathscr{R}} dr\, M_1(r\hat{K}_{\mathbf{x}_1}, r\,\partial\hat{K}_{\mathbf{x}_1}/r\hat{K}_{\mathbf{x}_2})$, and

$$I_0^{\lambda}(\mathbf{x}_1, \mathbf{x}_2) = \left(\prod_{j=1}^{\lambda} \int_{\mathscr{R}} dr_j\right) \int_{r_j\,\partial\hat{K}_{\mathbf{x}_1}/r_j\hat{K}_{\mathbf{x}_2}} d\mathbf{y}_j\, \Delta_{11}(\mathbf{n}_{\mathbf{y}_1}\mathbf{n}_{\mathbf{y}_2}) \cdots \Delta_{(\lambda-1)1}(\mathbf{n}_{\mathbf{y}_1}\cdots\mathbf{n}_{\mathbf{y}_\lambda}) \tag{53}$$

For $|\mathbf{x}_2 - \mathbf{x}_1| > 2R$ one obtains $I_0^{\lambda} = \langle \chi^{\lambda}(\bigcup_{j=1}^{\lambda} K_j, \mathbf{x}_i)\rangle = \bar{I}_0^{\lambda}$, i.e., the mean value of the $(d-\lambda)$-dimensional volume of the intersection of λ grain boundaries given by Eq. (40). For values $l \neq 0$ the expression (49) cannot be written as product of two factors $I_0^{\lambda_i}$. Nevertheless, one can simplify the expression (50) by introducing the boundaries

$$Y_j^{(1)} := r_j\,\partial\hat{K}_{\mathbf{x}_1}/r_j\hat{K}_{\mathbf{x}_2}, \qquad Y_j^{(2)} := r_j\,\partial\hat{K}_{\mathbf{x}_2}/r_j\hat{K}_{\mathbf{x}_1}, \qquad Y_j^{(12)} := r_j\,\partial\hat{K}_{\mathbf{x}_1} \cap r_j\,\partial\hat{K}_{\mathbf{x}_2} \tag{54}$$

and applying the decomposition rule (18) so that

$$\begin{aligned} S_l^{\lambda_1\lambda_2}(\mathbf{x}_1, \mathbf{x}_2) = {} & \left(\prod_{i=1}^{\lambda_1+\lambda_2-l} \int_{\mathscr{R}} dr_i\right) \prod_{j=\lambda_1-l+1}^{\lambda_1} \int_{Y_j^{(12)}} \frac{d\mathbf{y}_j}{\sin\phi_j} \\ & \times \prod_{j'=1}^{\lambda_1-l} \int_{Y_{j'}^{(2)}} d\mathbf{y}_{j'} \prod_{j''=\lambda_1+1}^{\lambda_1+\lambda_2-l} \int_{Y_{j''}^{(2)}} d\mathbf{y}_{j''} \\ & \times \Delta_{11}(\mathbf{n}_{\mathbf{y}_1}^1\mathbf{n}_{\mathbf{y}_2}^1)\, \Delta_{21}(\mathbf{n}_{\mathbf{y}_1}^1\mathbf{n}_{\mathbf{y}_2}^1\mathbf{n}_{\mathbf{y}_3}^1) \cdots \Delta_{(\lambda_1-1)1}(\mathbf{n}_{\mathbf{y}_1}^1\cdots\mathbf{n}_{\mathbf{y}_{\lambda 1}}^1) \\ & \times \Delta_{11}(\mathbf{n}_{\mathbf{y}_{\lambda_1}-l+1}^2\mathbf{n}_{\mathbf{y}_{\lambda_1}-l+2}^2) \cdots \Delta_{(\lambda_2-1)1}(\mathbf{n}_{\mathbf{y}_{\lambda_1}-l+1}^2\cdots\mathbf{n}_{\mathbf{y}_{\lambda_2}}^2) \end{aligned} \tag{55}$$

where ϕ_j is the angle between the normals $\mathbf{n}_j^1$ and $\mathbf{n}_j^2$ of $\hat{K}_{\mathbf{x}_1}$ and $\hat{K}_{\mathbf{x}_2}$ at $\mathbf{y}_j$. The Jacobians $\Delta_{11}^{(2)}(\mathbf{n}_{\mathbf{y}_1}\mathbf{n}_{\mathbf{y}_2})$ and $\Delta_{21}^{(3)}(\mathbf{n}_{\mathbf{y}_1}^1\mathbf{n}_{\mathbf{y}_2}^1\mathbf{n}_{\mathbf{y}_3}^1)$ are given by Eqs. (21) and (22), respectively. Thus, the geometric factors $S_l^{\lambda_1\lambda_2}(\mathbf{x}_1, \mathbf{x}_2)$ in the structure functions, Eq. (49), are averages of the volume elements $\Delta_{ij}^{(d)}(\mathbf{r}_x)$ at intersection points of grains K_i which are explicitly given by Eqs. (20)–(22). The advantage of the expression (55) instead of Eq. (50) is that it involves only independent integrals over grain boundaries Y_j without referring to common intersection points $\mathbf{x}_1$ and $\mathbf{x}_2$ as in Eq. (50).

It should be noted that the functions $S_{l>0}^{\lambda_1\lambda_2}(\mathbf{x}_1, \mathbf{x}_2) = 0$ vanishes for $|\mathbf{x}_2 - \mathbf{x}_1| > 2R$ in contrast to $S_0^{\lambda_1\lambda_2}(\mathbf{x}_1, \mathbf{x}_2)$. In particular, one finds the following expressions where $\mathbf{n}_\mathbf{y}$ denotes the normal of K at $\mathbf{y} \in \partial K$. The vector $\mathbf{n}_\mathbf{y}^i$ is the normal of $K_{\mathbf{x}_i}$ at the intersection $\mathbf{y} \in \partial K_{\mathbf{x}_1} \cap K_{\mathbf{x}_2}$ and $\phi(\mathbf{n}_1, \mathbf{n}_2)$ denotes the angle between the two normals $\mathbf{n}_i$. The definition of the integration domains Y_i are given by Eq. (54). Since our interest is focused primarily on two and three-dimensional spatial structures we give here the explicit expressions for $\lambda_i \leqslant 3$:

$$S_1^{11} = \int_{\mathscr{R}} dr \int_{Y^{(12)}} d\mathbf{y} \frac{1}{\sin \phi(\mathbf{n}_\mathbf{y}^1 \mathbf{n}_\mathbf{y}^2)}$$

$$S_1^{21} = \prod_{i=1}^{2} \int_{\mathscr{R}} dr_i \int_{Y_1^{(12)}} d\mathbf{y}_1 \int_{Y_2^{(1)}} d\mathbf{y}_2 \frac{\sin \phi(\mathbf{n}_{\mathbf{y}_1}^1 \mathbf{n}_{\mathbf{y}_2})}{\sin \phi(\mathbf{n}_{\mathbf{y}_1}^1 \mathbf{n}_{\mathbf{y}_1}^2)}$$

$$S_1^{22} = \prod_{i=1}^{3} \int_{\mathscr{R}} dr_i \int_{Y_1^{(12)}} d\mathbf{y}_1 \int_{Y_2^{(1)}} d\mathbf{y}_2 \int_{Y_3^{(2)}} d\mathbf{y}_3 \frac{\sin \phi(\mathbf{n}_{\mathbf{y}_1}^1 \mathbf{n}_{\mathbf{y}_2}) \sin \phi(\mathbf{n}_{\mathbf{y}_1}^2 \mathbf{n}_{\mathbf{y}_3})}{\sin \phi(\mathbf{n}_{\mathbf{y}_1}^1 \mathbf{n}_{\mathbf{y}_1}^2)}$$

$$S_2^{22} = \prod_{i=1}^{2} \int_{\mathscr{R}} dr_i \int_{Y_i^{(12)}} d\mathbf{y}_i \frac{\sin \phi(\mathbf{n}_{\mathbf{y}_1}^1 \mathbf{n}_{\mathbf{y}_2}^1) \sin \phi(\mathbf{n}_{\mathbf{y}_1}^2 \mathbf{n}_{\mathbf{y}_2}^2)}{\sin \phi(\mathbf{n}_{\mathbf{y}_1}^1 \mathbf{n}_{\mathbf{y}_1}^2) \sin \phi(\mathbf{n}_{\mathbf{y}_2}^1 \mathbf{n}_{\mathbf{y}_2}^2)}$$

$$S_1^{31} = \prod_{i=1}^{3} \int_{\mathscr{R}} dr_i \int_{Y_1^{(12)}} d\mathbf{y}_1 \int_{Y_{i>1}^{(1)}} d\mathbf{y}_i \frac{|(\mathbf{n}_{\mathbf{y}_1}^1 \times \mathbf{n}_{\mathbf{y}_2}) \mathbf{n}_{\mathbf{y}_3}|}{\sin \phi(\mathbf{n}_{\mathbf{y}_1}^1 \mathbf{n}_{\mathbf{y}_1}^2)}$$

$$S_1^{32} = \prod_{i=1}^{4} \int_{\mathscr{R}} dr_i \int_{Y_1^{(12)}} d\mathbf{y}_1 \int_{Y_{i=2,3}^{(1)}} d\mathbf{y}_i \times \int_{Y_4^{(2)}} d\mathbf{y}_4 \frac{|(\mathbf{n}_{\mathbf{y}_1}^1 \times \mathbf{n}_{\mathbf{y}_2}) \mathbf{n}_{\mathbf{y}_3}| \sin \phi(\mathbf{n}_{\mathbf{y}_1}^2 \mathbf{n}_{\mathbf{y}_4})}{\sin \phi(\mathbf{n}_{\mathbf{y}_1}^1 \mathbf{n}_{\mathbf{y}_1}^2)} \tag{56}$$

