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A morphological model for complex fluids

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Abstract. A new model is proposed for the study of porous media and complex fluids using morphological measures to describe homogeneous spatial domains of the constituents. Under rather natural assumptions a general expression for the Hamiltonian can be given extending the model of Widom and Rowlinson for penetrable spheres. The Hamiltonian includes energy contributions related to the volume, surface area, mean curvature, and the Euler characteristic of the configuration generated by overlapping sets of arbitrary shapes. Phase diagrams of the model are calculated and discussed. In particular, we find that the Euler characteristic in the Hamiltonian stabilizes a highly connected bicontinuous structure, resembling the middle phase in oil–water microemulsions.

1. Introduction

A characteristic feature of complex fluids and porous media is homogeneous spatial domains of phases on a mesoscopic scale [1]. For instance, microemulsions exhibit a bicontinuous structure of homogeneous oil and water phases stabilized by amphiphilic surfactants assembled on the oil–water interface. The thermodynamics and bulk properties of such composite materials depend often on the morphology of its constituents, i.e., on the spatial structure of the homogeneous domains. Therefore, a statistical theory should include geometrical as well as topological descriptors to characterize the size, shape and connectivity of the aggregating mesophases in such media [2].

In this paper we focus on the morphological aspects of two-component media by employing Minkowski functionals, known from integral geometry [3, 4], as suitable descriptors of spatial patterns. In a d-dimensional space, these functionals constitute a distinguished family of $d + 1$ morphological measures which share the common features of being additive, motion-invariant and continuous. In $d = 3$ they are related with familiar measures: covered volume, surface area, integral mean curvature and the Euler characteristic. For completeness we collect together in section 2 some expressions from integral geometry which are required to formulate our model which is introduced in section 3. Our approach is an extension of the widely studied Widom–Rowlinson (WR) model of continuum fluids [5] and may be outlined as follows.

(i) Each configuration of component (I) is assumed to be the union of mutually penetrable convex sets (‘grains’) embedded in the host component (II). The form of the grains is otherwise arbitrary; they may be balls, flat discs, thin sticks etc.

(ii) The energy of a configuration is assumed to be a morphological measure, i.e., an additive, motion-invariant and continuous functional of the position and orientation of the grains. Thus the Hamiltonian of our model is a linear combination of Minkowski functionals

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on the configuration space of the grains and depends in particular on the integral mean curvature and Euler characteristic of the homogeneous domains.

(iii) The partition function is defined as an integral over the Euclidean motions, i.e., translations and rotations of the penetrable grains, weighted by the Boltzmann factor.

The WR model only accounts for the volume covered by spherical grains and shows a liquid–vapour transition. A mean-field approximation is applied to study the modifications of the phase transition caused by the surface area and curvature terms. We focus primarily on effects due to the Euler characteristic X, which is related to the integral Gaussian curvature of the interface between the mesophases and has the attributes of a topological order parameter; configurations with $X > 0$ consist typically of isolated grain clusters dispersed in the host component, whereas multiply connected aggregates of grains yield $X < 0$. We find that for $d = 3$ the Euler term in the Hamiltonian induces an additional continuous phase transition and a *triple point*. One of the three coexisting fluid phases shows a negative Euler characteristic which indicates a highly connected bicontinuous structure, resembling the middle phase in oil–water microemulsions where the surfactants saturate the oil–water interface.

2. Minkowski functionals

The aim of this section is the morphological characterization of random structures typical for the structure of mesoscopic phases. We consider a two-component medium filling a cube Ω with volume $V = L^d$. Component (I) is a collection of penetrable grains represented by compact, i.e., closed and bounded, convex sets $K_i \subset \mathbb{E}^d, i = 1, \ldots, N$. Thus, a configuration is given by $K^N = \cup_{i=1}^N K_i$. The complement $\Omega \backslash K^N$ constitutes component (II), i.e., the region in space which is not covered by one of the sets K_i. To avoid finite-size effects we assume periodic boundary conditions on $\partial\Omega$. For an arbitrary set K the Euler characteristic X can now be defined by $X(K) := 1$ if $K \neq \emptyset$ is convex, and $X(K) := 0$ if $K = \emptyset$ is the empty set. For unions of convex sets K, K' the Euler characteristic is given by the additivity relation