$$S_2^{32} = \prod_{i=1}^{3} \int_{\mathscr{R}} dr_i \int_{Y_{i=2,3}^{(12)}} d\mathbf{y}_i \int_{Y_3^{(1)}} d\mathbf{y}_3 \frac{|(\mathbf{n}_{\mathbf{y}_1}^1 \times \mathbf{n}_{\mathbf{y}_2}^1) \mathbf{n}_{\mathbf{y}_3}| \sin \phi(\mathbf{n}_{\mathbf{y}_1}^2 \mathbf{n}_{\mathbf{y}_2}^2)}{\sin \phi(\mathbf{n}_{\mathbf{y}_1}^1 \mathbf{n}_{\mathbf{y}_1}^2) \sin \phi(\mathbf{n}_{\mathbf{y}_2}^1 \mathbf{n}_{\mathbf{y}_2}^2)}$$

$$S_1^{33} = \prod_{i=1}^{5} \int_{\mathscr{R}} dr_i \int_{Y_1^{(12)}} d\mathbf{y}_1 \int_{Y_{i=1,2}^{(1)}} d\mathbf{y}_i \int_{Y_{j=4,5}^{(2)}} d\mathbf{y}_j \frac{|(\mathbf{n}_{\mathbf{y}_1}^1 \times \mathbf{n}_{\mathbf{y}_2}) \mathbf{n}_{\mathbf{y}_3}| \, |(\mathbf{n}_{\mathbf{y}_1}^2 \times \mathbf{n}_{\mathbf{y}_4}) \mathbf{n}_{\mathbf{y}_5}|}{\sin \phi(\mathbf{n}_{\mathbf{y}_1}^1 \mathbf{n}_{\mathbf{y}_1}^2)}$$

$$S_2^{33} = \prod_{i=1}^{4} \int_{\mathscr{R}} dr_i \int_{Y_{i=1,2}^{(12)}} d\mathbf{y}_i \int_{Y_3^{(1)}} d\mathbf{y}_3 \int_{Y_4^{(2)}} d\mathbf{y}_4 \frac{|(\mathbf{n}_{\mathbf{y}_1}^1 \times \mathbf{n}_{\mathbf{y}_2}^1) \mathbf{n}_{\mathbf{y}_3}| \, |(\mathbf{n}_{\mathbf{y}_1}^2 \times \mathbf{n}_{\mathbf{y}_2}^2) \mathbf{n}_{\mathbf{y}_4}|}{\sin \phi(\mathbf{n}_{\mathbf{y}_1}^1 \mathbf{n}_{\mathbf{y}_1}^2) \sin \phi(\mathbf{n}_{\mathbf{y}_2}^1 \mathbf{n}_{\mathbf{y}_2}^2)}$$

$$S_3^{33} = \prod_{i=1}^{3} \int_{\mathscr{R}} dr_i \int_{Y_i^{(12)}} d\mathbf{y}_i \frac{|(\mathbf{n}_{\mathbf{y}_1}^1 \times \mathbf{n}_{\mathbf{y}_2}^1) \mathbf{n}_{\mathbf{y}_3}^1| \, |(\mathbf{n}_{\mathbf{y}_1}^2 \times \mathbf{n}_{\mathbf{y}_2}^2) \mathbf{n}_{\mathbf{y}_3}^2|}{\sin \phi(\mathbf{n}_{\mathbf{y}_1}^1 \mathbf{n}_{\mathbf{y}_1}^2) \sin \phi(\mathbf{n}_{\mathbf{y}_2}^1 \mathbf{n}_{\mathbf{y}_2}^2) \sin \phi(\mathbf{n}_{\mathbf{y}_3}^1 \mathbf{n}_{\mathbf{y}_3}^2)}$$

The general expression Eq. (55) for the coefficients $S_l^{\lambda_1\lambda_2}(\mathbf{x}_1, \mathbf{x}_2)$ is the main result of this section since they determine the correlation functions, Eq. (49), besides combinatorial factors. The main difficulty in evaluating the coefficients resides in an useful parameterization of the boundaries $Y_j^{(1)}(\mathbf{x}_1, \mathbf{x}_2)$, $Y_j^{(2)}(\mathbf{x}_1, \mathbf{x}_2)$ of a single grain K and their intersection $Y_j^{(12)}(\mathbf{x}_1, \mathbf{x}_2)$ which depend on the relative position of the grains. For discs and spheres the parameterization is straightforward so that the integrals in Eq. (56) can be performed analytically. For more complex shapes the integrals over a single grain boundary ∂K can be calculated numerically without much effort since the dimensions of the manifolds Y_j are low.

Example 3.1. One obtains for discs B_R of radius R in two dimensions the geometric structure amplitudes

$$
\begin{aligned}
S_1^{\lambda 0}(\mathbf{x}_1, \mathbf{x}_2) &= I_0^{\lambda} \\
S_1^{11}(\mathbf{x}_1, \mathbf{x}_2) &= \frac{2}{\sin \Phi} = \frac{2R}{|\mathbf{x}_2 - \mathbf{x}_1| \sqrt{1 - (\mathbf{x}_2 - \mathbf{x}_1)^2/(2R)^2}} \\
S_1^{21}(\mathbf{x}_1, \mathbf{x}_2) &= S_1^{11} R \int_0^{\pi + \Phi} d\phi \, |\sin(\phi)| = \frac{2R}{\sin \Phi} (3 - \cos \Phi) \\
S_1^{22}(\mathbf{x}_1, \mathbf{x}_2) &= \frac{2R^2}{\sin \Phi} (3 - \cos \Phi)^2 \\
S_2^{22}(\mathbf{x}_1, \mathbf{x}_2) &= 2 \frac{\sin^2(\pi - \Phi)}{\sin^2 \Phi} + 8\pi R^2 \delta(\mathbf{x}_1 - \mathbf{x}_2) = 2 + 8\pi R^2 \delta(\mathbf{x}_1 - \mathbf{x}_2)
\end{aligned}
\tag{57}
$$

with $S_{l>0}^{\lambda_1\lambda_2} = 0$ for $|\mathbf{x}_2 - \mathbf{x}_1| > 2R$. The opening angle Φ $(0 \leqslant \Phi \leqslant \pi)$ at the intersection point $Y^{(12)} = \partial K_{\mathbf{x}_1} \cap \partial K_{\mathbf{x}_2}$ of two discs is defined by $\sin(\Phi/2) = s$ and $s = (|\mathbf{x}_1 - \mathbf{x}_2|)/(2R)$. The last expression $S_2^{22}(\mathbf{x}_1, \mathbf{x}_2)$ contains a term localized at $\mathbf{x}_1 = \mathbf{x}_2$, i.e., a δ-distribution due to the intersection $Y^{(12)} = \partial B_R$, in accordance with the general relations

$$
\begin{aligned}
\int d\mathbf{x}_2 \, S_2^{22}(\mathbf{x}_1, \mathbf{x}_2) &= \int dg (M_0^2(K_1 \cap gK_2))^2 = 4I_\chi \\
S_2^{22}(\mathbf{x}_1 = \mathbf{x}_2) &= \int \int dg \, dg' (\chi^2(gK \cap g'K, \mathbf{x}_1))^2 = 2I_\chi \delta(\mathbf{x}_1 - \mathbf{x}_2)
\end{aligned}
\tag{58}
$$

in two dimensions with $I_\chi = \int dg \, \chi(K \cap gK) = 2(W_0(K) + W_1(K)^2/\pi) = 4\pi R^2$.

4. SECOND ORDER MOMENTS OF MINKOWSKI FUNCTIONALS

The moments of the volume $V(\mathscr{A}) = M_0(\mathscr{A})$ can be written as integrals of the structure functions defined in Eq. (44),

$$m^{(gk)}_{\underbrace{0\cdots0}_{n\text{-times}}}(\rho) = \frac{\langle (V(\mathscr{A}) - \langle V(\mathscr{A})\rangle)^n\rangle}{|\Omega|} = \left(\prod_{i=2}^{n}\int_{\mathbb{R}^d} d\mathbf{x}_i\right) \overbrace{S^{0\cdots0}}^{n\text{-times}}(\rho; 0, \mathbf{x}_2, ..., \mathbf{x}_n) \tag{59}$$

Here, the index (gk) indicates that these values are grand-canonical moments averaged, with fluctuating particle numbers but fixed mean density $\rho = \langle N\rangle/|\Omega|$. For fixed particle number N the canonical moments $m^{(k)}(\rho)$ differ which is shown in the following section. Whenever not indicated, the grand-canonical average is meant.

4.1. Curvature-Weighted Structure Functions

In order to calculate moments of Minkowski functional the correlation functions $S^{\lambda_1\cdots\lambda_n}(N; \mathbf{x}_1, ..., \mathbf{x}_n)$, Eq. (47), are weighted, i.e., multiplied with the local Minkowski functionals,

$$M^{\lambda_1\lambda_2\cdots\lambda_n}_{\nu_1\nu_2\cdots\nu_n}(N; \mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_n) = \left\langle \prod_{i=1}^{n} [M_{\nu_i}(\mathscr{A}, \mathbf{x}_i)\,\chi^{\lambda_i}(\mathscr{A}, \mathbf{x}_i) - M^{\lambda_i}_{\nu_i}(N; \mathbf{x}_i)] \right\rangle \tag{60}$$

and $M^{\lambda}_{\nu}(N; \mathbf{x}) = \langle M_\nu(\mathscr{A}, \mathbf{x})\,\chi^\lambda(\mathscr{A}, \mathbf{x}_i)\rangle = m^\lambda_\nu(N)$ for homogeneous distributions of grains. The weighted correlation functions $M^{\{\lambda_i\}}_{\{\nu_i\}}(N; \{\mathbf{x}_i\})$ contains different types of morphological informations. Whereas the position is given by $\mathbf{x}_i$, the indices λ_i describe the type of surface and ν_i the local geometry given by the curvature $S_{\lambda-1}$. There are two constraints on the indices of the correlation functions given in Eq. (60): First, $\lambda_i \leqslant \nu_i$ because of $W_\nu(\mathscr{A}, \mathbf{x}) = 0$ for $\nu < \lambda$ and $\mathbf{x} \in \partial^\lambda\mathscr{A}$. Second, $\nu_i = 0$ if $\lambda_i = 0$ because of $W_\nu(\mathscr{A}, \mathbf{x}) = 0$ "almost sure" for $\nu \geqslant 1$ and $\mathbf{x} \in \mathscr{A}$ arbitrarily chosen. Although $\chi^0(\mathscr{A}, \mathbf{x}) = 1$ for $\mathbf{x} \in \partial^\nu\mathscr{A}$ one obtains for the average $S^0_\nu =$ for $\nu \geqslant 1$.

$W^\lambda_\nu(\mathbf{x})$ measures the probability that $\mathbf{x}$ is located on the partition $\partial^\lambda\mathscr{A}$ weighted by the local curvature (geometry) W_ν. It should be noted that as soon as an upper index occurs $W^\lambda_\nu(\mathbf{x})$ is not a functional but a distribution (in contrast to $W_\nu(\mathbf{x})$), defined only in combination with an integral over the position $\mathbf{x}$.

The second order moments of the Minkowski functionals, i.e., of $\delta M_\nu(\mathscr{A}) = M_\nu(\mathscr{A}) - \langle M_\nu(\mathscr{A}) \rangle$ can now be written as integrated structure functions

$$m_{\nu\mu}(N) = \frac{\langle \delta M_\nu(\mathscr{A})\, \delta M_\mu(\mathscr{A}) \rangle}{|\Omega|} = \sum_{\lambda_1=1}^{\nu} \sum_{\lambda_1=1}^{\mu} \int_{\mathbb{R}^d} d\mathbf{x}\, M_{\nu\mu}^{\lambda_1\lambda_2}(N; 0, \mathbf{x}) \tag{61}$$

where the sum runs over contributions stemming from $(d-\lambda_i)$-dimensional intersections $\mathscr{A}^{(\lambda_i)}$. Analogous to Eq. (49), one finds for the curvature-weighted structure functions

$$\begin{aligned}
M_{00}^{00}(N; \mathbf{x}_1, \mathbf{x}_2) &= \left(1 - \frac{V(\mathbf{x}_1, \mathbf{x}_2)}{|\Omega|}\right)^N - \left(1 - \frac{V}{|\Omega|}\right)^{2N} \\
M_{\nu 0}^{\lambda 0}(N; \mathbf{x}_1, \mathbf{x}_2) &= (-1)^{\lambda+1} \binom{N}{\lambda} \left(\left(1 - \frac{V}{|\Omega|}\right)^{2N-\lambda} \frac{\bar{I}_\nu^\lambda}{|\Omega|^\lambda} \right. \\
&\quad \left. - \left(1 - \frac{V(\mathbf{x}_1, \mathbf{x}_2)}{|\Omega|}\right)^{N-\lambda} \frac{I_\nu^\lambda(\mathbf{x}_1, \mathbf{x}_2)}{|\Omega|^\lambda} \right) \\
M_{\nu_1\nu_2}^{\lambda_1\lambda_2}(N; \mathbf{x}_1, \mathbf{x}_2) &= (-1)^{\lambda_1+\lambda_2} \sum_{l=0}^{\lambda_2} \binom{N}{\lambda_1} \binom{\lambda_1}{l} \binom{N-\lambda_1}{\lambda_2 - l} \\
&\quad \times \left| \frac{M_{\nu_1\nu_2;\, l}^{\lambda_1\lambda_2}}{|\Omega|^{\lambda_1+\lambda_2-l}} \left(1 - \frac{V(\mathbf{x}_1, \mathbf{x}_2)}{|\Omega|}\right)^{N-\lambda_1-\lambda_2+l} \right| \\
&\quad - (-1)^{\lambda_1+\lambda_2} \binom{N}{\lambda_1} \binom{N}{\lambda_2} \frac{\bar{I}_{\nu_1}^{\lambda_1} \bar{I}_{\nu_2}^{\lambda_2}}{|\Omega|^{\lambda_1+\lambda_2}} \left(1 - \frac{V}{|\Omega|}\right)^{2N-\lambda_1-\lambda_2}
\end{aligned} \tag{62}$$

with $(\lambda_i > 0)$

$$\begin{aligned}
M_{\nu_1\nu_2;\, l}^{\lambda_1\lambda_2}(\mathbf{x}_1, \mathbf{x}_2) &= S_l^{\lambda_1\lambda_2} \times \left\{ M_{\nu_1}\left(\bigcap_{j=1}^{\lambda_1} r_j K_{\mathbf{y}_j}, \mathbf{x}_1 \right) M_{\nu_2}\left(\bigcap_{j=\lambda_1-l+1}^{\lambda_1+\lambda_2-l} r_j K_{\mathbf{y}_j}, \mathbf{x}_2 \right) \right\} \\
&= (-1)^{\lambda_1+\lambda_2} S_l^{\lambda_1\lambda_2} \\
&\quad \times \left\{ M_{\nu_1}\left(\bigcup_{j=1}^{\lambda_1} r_j K_{\mathbf{y}_j}, \mathbf{x}_1 \right) M_{\nu_2}\left(\bigcup_{j=\lambda_1-l+1}^{\lambda_1+\lambda_2-l} r_j K_{\mathbf{y}_j}, \mathbf{x}_2 \right) \right\}
\end{aligned} \tag{63}$$

where $S_l^{\lambda_1\lambda_2}$ denotes the expression given in Eq. (55), so that Eq. (63) is actually an integration of $M_{\nu_1}(\{r_j, \mathbf{y}_j\})\, M_{\nu_2}(\{r_j, \mathbf{y}_j\})$ over the rotations r_j and locations $\mathbf{y}_j$ of the $\lambda_1 + \lambda_2 - l$ grains K_i using the volume elements $\Delta_{ij}^{(d)}$

given in Eq. (20), i.e., the Jacobians as weights for the kinematic densities. The local Minkowski functionals $M_\nu(K, \mathbf{x}_i)$ are defined by Eq. (25) and depend only on the coordinates $\mathbf{y}_i$ but not on $\mathbf{x}_i$ due to the motion invariance of Minkowski functionals. Eq. (62) resembles the same structure than Eq. (37) for the mean values $m_\nu(N)$ but with distance-dependent geometric amplitudes $M^{\lambda_1\lambda_2}_{\nu_1\nu_2;\,l}$ instead of constant coefficients $\bar{I}^\lambda_\nu$.

Remark 1. Note, that $M^{\lambda_1\lambda_2}_{\nu_1\nu_2;\,l>0}(N; \mathbf{x}_1, \mathbf{x}_2) = 0$ vanishes for distances $|\mathbf{x}_2 - \mathbf{x}_1| > 2R$ larger than the contact distance $2R$ given by Eq. (51).

Remark 2. The integration $S^{\lambda_1\lambda_2}_l$ in Eq. (63) corresponds to the average $\langle \cdot \rangle$ over positions and orientations of $\lambda_1 + \lambda_2 - l$ grains.

This interpretation of Eq. (63) is more convenient for evaluating the integrals for sticks in Subsection 4.3, for instance.

$$M^{\lambda_1\lambda_2}_{\nu_1\nu_2;\,l}(\mathbf{x}_1, \mathbf{x}_2) = \left\langle M_{\nu_1}\left(\bigcap_{i=1}^{\lambda_1} \partial K_i, \mathbf{x}_1\right) M_{\nu_1}\left(\bigcap_{i=\lambda_1-l+1}^{\lambda_1+\lambda_2-l} \partial K_i, \mathbf{x}_2\right)\right\rangle \tag{64}$$

The curvature-weighted functionals $M^{\lambda_1\lambda_2}_{\nu_1\nu_2;\,0}$ can be decomposed into the product of two structure functions ($\lambda_i > \nu_i$)

$$M^{\lambda_1\lambda_2}_{\nu_1\nu_2;\,0}(\mathbf{x}_1, \mathbf{x}_2) = I^{\lambda_1}_{\nu_1}(\mathbf{x}_1, \mathbf{x}_2)\, I^{\lambda_2}_{\nu_2}(\mathbf{x}_2, \mathbf{x}_1) \tag{65}$$

with ($\lambda > 0$)

$$\begin{aligned} I^\lambda_\nu(\mathbf{x}_1, \mathbf{x}_2) = \prod_{j=1}^{\lambda} \int_{\mathscr{R}} dr_j \int_{r_j\,\partial\hat{K}_{\mathbf{x}_1}/r_j\hat{K}_{\mathbf{x}_2}} d\mathbf{y}_j\, \Delta_{11}(\mathbf{n}_{\mathbf{y}_1}\mathbf{n}_{\mathbf{y}_2}) \cdots \\ \times \Delta_{(\lambda-1)\,1}(\mathbf{n}_{\mathbf{y}_1} \cdots \mathbf{n}_{\mathbf{y}_\lambda})\, M_\nu\left(\bigcap_{j=1}^{\lambda} r_j K_{\mathbf{y}_j}, \mathbf{x}_1\right) \end{aligned} \tag{66}$$

and $I^0_{\nu>0} = 0$, $I^0_0 = 1$. In general, one finds

$$I^1_\nu(\mathbf{x}_1, \mathbf{x}_2) = \int_{\mathscr{R}} dr \int_{r\,\partial\hat{K}_{x_1}/r\hat{K}_{x_2}} dy\, M_\nu(rK_y, x_1) = \int_{\mathscr{R}} dr\, M_\nu(rK_{x_1}, +2K_{x_1}/rK_{x_2}) \tag{67}$$

Remark 1. In the limit $|\mathbf{x}_2 - \mathbf{x}_1| > 2R$ one obtains $I^\lambda_\nu(\mathbf{x}_1, \mathbf{x}_2) = \langle M^\lambda_\nu(\bigcup_{j=1}^{\lambda} K_j, \mathbf{x}_i)\rangle = \bar{I}^\lambda_\nu$, i.e., the averaged local Minkowski functionals given by Eq. (34).

Remark 2. Although it is possible to derive explicit expressions for second order moments of Minkowski functionals (see Eqs. (61) and (62)),

the actual evaluation is quite difficult for non-spherical shapes. In order to study the dependence on shape and orientation of the grains similar general results as for the mean values (8) or at least reliable approximations would be useful for many applications in statistical physics.

4.2. Canonical Versus Grand-Canonical Ensembles

Averages $\langle \cdot \rangle_N$ are calculated in the Boolean model first at fixed particle numbers N. Using a Poisson distribution

$$P_N(\rho) = \frac{(\rho\Omega)^N}{N!} e^{-\rho\Omega} \tag{68}$$

of N grains in the volume Ω with density ρ one may define a grand-canonical average at fixed density (intensity) but fluctuating particle number N by

$$\langle \cdot \rangle_\rho = \sum_{N=0}^{\infty} P_N(\rho) \langle \cdot \rangle_N \tag{69}$$

In the Boolean model mean values $m_\nu(\rho)$ of morphological measures obtained at fixed particle number (canonical ensemble) or at fixed intensity (grand-canonical ensemble) become identical in the thermodynamic limit $N, \Omega \to \infty$, $\rho = N/|\Omega|$. This is not the case for variances or higher order moments. Note, that for the definition of grand-canonical averages at fixed density ρ no thermodynamic limit is needed.

It is well known that the difference $\delta C = C_p - C_V > 0$ between the specific heat at constant pressure C_p and at constant volume C_v, i.e., the difference in the second order moment of the energy is given by the thermodynamic relation $\delta C = T(\partial p/\partial T)_V (\partial V/\partial T)_p$. In the following a similar expression is derived for the difference $\delta m_{\nu_1\nu_2}(\rho) = m^{(gk)}_{\nu_1\nu_2} - m^{(k)}_{\nu_1\nu_2}$ of the moments at constant grain number (canonical ensemble, Bernoulli distribution) and at constant density but fluctuating number (grand-canonical ensemble, Poisson distribution) in the Boolean model.

Using the canonical correlation function $S^{00}(\mathbf{x})$, $\mathbf{x} = \mathbf{x}_2 - \mathbf{x}_1$ given by Eq. (49) one obtains for the canonical moments of the volume ($\rho = N/|\Omega|$, $V(K) = M_0(K)$) in the thermodynamic limit $N, \Omega \to \infty$

$$\begin{aligned} m^{(k)}_{00}(N) &= \int_\Omega d\mathbf{x}\, S^{00}(N, \mathbf{x}) = \int_\Omega d\mathbf{x} \left(S^{00}(\rho; \mathbf{x}) - \frac{1}{|\Omega|} \delta S^{00}(\rho; \mathbf{x}) + \mathcal{O}(|\Omega|^{-2}) \right) \\ &\sim \frac{N(N-1)}{2\,|\Omega|^2} \int_\Omega d\mathbf{x}\, V(K \cap K_{\mathbf{x}})^2 + \mathcal{O}\left(\rho^3, \frac{1}{|\Omega|}\right) \end{aligned} \tag{70}$$

with the grand-canonical structure function and its finite-volume distortion ($\mathbf{x} = \mathbf{x}_2 - \mathbf{x}_1$) at constant density ρ (i.e., $N(\varepsilon) = \rho\,|\Omega|$ is an function of $\varepsilon = |\Omega|^{-1}$ in an expansion of Eq. (49)):

$$\begin{aligned} S^{00}(\rho; \mathbf{x}) &= e^{-\rho V(\mathbf{x}_1, \mathbf{x}_2)} - e^{-2\rho V} \\ \delta S^{00}(\rho; \mathbf{x}) &= \tfrac{1}{2}\rho V(\mathbf{x}_1, \mathbf{x}_2)^2\, e^{-\rho V(\mathbf{x}_1, \mathbf{x}_2)} - \rho V^2 e^{-2\rho V} \end{aligned} \tag{71}$$

Using the Poisson distribution $P_N(\rho)$ of N grains in the volume Ω with density ρ, the relation (69) for the averages, and Eq. (49) one obtains the grand-canonical moments

$$\begin{aligned} m_{00}^{(gk)}(\rho) &= \sum_{N=0}^{\infty} P_N \langle V^2 \rangle_N - \left(\sum_{N=0}^{\infty} P_N \langle V \rangle_N \right)^2 \\ &= \int_{\Omega} d\mathbf{x}\; S^{00}(\rho; \mathbf{x}) \\ &\sim \rho V^2 - 2\rho^2 V^3 + \frac{\rho^2}{2} \int_{\Omega} d\mathbf{x}\; V(K \cap K_{\mathbf{x}})^2 + \mathcal{O}(\rho^3) \end{aligned} \tag{72}$$

It should be noted that $m_{00}^{(gk)}(\rho) \neq m_{00}^{(k)}(\rho)$ defined by $m_{00}^{(k)}(\rho) = \lim m_{00}^{(k)}(N)$ for $N, \Omega \to \infty$, $\rho = N/|\Omega|$ fixed. The difference $\delta m_{00}(\rho) = m_{00}^{(gk)}(\rho) - m_{00}^{(k)}(\rho)$ of the canonical and grand-canonical moments are then given by

$$\begin{aligned} \delta m_{00}(\rho) &= \lim_{N, \Omega \to \infty} \int \frac{d\mathbf{x}}{|\Omega|}\, \delta S^{00}(\mathbf{x}) = \lim_{|\mathbf{x}| \to \infty} \delta S^{00}(\mathbf{x}) \\ &= \rho V^2 e^{-2\rho V} \approx \rho V^2 - 2\rho^2 V^3 + \mathcal{O}((\rho V)^3) \end{aligned} \tag{73}$$

Although the difference $\delta S^{00}/\Omega$ in the canonical and grand-canonical correlation function $S^{00}(\mathbf{x})$ vanishes in the thermodynamic limit, integrals of them differ. The grand-canonical function is equal to zero for distance $|\mathbf{x}| > 2R$ larger than the diameter whereas the canonical function is negative. Although for fixed distance $|\mathbf{x}| > 2R$ the value $g^{(k)}(\mathbf{x}) \sim 1/|\Omega|$ vanishes an integral over all distances larger than the diameter, i.e., over a volume $\sim |\Omega|$ remains finite. Generally, one finds for the difference of the second order moments

$$\delta m_{\nu\mu}(\rho) = m_{\nu\mu}^{(gk)}(\rho) - m_{\nu\mu}^{(k)}(\rho) = \lim_{N, \Omega \to \infty} \int \frac{d\mathbf{x}}{|\Omega|}\, \delta M_{\nu\mu}(\mathbf{x}) \tag{74}$$

where the differences in the structure function in the thermodynamical limit is given by

$$
\begin{aligned}
S^{\lambda_1\lambda_2}(N) &\to S^{\lambda_1\lambda_2}(\rho) - \frac{1}{|\Omega|}\,\delta S^{\lambda_1\lambda_2}(\rho) + \mathcal{O}(|\Omega|^{-2}) \\
M^{\lambda_1\lambda_2}_{\nu_1\nu_2}(N) &\to M^{\lambda_1\lambda_2}_{\nu_1\nu_2}(\rho) - \frac{1}{|\Omega|}\,\delta M^{\lambda_1\lambda_2}_{\nu_1\nu_2} + \mathcal{O}(|\Omega|^{-2})
\end{aligned}
\tag{75}
$$

with (see Eqs. (39), (42), (49), and (62))

$$
\begin{aligned}
M^{\lambda}_{\nu}(\rho) &= (-1)^{\lambda+1}\frac{\rho^{\lambda}}{\lambda!}\,e^{-\rho V}\bar{I}^{\lambda}_{\nu} \\
M^{00}_{00}(\rho) &= e^{-\rho V(\mathbf{x}_1,\mathbf{x}_2)} - e^{-2\rho V} \\
M^{\lambda 0}_{\nu 0}(\rho) &= (-1)^{\lambda+1}\frac{\rho^{\lambda}}{\lambda!}\,(\bar{I}^{\lambda}_{\nu}e^{-2\rho V} - I^{\lambda}_{\nu}e^{-\rho V(\mathbf{x}_1,\mathbf{x}_2)}) \\
M^{\lambda_1\lambda_2}_{\nu_1\nu_2}(\rho) &= (-1)^{\lambda_1+\lambda_2}\,e^{-\rho V(\mathbf{x}_1,\mathbf{x}_2)}\sum_{l=0}^{\lambda_2}\frac{\rho^{\lambda_1+\lambda_2-l}}{l!\,(\lambda_1-l)!\,(\lambda_2-l)!}\,M^{\lambda_1\lambda_2}_{\nu_1\nu_2;\,l} - M^{\lambda_1}_{\nu_1}M^{\lambda_2}_{\nu_2} \\
\delta M^{\lambda}_{\nu}(\rho) &= (-1)^{\delta_{0\lambda}}\frac{\rho^2V^2 - 2\rho\lambda V + \lambda(\lambda-1)}{2\rho}\,M^{\lambda}_{\nu}(\rho) \\
\delta M^{\lambda_1\lambda_2}_{\nu_1\nu_2}(\rho) &= (-1)^{\lambda_1+\lambda_2}\,e^{-\rho V(\mathbf{x}_1,\mathbf{x}_2)}\sum_{l=0}^{\lambda_2}\frac{\rho^{\lambda_1+\lambda_2-l}}{l!\,(\lambda_1-l)!\,(\lambda_2-l)!}\,\delta M^{\lambda_1\lambda_2}_{\nu_1\nu_2;\,l} \\
&\quad - \delta M^{\lambda_1}_{\nu_1}M^{\lambda_2}_{\nu_2} - M^{\lambda_1}_{\nu_1}\,\delta M^{\lambda_2}_{\nu_2} \\
\delta M^{\lambda_1\lambda_2}_{\nu_1\nu_2;\,l}(\rho) &= (-1)^{\delta_{0\lambda_1}+\delta_{0\lambda_2}}\frac{\begin{pmatrix}(\rho V(\mathbf{x}_1,\mathbf{x}_2))^2 - 2\rho(\lambda_1+\lambda_2-l)\;V(\mathbf{x}_1,\mathbf{x}_2) \\ +(\lambda_1+\lambda_2-l)(\lambda_1+\lambda_2-l-1)\end{pmatrix}}{2\rho} \\
&\quad \times M^{\lambda_1\lambda_2}_{\nu_1\nu_2;\,l}(\rho)
\end{aligned}
\tag{76}
$$

and $(\delta)\,S^{\lambda} = (-1)^{\lambda+1}\,M^{\lambda}_{0}$, $(\delta)\,S^{\lambda 0} = (-1)^{\lambda+1}\,M^{\lambda 0}_{00}$, $(\delta)\,S^{\lambda_1\lambda_2} = (-1)^{\lambda_1+\lambda_2}\,M^{\lambda_1\lambda_2}_{00}$. In the limit $|\mathbf{x}_2 - \mathbf{x}_1| \to \infty$ only the term $l=0$ of $\delta M^{\lambda_1\lambda_2}_{\nu_1\nu_2;\,l}$ does not vanish and one obtains

$$
\delta M^{\lambda_1\lambda_2}_{\nu_1\nu_2} = (-1)^{\delta_{0\lambda_1}+\delta_{0\lambda_2}}\frac{\rho^{\lambda_1+\lambda_2}}{\lambda_1!\lambda_2!}\,e^{-2\rho V}\bar{I}^{\lambda_1}_{\nu_1}\bar{I}^{\lambda_2}_{\nu_2}\left(\rho V^2 - (\lambda_1+\lambda_2)\;V + \frac{\lambda_1\lambda_2}{\rho}\right) \tag{77}
$$

so that using Eq. (74) the difference of the moments reads

$$\delta m_{\nu_1\nu_2}(\rho) = \sum_{\lambda_1=1}^{\nu_1} \sum_{\lambda_2=1}^{\nu_2} \delta M_{\nu_1\nu_2}^{\lambda_1\lambda_2} = \rho \frac{\partial m_{\nu_1}(\rho)}{\partial \rho} \frac{\partial m_{\nu_2}(\rho)}{\partial \rho} \tag{78}$$

Thus, the difference of canonical and grand-canonical moments is given solely by derivatives of their mean values, Eq. (8). The relation (78) can immediately be applied to the specific heat difference $C_\mu - C_N$ (Joule–Thomson effect) in the Widom–Rowlinson model and the morphological model[19] discussed in Section 5.

4.3. Examples of Second Order Moments

The explicit expressions (61)–(63) for the moments of Minkowski functionals in the Boolean model are general and applicable for arbitrary shapes. Of particular interest are d-dimensional spheres since it is the most often used and most convenient shape. In order to test the general formula (62) and to study the dependence on shape and orientation we illustrate the results also by random distributions of sticks in two dimensions.

Example 1: Two Discs, $N=2$. Using the additivity relation (3), the kinematic formula (5), and the relation $\chi(K)^2 = \chi(K) = 1$ for a convex grain K one obtains the mean value and the second order moment

$$\begin{aligned} \langle \chi(K_1 \cup K_2) \rangle &= 2 - \frac{4\pi R^2}{|\Omega|} \\ \langle \delta\chi(K_1 \cup K_2)^2 \rangle &= \frac{4\pi R^2}{|\Omega|} - \frac{16\pi^2 R^4}{|\Omega|^2} \end{aligned} \tag{79}$$

of the Euler characteristic for two discs of radius R. Applying Eq. (61) and Eq. (62) one obtains

$$\begin{aligned} |\Omega|^2 M_{\nu_1\nu_2}^{11} &= -4M_{\nu_1}M_{\nu_2}\left(1 - \frac{V}{|\Omega|}\right) + 2M_{\nu_1\nu_2;\,0}^{11} + 2M_{\nu_1\nu_2;\,1}^{11}(|\Omega| - V(\mathbf{x}_1, \mathbf{x}_2)) \\ |\Omega|^2 M_{2\nu_2}^{21} &= 2\frac{\bar{I}_2^2 M_{\nu_2}}{|\Omega|}\left(1 - \frac{V}{|\Omega|}\right) - 2M_{2\nu_2;\,1}^{21} \\ |\Omega|^2 M_{22}^{22} &= -\left(\frac{\bar{I}_2^2}{|\Omega|}\right)^2 + M_{22;\,2}^{22} \end{aligned} \tag{80}$$

so that one recovers the result (79) for two discs of radius R with $\bar{I}_2^2 = 2R^2$, $V = R^2(\pi + \Phi + \sin\Phi)$, $\sin(\Phi/2) = (|\mathbf{x}_1 - \mathbf{x}_2|)/(2R)$, and

$$\begin{aligned} M^{11}_{22;\,0} &= (\pi + \Phi)^2/(4\pi^4) \\ M^{11}_{22;\,1} &= \frac{1}{2\pi^4 R^2 \sin\Phi} \\ M^{21}_{22;\,1} &= \frac{2\pi - \sin\Phi - (\pi - \Phi)\cos\Phi}{2\pi^4 \sin\Phi} \\ M^{22}_{22;\,2} &= \frac{(\pi - \Phi)^2}{2\pi^4} + R^2\left(\frac{1}{\pi} - \frac{4}{\pi^3}\right)\delta(\mathbf{x}_1 - \mathbf{x}_2) \end{aligned} \tag{81}$$

(see Eq. (97)). Note, that the integration $\int d^2\mathbf{x}_2 = 2\pi R^2 \int_0^\pi d\Phi \sin\Phi$ is restricted to values $\mathbf{x}_2 < 2R$ only for the terms $M^{11}_{22;\,1}$, $M^{21}_{22;\,1}$, and $M^{22}_{22;\,2}$, whereas $M^{11}_{22;\,0}$ and the constants M_ν are integrated over Ω.

Example 2: *N* Sticks in One Dimension. For a distribution of Poisson distributed sticks of length r in one spatial dimension the expressions (61)–(55) reduce to

$$\begin{aligned} S^{00} &= e^{-\rho[2r - \Theta(r - |x_1 - x_2|)(r - |x_1 - x_2|)]} - e^{-2r\rho} \\ S^{10} &= -(\rho S^{00} - \rho e^{-2r\rho})/2 \\ S^{11} &= (\rho S^{00} - 3\rho e^{-2r\rho} + e^{-2r\rho}\,\delta(r - |x_1 - x_2|) + 2e^{-r\rho}\delta(|x_1 - x_2|))\,\rho/4 \end{aligned} \tag{82}$$

so that one finds the second order moments

$$\begin{aligned} m_{00}(\rho) &= \frac{2}{\rho}\,(e^{-\rho r} - (1 + \rho r)\,e^{-2\rho r}) \\ m_{10}(\rho) &= -(e^{-\rho r} - (1 + 2\rho r)\,e^{-2\rho r})/2 \\ m_{11}(\rho) &= \rho(e^{-\rho r} - 2\rho r e^{-2\rho r})/4 \end{aligned} \tag{83}$$

plotted in Fig. 2.

Example 3: *N* Sticks in Two Dimensions. For sticks of length L one finds $W_0 = 0$, $W_1 = L$, $W_2 = \pi$, and therefore $M_0 = 0$, $M_1 = L/\pi$, $M_2 = 1/\pi$. Using the additivity relation (3) one obtains the mean values $m_0(N) = 0$, $m_1(N) = NM_1/|\Omega|$, and

$$m_2(N) = \frac{N}{\pi\,|\Omega|} - \frac{N(N-1)}{2\pi\,|\Omega|}\,P_2 \to \frac{\rho}{\pi} - \left(\frac{L\rho}{\pi}\right)^2 \tag{84}$$

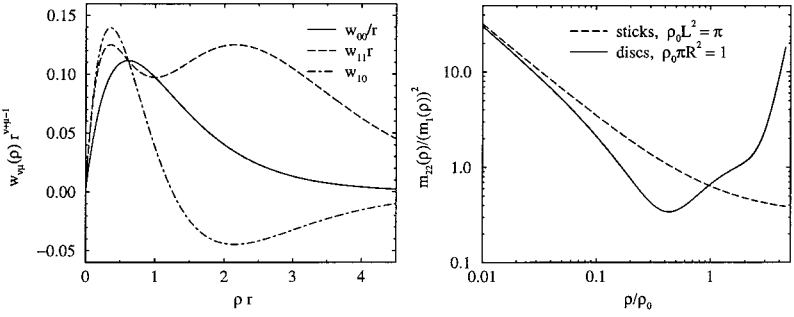

Fig. 2. (a) Second order measures $w_{\nu\mu}(\rho)$ of the one-dimensional volume ($\nu=0$) and of the Euler characteristic ($\nu=1$) for Poisson distributed sticks of length r in one dimension as function of the density ρr (see Eq. (83)). (b) Grand-canonical second order moments $m_{22}(\rho)$ of the curvature for sticks of length L and discs of radius R in two dimensions. The zero ρ_0 of the Euler characteristic $m_2(\rho)$ and the length $m_1(\rho)$ of the boundary length is used to normalize the density and the curvature, respectively. Note, that for $\rho=\rho_0$ the variances are almost equal.

where $P_2=\int (dS'/|\Omega|)\,\chi(S\cap S')=2L^2/\pi\,|\Omega|$ denotes the probability that two sticks intersect. The second order moments $m_{\nu\mu}(N)=0$ vanish identical, except for

$$m_{22}(N)=\frac{N(N-1)}{2\pi^2\,|\Omega|}P_2-\frac{N(N-1)}{2\,|\Omega|}\left(\frac{2L^2}{\pi^2\,|\Omega|}\right)^2 \tag{85}$$

In the thermodynamic limit N, $|\Omega|\to\infty$ one obtains the canonical moment $m_{22}^{(k)}(\rho)=\rho^2(L^2/\pi^3)$. The grand-canonical moment is given by Eq. (78), i.e., $m_{22}^{(gk)}(\rho)=(\rho/\pi^2)+(L^2\rho^2/\pi^3)$. Now, the expression (66) can be applied yielding the integrals $I_2^1=1/\pi$, $I_2^2=2L^2/\pi^2$ for sticks. Therefore, one finds $\bar I_2^1=1/\pi$, $\bar I_2^2=2L^2/\pi^2$ in accordance with Eq. (33). Using the general result (62),

$$\begin{aligned}
M_{22}^{11}&=-\frac{N}{|\Omega|^2}\frac{1}{\pi^2}+\frac{N}{|\Omega|}M_{22;\,1}^{11}\\
M_{22}^{21}&=\frac{N(N-1)}{|\Omega|^3}\frac{2L^2}{\pi^3}-\frac{N(N-1)}{|\Omega|^2}M_{22;\,1}^{21}\\
M_{22}^{22}&=-\frac{N(N-1)(4N-6)}{|\Omega|^4}\frac{L^4}{\pi^4}+\frac{N(N-1)(N-2)}{|\Omega|^3}M_{22;\,1}^{22}+\frac{N(N-1)}{2\,|\Omega|^2}M_{22;\,2}^{22}
\end{aligned} \tag{86}$$

with

$$M^{11}_{22;\,1} = \frac{\delta^{(2)}(\mathbf{x}_1 - \mathbf{x}_2)}{2\pi^2} + \frac{\delta^{(1)}(|\mathbf{x}_1 - \mathbf{x}_2| - L)}{4\pi^3 L}$$
$$M^{21}_{22;\,1} = \frac{L}{\pi^4\,|\mathbf{x}_1 - \mathbf{x}_2|}, \qquad M^{22}_{22;\,1} = \frac{2L^3}{\pi^5\,|\mathbf{x}_1 - \mathbf{x}_2|}, \qquad M^{22}_{22;\,2} = \frac{2L^2}{\pi^3}\,\delta(\mathbf{x}_1 - \mathbf{x}_2) \tag{87}$$

one recovers Eq. (85),

$$m_{22}(N) = \int_{\Omega} d\mathbf{x}_2\, M^{22}_{22}(N, \mathbf{x}_1, \mathbf{x}_2) = \frac{N(N-1)}{|\Omega|^2}\frac{L^2}{\pi^3} - \frac{N(N-1)}{|\Omega|^3}\frac{2L^4}{\pi^4} \tag{88}$$

Here, the expression

$$\begin{aligned} M_2(rS_{\mathbf{y}}, \mathbf{x}) &= \frac{\delta(|\mathbf{x} - \mathbf{y}| - L)}{2\pi\,|\mathbf{x} - \mathbf{y}|}\,\delta(\Phi) + \frac{1}{2\pi}\,\delta(\mathbf{x} - \mathbf{y}) \\ &= \frac{\delta(|\mathbf{x} - \mathbf{y}'| - L/2)}{2\pi\,|\mathbf{x} - \mathbf{y}'|}\,(\delta(\Phi) + \delta(\Phi - \pi)) \end{aligned} \tag{89}$$

for the local Minkowski functionals of a stick $S_{\mathbf{y}}$ of length L has been used where $\mathbf{y}$ ($\mathbf{y}'$) denotes the position of one end point (the midpoint) and Φ the angle between $\mathbf{x} - \mathbf{y}$ and the direction of the stick axes (orientation $r = \Phi$). One recovers

$$\begin{aligned} M_2(S) &= \int M_2(rS_{\mathbf{y}}, \mathbf{x})\, d\mathbf{x} = \frac{1}{\pi} = \int M_2(rS_{\mathbf{y}}, \mathbf{x})\, dS \\ &= \frac{1}{2\pi} + \frac{1}{2\pi}\int_0^{\infty} dr\, r \int_0^{2\pi} d\Phi\, \frac{\delta(r - L)}{r}\,\delta(\Phi) \end{aligned}$$

and with

$$M_2(\partial S \cap \partial S', \mathbf{x}) = \delta(\mathbf{x} - \mathbf{y})\, 2\left(\frac{\phi}{2\pi^2} + \frac{\pi - \phi}{2\pi^2}\right) \tag{90}$$

the integral

$$I_2^2 = \langle M_2(\partial S \cap \partial S', \mathbf{x}) \rangle = \frac{2L^2}{\pi^2}\int_0^{\pi} \frac{d\phi}{\pi}\,\phi \sin\phi = \frac{2L^2}{\pi^2}$$

where $\mathbf{y}$ denotes the intersection point of the two sticks and ϕ the enclosed angle. Note the relation $\delta(\mathbf{x}-\mathbf{y}) = (\delta(|\mathbf{x}-\mathbf{y}|)/|\mathbf{x}|)\,\delta(\Phi)$ if one transform to spherical coordinates $\mathbf{y} = (|\mathbf{y}|, \Phi)$ where $\Phi = 0$ denotes the direction of $\mathbf{x}$.

Example 4: *N* Discs in Two Dimensions. The volume of two overlapping spheres of radius R and distance r in d dimensions is given by

$$V(r) = 2 \cdot \omega_d R^d - \omega_{d-1} \int_r^{2R} \left(R^2 - \left(\frac{x}{2}\right)^2 \right)^{(d-1)/2} dx \tag{91}$$

and for discs in two dimensions

$$V(\mathbf{x}_1, \mathbf{x}_2) = V\left(1 + \frac{2}{\pi} \arcsin(s) + \frac{2}{\pi} s\sqrt{1-s^2}\right) \tag{92}$$

with $V = \pi R^2$ and $s = (|\mathbf{x}_1 - \mathbf{x}_2|)/(2R)$. The boundary length of a disc which is not covered by another disc at distance r reads $F(\mathbf{x}_1, \mathbf{x}_2) = R(\pi + 2\arcsin(s))$ and the opening angle Φ at the intersection point $\partial K_{\mathbf{x}_1} \cap \partial K_{\mathbf{x}_2}$ of two discs is given by $\sin(\Phi/2) = s$ $(0 \leqslant \Phi \leqslant \pi)$. Often an angle Θ is defined in the literature on overlapping spheres by $\cos\Theta = |\mathbf{x}_1 - \mathbf{x}_2|/(2R)$, $0 \leqslant \Theta \leqslant \pi/2$, and therefore, $\Phi = \pi - 2\Theta$. Then, one obtains for an ensemble of discs of radius R and density ρ in two dimensions the structure functions

$$\begin{aligned} I_0^1 &= R\left(\pi + 2\arcsin\frac{|\mathbf{x}_2 - \mathbf{x}_1|}{2R}\right) = R(\pi + \Phi) \\ I_0^2 &= R^2 \iint_0^{\pi+\Phi} d\phi\, d\phi'\, |\sin(\phi - \phi')| = 2R^2(\pi + 3\Phi - \sin\Phi) \\ &= 2R^2(4\pi - 6\Theta - \sin 2\Theta) \end{aligned} \tag{93}$$

with $I_0^1 = \bar{I}_0^1 = 2\pi R$, $I_0^2 = \bar{I}_0^2 = 8\pi R^2$ for $|\mathbf{x}_2 - \mathbf{x}_1| > 2R$ and

$$\begin{aligned} I_\lambda^1 &= R^{2-\lambda} \frac{\pi + \Phi}{2\pi^\lambda} \\ I_2^2 &= \frac{R^2}{2\pi^2} \iint_0^{\pi+\Phi} d\phi\, d\phi'\, |\delta\tilde{\phi}|\, |\sin(\delta\tilde{\phi})| \\ &= \frac{R^2}{2\pi^2}(4\pi\Phi + 4 + 4\cos\Phi - 2(\pi - \Phi)\sin\Phi) \\ &= 2\frac{R^2}{\pi^2}(\pi^2 - 2\pi\Theta + 1 - \cos 2\Theta - \Theta \sin 2\Theta) \end{aligned} \tag{94}$$

with $\delta\tilde{\phi} = \tilde{\phi} - \tilde{\phi}'$ and

$$\tilde{\phi} = \begin{cases} \phi, & \phi \leqslant \pi \\ 2\pi - \phi, & \phi > \pi \end{cases} \tag{95}$$

In the limit $|\mathbf{x}_2 - \mathbf{x}_1| > 2R$ one finds $I_1^1(\mathbf{x}_1, \mathbf{x}_2) = \bar{I}_1^1 = R$, $I_2^1(\mathbf{x}_1, \mathbf{x}_2) = \bar{I}_2^1 = 1/\pi$, and $I_2^2(\mathbf{x}_1, \mathbf{x}_2) = \bar{I}_2^2 = 2R^2$. The local Minkowski functionals defined by Eq. (23) read ($i, \lambda = 1, 2$)

$$\begin{aligned} M_\lambda(K_{\mathbf{y}}, \mathbf{x}_i) &= R^{1-\lambda}/(2\pi^\lambda) \\ M_2(K_{\mathbf{y}_1} \cap K_{\mathbf{y}_2}, \mathbf{x}_i) &= \frac{1}{\pi^2} \arcsin\left(\frac{|\mathbf{y}_2 - \mathbf{y}_1|}{2R}\right) \end{aligned} \tag{96}$$

yielding the constrained structure functions (see Eq. (55) and (63))

$$\begin{aligned} M^{11}_{\nu\mu;\,1}(\mathbf{x}_1, \mathbf{x}_2) &= \frac{R^{2-\nu-\mu}}{2\pi^{\nu+\mu} \sin \Phi} \\ M^{21}_{2\nu;\,1}(\mathbf{x}_1, \mathbf{x}_2) &= \frac{R^{2-\nu}}{2\pi^{2+\nu} \sin \Phi} \int_0^{\pi+\Phi} d\phi \; |\tilde{\phi}| \; |\sin(\tilde{\phi})| \\ &= \frac{R^{2-\nu}}{2\pi^{2+\nu} \sin \Phi} (2\pi - \sin \Phi - (\pi - \Phi) \cos \Phi) \\ &= \frac{R^{2-\nu}}{4\pi^{2+\nu} \sin \Theta \cos \Theta} (2\pi - \sin 2\Theta + 2\Theta \cos 2\Theta) \\ M^{22}_{22;\,1}(\mathbf{x}_1, \mathbf{x}_2) &= \frac{R^2}{2\pi^4 \sin \Phi} \left(\int_0^{\pi+\Phi} d\phi \; |\phi| \; |\sin(\phi)| \right)^2 \\ &= \frac{R^2}{2\pi^4 \sin \Phi} (2\pi - \sin \Phi - (\pi - \Phi) \cos \Phi)^2 \\ M^{22}_{22;\,2}(\mathbf{x}_1, \mathbf{x}_2) &= \frac{(\pi - \Phi)^2}{2\pi^4} + R^2 \left(\frac{1}{\pi} - \frac{4}{\pi^3} \right) \delta(\mathbf{x}_1 - \mathbf{x}_2) \end{aligned} \tag{97}$$

with $S_{I \geq 0}^{\lambda_1 \lambda_2} = 0$ for $|\mathbf{x}_2 - \mathbf{x}_1| > 2R$. The last expression contains a term localized at $\mathbf{x}_1 = \mathbf{x}_2$, i.e., proportional to a δ-distribution. The Euler characteristic contains a term proportional to a sum over all uncovered *points* where the boundaries of two discs intersect. Therefore, the second order moment of χ contains a sum of the squared local Euler characteristic at these points. This contribution can be written as a single integral over $\mathbf{x}_1$ or, alternatively, as a double integral over a structure function which contains a delta distribution.

Remark. Note, that in contrast to I_2^2 and $M_{2v;1}^{21}$ the intgrals

$$\int_0^{\pi+\Phi} d\phi\ |\phi|\ |\sin(\phi)| = 2\pi + \sin\Phi - (\pi+\Phi)\cos\Phi$$
$$\iint_0^{\pi+\Phi} d\phi\, d\phi'\ |\phi-\phi'|\ |\sin(\phi-\phi')| = 4\pi\Phi + 12 - 4\cos\Phi - 2(\pi+\Phi)\sin\Phi \tag{98}$$

where $\tilde{\phi}$ is replaced by ϕ do not give the correct results, Eqs. (94) and (97).

With the explicit expressions (57) and (97) one finds for the structure functions

$$\begin{aligned}
S^{10}(\mathbf{x}_1,\mathbf{x}_2) &= -R\rho(\pi+\Phi)\, e^{-\rho V(\mathbf{x}_1,\mathbf{x}_2)} + 2\pi R\rho e^{-2\rho V}\\
S^{20}(\mathbf{x}_1,\mathbf{x}_2) &= -\frac{1}{2}\rho^2 e^{-\rho V(\mathbf{x}_1,\mathbf{x}_2)} I_0^2 + \bar{I}_0^2\frac{\rho^2}{2}\, e^{-2\rho V}\\
&= -\frac{(R\rho)^2}{2}(2\pi + 6\Phi - 2\sin\Phi)\, e^{-\rho V(\mathbf{x}_1,\mathbf{x}_2)} + 4\pi R^2\rho^2 e^{-2\rho V}\\
S^{11}(\mathbf{x}_1,\mathbf{x}_2) &= ((I_0^1\rho)^2 + S_1^{11}\rho)\, e^{-\rho V(\mathbf{x}_1,\mathbf{x}_2)} - (\bar{I}_0^1\rho)^2\, e^{-2\rho V}\\
S^{21}(\mathbf{x}_1,\mathbf{x}_2) &= \left(I_0^2 I_0^1\frac{\rho^3}{2} + S_1^{21}\rho^2\right) e^{-\rho V(\mathbf{x}_1,\mathbf{x}_2)} - \frac{1}{2}\bar{I}_0^1\bar{I}_0^2\rho^3 e^{-2\rho V}\\
S^{22}(\mathbf{x}_1,\mathbf{x}_2) &= \left((I_0^2)^2\frac{\rho^4}{4} + S_1^{22}\rho^3 + S_2^{22}\frac{\rho^2}{2}\right) e^{-\rho V(\mathbf{x}_1,\mathbf{x}_2)} - \frac{1}{4}(\bar{I}_0^2\rho^2)^2\, e^{-2\rho V}
\end{aligned} \tag{99}$$

and for the Minkowski functions

$$\begin{aligned}
M_{v0}^{10}(\mathbf{x}_1,\mathbf{x}_2) &= S^{10}/(2\pi^v R^{v-1})\\
&= R^{2-v}\pi^{1-v}\rho e^{-2\rho V} - R^{2-v}\frac{\pi+\Phi}{2\pi^v}\rho e^{-\rho V(\mathbf{x}_1,\mathbf{x}_2)}\\
M_{20}^{20}(\mathbf{x}_1,\mathbf{x}_2) &= I_2^2\frac{\rho^2}{2}\, e^{-\rho V(\mathbf{x}_1,\mathbf{x}_2)} - \bar{I}_2^2\frac{\rho^2}{2}\, e^{-2\rho V}\\
&= \frac{\rho^2 R^2}{4\pi^2}\, e^{-\rho V(\mathbf{x}_1,\mathbf{x}_2)}(4\pi\Phi + 4 + 4\cos\Phi - 2(\pi-\Phi)\sin\Phi)\\
&\quad - R^2\rho^2 e^{-2\rho V}
\end{aligned}$$

$$M^{11}_{\nu\mu}(\mathbf{x}_1, \mathbf{x}_2) = (I^1_\nu I^1_\mu \rho^2 + M^{11}_{\nu\mu;\,1}\rho)\, e^{-\rho V(\mathbf{x}_1, \mathbf{x}_2)} - \bar{I}^1_\nu \bar{I}^1_\mu \rho^2 e^{-2\rho V}$$

$$= \frac{R^2\rho}{4(\pi R)^{\nu+\mu}}\, e^{-\rho V(\mathbf{x}_1, \mathbf{x}_2)} \left(\rho R^2(\pi+\Phi)^2 + \frac{2}{\sin\Phi}\right) - \frac{(\pi R^2\rho)^2}{(\pi R)^{\nu+\mu}}\, e^{-2\rho V}$$

$$M^{21}_{2\mu}(\mathbf{x}_1, \mathbf{x}_2) = -\left(I^2_2 I^1_\mu \frac{\rho^3}{2} + M^{21}_{2\mu;\,1}\rho^2\right) e^{-\rho V(\mathbf{x}_1, \mathbf{x}_2)} + \bar{I}^2_2 \bar{I}^1_\mu \frac{\rho^3}{2}\, e^{-2\rho V}$$

$$= (\pi R)^{1-\mu}\,(\rho R)^3\, e^{-2\rho V} - \frac{R^{2-\mu}\rho^2}{2\pi^{2+\mu}}\, e^{-\rho V(\mathbf{x}_1, \mathbf{x}_2)}$$

$$\times \left(\frac{2\pi - \sin\Phi - (\pi-\Phi)\cos\Phi}{\sin\Phi}\right.$$

$$\left. + \rho R^2(\pi+\Phi)\left(\pi\Phi + 1 + \cos\Phi - \frac{\pi-\Phi}{2}\sin\Phi\right)\right)$$

$$M^{22}_{22}(\mathbf{x}_1, \mathbf{x}_2) = \left((I^2_2)^2 \frac{\rho^4}{4} + M^{22}_{22;\,1}\rho^3 + M^{22}_{22,\,2}\frac{\rho^2}{2}\right) e^{-\rho V(\mathbf{x}_1, \mathbf{x}_2)} - \left(\bar{I}^2_2 \frac{\rho^2}{2}\right)^2 e^{-2\rho V}$$

$$= \left(\frac{R\rho}{\pi}\right)^4 e^{-\rho V(\mathbf{x}_1, \mathbf{x}_2)} \left(\pi\Phi + 1 + \cos\Phi - \frac{\pi-\Phi}{2}\sin\Phi\right)^2$$

$$+ \rho^3 \frac{R^2}{2\pi^4 \sin\Phi}\, e^{-\rho V(\mathbf{x}_1, \mathbf{x}_2)} (2\pi - \sin\Phi - (\pi-\Phi)\cos\Phi)^2$$

$$+ \rho^2 \left(\frac{\pi-\Phi}{2\pi^2}\right)^2 e^{-\rho V(\mathbf{x}_1, \mathbf{x}_2)} - (R\rho)^4\, e^{-2\rho V}$$

$$+ \frac{1}{2}\rho^2 R^2 \left(\frac{1}{\pi} - \frac{4}{\pi^3}\right) e^{-\rho V}\, \delta((\mathbf{x}_1 - \mathbf{x}_2) \tag{100}$$

In Fig. 3 the exact grand-canonical second order moments $m_{\nu\mu}(\rho)$ of the Minkowski measures are shown for discs in two dimensions (see Eq. (61), (74) and the normalization Eq. (2)). It should be noted that the variances for the Euler-characteristic w_{22} are large compared to the area and boundary length which are similar to the second order moments w_{00}, w_{01} and w_{11} in one dimension shown in Fig. 2. The second order moment of the Euler-characteristic w_{22} exhibit a maximum at a density close to the zero $m_0\rho_0 = 1$ with $w_2(\rho_0) = 0$.

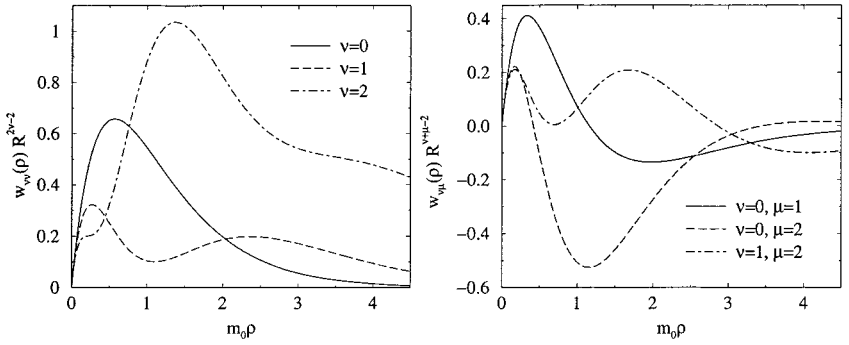

Fig. 3. Grand-canonical second order measures $w_{\nu\mu}(\rho)$ for the area F ($\nu=0$), perimeter U ($\nu=1$), and Euler characteristic χ ($\nu=2$) of Poisson distributed discs of radius R ($m_0=\pi R^2$) in two dimensions as function of the density $\pi R^2\rho$. It should be noted that the functional form of the variances becomes more complex with increasing index ν. The boundary length w_{11} exhibit two fluctuation maxima and the Euler characteristic shows a single (large) maxima but additionally two shoulders.

5. APPLICATION: MORPHOLOGICAL THERMODYNAMICS

Homogeneous spatial domains of phases on a mesoscopic scale are a characteristic feature of many composite media such as porous materials or complex fluids shown in Fig. 1. The spatial structure of such composite media may be described by randomly distributed, overlapping spheres, i.e., by configurations of a germ grain model (see Fig. 1). In contrast to the Boolean model used in stochastic geometry it is necessary for physical applications to introduce interactions between the grains in order to capture correlations of the particle. Therefore, a statistical theory should include morphological descriptors to characterize size, shape and connectivity of the aggregating mesophases shown in Fig. 1, for instance.

The Widom–Rowlinson model is an important example of such an interacting model of stochastic geometries used mainly in the statistical physics of fluids where the interaction is given by the volume of overlapping spheres.[19] A general extension of this model rest on the Minkowski functionals of the overlapped region in space, i.e., on surface tension and curvature energies additionally to the volume of the spheres.[5–7, 12]

Such a morphological thermodynamics may be outlined as follows: Each configuration of component (I) is assumed to be the union of mutually penetrable convex grains $\mathscr{A}_N=\bigcup_{i=1}^{N} g_i K$. embedded in the host component (II). The form of the grains is otherwise arbitrary; they may be balls, flat discs, or thin sticks. The Boltzmann weights are specified by the Hamiltonian

$$\mathscr{H}(\mathscr{A}_N)=\sum_{\nu=0}^{d} h_\nu M_\nu\left(\bigcup_{i=1}^{N} g_i K_i\right) \tag{101}$$

which is a linear combination of Minkowski functionals on the configuration space of the grains. It should be emphasized that the Hamiltonian (Eq. (101)) constitutes the most general model for composite media assuming additivity of the energy of the homogeneous, mesoscopic components. The configurational partition function is taken to be

$$Z_N(T, V) = \frac{1}{N!\, \Lambda^{Nd}} \int \exp\left\{ -\beta \mathscr{H}\left(\bigcup_{i=1}^{N} g_i K \right) \right\} \prod_{j=1}^{N} dg_j \tag{102}$$

The integral denotes averages over the motions of the grains with dg being the invariant Haar measure on the group of motion. The length Λ is a scale of resolution for the translational degrees of freedom of the grains which are restricted to a cube of volume V. Given the partition function $Z_N(T, D)$ of the spatial configurations $\mathscr{A} \cap D$ in a domain D (volume $V = |D|$) at fixed particle number N and temperature temperature T, the free energy equals the logarithm $F(T, N, D) = -k_B T \log Z_N(T, D)$. Thermodynamic potentials are related by Legendre transformations so that the grand canonical potential $\Omega(T, \mu, D) = F - \mu N = -k_B T \log \Xi(T, \mu, D)$ is given by the grand-canonical partition sum $\Xi(T, \mu, V) = \sum_{N=0}^{\infty} e^{\beta \mu N} Z_N(T, V)$. The internal energy, i.e., the expectation value of the energy (101),

$$U(N, T, D) = \left. \frac{\partial \beta F}{\partial \beta} \right|_{NV} = \langle \mathscr{H} \rangle_{TNV} = \sum_{\nu=0}^{d} h_\nu \bar{M}_\nu(N, T, V) \tag{103}$$

is given by the mean values $\bar{M}_\nu(N, T, V)$ of the Minkowski functionals in the Gibbsian ensemble at constant particle number N. In the thermodynamic limit one obtains

$$f(T, \rho) = \lim_{N, V \to \infty} \frac{1}{V} F(T, N, V) = k_B T(\rho \log \rho - \rho) - k_B T \int_0^\rho d\rho' \log z(T, \rho') \tag{104}$$

with $\rho = N/V$ and the fugacity $z(T, \rho) = \rho Z_{N+1}/Z_N$. Then, the chemical potential

$$\mu(T, \rho) = \left. \frac{\partial F}{\partial N} \right|_T = k_B T \log \rho - k_B T \log z(T, \rho) \tag{105}$$

and the pressure

$$p = -\left. \frac{\partial F}{\partial V} \right|_T = \rho \frac{\partial f(T, \rho)}{\rho} - f(T, \rho) = k_B T \rho - k_B T \int_0^\rho d\rho' \frac{\rho'}{z(T, \rho')} \frac{\partial z(T, \rho')}{\partial \rho'} \tag{106}$$

can be expressed in terms of the fugacity $z(T, \rho)$ which is the generating functional for the cumulants of the geometric measures in a Gibbsian ensemble. Expanding in powers of the inverse temperature $\beta = 1/(k_B T)$ and using the kinematic formulae (5) for the average over the position and orientation of identical grains K in a homogeneous and isotropic ensemble one obtains the explicit expression

$$z(T, \rho) = 1 + \sum_{\nu=0}^{d} \beta h_\nu \sum_{\mu=0}^{\nu} \binom{\nu}{\mu} m_\mu(K)\, m_{\nu-\nu}(\rho) + \mathcal{O}(\beta^2) \tag{107}$$

The intensities $m_\nu(\rho)$ do not depend on the temperature and can be calculated within the Boolean model (see Eq. (8)).

The second derivatives of the free energy, namely the specific heat

$$\begin{aligned} C_N &= T \frac{\partial S}{\partial T}\bigg|_{NV} = -T \frac{\partial^2 F(T, N, V)}{\partial T^2}\bigg|_{NV} = \frac{\langle (\Delta \mathcal{H})^2 \rangle_k}{k_B T^2} \\ &= \frac{V}{k_B T^2} \sum_{\nu, \mu=0}^{d} h_\nu h_\mu m_{\nu\mu}^{(k)}(\rho, T) \end{aligned} \tag{108}$$

is given by the second order moment of the Hamiltonian (101), i.e., by the the second order moments of the Minkowski measures. Here, the index (k) refers to a canonical ensemble where the average is performed at constant particle number N and temperature T. The specific heat at constant chemical potential μ,

$$\begin{aligned} C_\mu &= -T \frac{\partial^2 \Omega}{\partial T^2}\bigg|_V \\ &= \frac{\mu(T, \rho)^2}{k_B T^2} \langle (\Delta N)^2 \rangle_{gk} + \frac{\langle (\Delta \mathcal{H})^2 \rangle_{gk}}{k_B T^2} - \frac{2\mu(T, \rho)}{k_B T^2} \langle \Delta N\, \Delta \mathcal{H} \rangle_{gk} \end{aligned} \tag{109}$$

is related to the second order moments

$$\langle (\Delta N)^2 \rangle_{gk} = -\frac{\partial^2 \beta \Omega}{\partial (\beta \mu)^2}\bigg|_V = k_B T \frac{\partial N}{\partial \mu}\bigg|_{TV} = \frac{N z(T, \rho)}{z(T, \rho) - \rho(\partial z(T, \rho)/\partial \rho)} \tag{110}$$

$$\langle (\Delta \mathcal{H})^2 \rangle_{gk} = \langle (\Delta N)^2 \rangle_{gk} \left(\frac{\partial \log z(T, \rho)}{\partial \beta} \right)^2 + \langle (\Delta \mathcal{H})^2 \rangle_k \tag{111}$$

Using the thermodynamic relation

$$C_\mu = T\left.\frac{\partial S}{\partial T}\right|_{\mu V} = C_N + T\left(\left.\frac{\partial \mu(T, N, V)}{\partial T}\right|_{NV}\right)^2 \Big/ \left.\frac{\partial \mu(T, N, V)}{\partial N}\right|_{TV} \tag{112}$$

between the specific heats at constant chemical potential C_μ and constant particle number C_N one obtains

$$C_\mu - C_N = \frac{Nk_B z(T, \rho)}{z(T, \rho) - \rho(\partial z(T, \rho)/\partial \rho)}\left(\beta\mu + \beta\frac{\partial \log z(T, \rho)}{\partial \beta}\right)^2 \tag{113}$$

and finally the relation

$$m_{\nu\mu}^{(gk)}(\rho) - m_{\nu\mu}^{(k)}(\rho) = \rho\frac{\partial m_\nu(\rho)}{\partial \rho}\frac{\partial m_\mu(\rho)}{\partial \rho} + \mathcal{O}(\beta^2) \tag{114}$$

for the grand-canonical and canonical second order moments of the Minkowski measures. Thus, a relation has been derived between the moments of morphological measures which is based only on thermodynamic arguments. Of course, it remains to calculate $m_{\nu\mu}(N, V)$ and $\bar{M}_\nu(N, V)$ in a canonical ensemble which has been done in the previous sections for the Boolean model of overlapping grains.

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