$$X(K \cup K') = X(K) + X(K') - X(K \cap K'). \tag{1}$$

Since the intersection of two convex sets is convex, one obtains X for an arbitrary configuration K^N by repeated application of the additivity relation (1). The functional X is motion-invariant, $X(gK^N) = X(K^N)$, where gK^N denotes the action of translations and rotations on K^N, and coincides with the Euler characteristic of algebraic topology when the latter is restricted to finite unions of convex compact sets. Since a single point $x \in \mathbb{E}^d$ is a convex set we can define a characteristic function of K^N by $I_{K^N}(x) := X(K^N \cap x)$, so that the volume covered by K^N is $W_0(K^N) := \int I_{K^N}(x)\ \mathrm{d}\mu(x)$. Here $\mathrm{d}\mu(x)$ denotes the motion-invariant volume element in $\mathbb{E}^d$. This relation motivates the definitions of the Minkowski functionals

$$W_\alpha(K^N) = \int X(K^N \cap E_\alpha)\ \mathrm{d}\mu(E_\alpha) \qquad \alpha = 0, \ldots, d-1 \tag{2}$$

and $W_d(K^N) = \omega_d X(K^N)$ with $\omega_d = \pi^{d/2}/\Gamma(1+d/2)$, where E_α is an α-dimensional plane in $\mathbb{E}^d$ and $\mathrm{d}\mu(E_\alpha)$ denotes its motion-invariant kinematical density [3, 4]. It is convenient to normalize the density $\mathrm{d}\mu(E_\alpha)$ so that for a d-dimensional ball B_r^d with radius r the Minkowski functionals are $W_\alpha(B_r^d) = \omega_d r^{d-\alpha}$. These functionals are familiar geometric quantities in disguise. For $d = 3$ we have, for instance, $W_0 = \mathcal{V}$, $W_1 = \mathcal{A}/3$, $W_2 = \mathcal{C}/3$, and $W_3 = (4\pi/3)X$ with the area $\mathcal{A}$ and integral mean curvature $\mathcal{C}$ of the surface exposed by a

coverage with volume $\mathcal{V}$ and Euler characteristic X. Obviously the Minkowski functionals W_α inherit the main features from the Euler characteristic; in particular they are

$$\begin{aligned} &\bullet \text{ additive :} \qquad W_\alpha(K \cup K') = W_\alpha(K) + W_\alpha(K') - W_\alpha(K \cap K') \\ &\bullet \text{ motion-invariant:} \qquad W_\alpha(gK) = W_\alpha(K) \\ &\bullet \text{ conditionally continuous.} \end{aligned} \tag{3}$$

Intuitively, 'continuity' means that an approximation of a convex body as a sequence of polyhedra K_n also yields an approximation of $W_\alpha(K)$ as $W_\alpha(K_n)$. This is relevant for the approximation of real configurations as unions of convex sets. The additivity relation is a common feature of thermodynamic potentials, e.g., the free energy of two mesoscopic domains of a system is often assumed to be the sum of the free energies of each domain.

The subsequent construction of our model rests on Hadwiger's theorem [3, 4] which states that the family of the $d + 1$ Minkowski functionals is *complete* in the following sense: if Φ is an additive, motion-invariant and continuous functional over the class of finite unions of convex sets, then it must be of the form $\Phi(K^N) = \sum_{\alpha=0}^{d} c_\alpha W_\alpha(K^N)$ with suitable coefficients $c_\alpha \in \mathbb{R}$ independent of K^N. Thus, the Minkowski functionals are essentially the only additive and motion-invariant measures of unions of convex sets.

3. The model

In order to set up a phenomenological model for the statistical morphology of a Gibbsian ensemble of configurations K^N, it is natural to adopt the properties (3) as criteria for the choice of an energy $\mathcal{H}(K^N)$. Then, Hadwiger's theorem forces $\mathcal{H}$ to take the form

$$\mathcal{H}(K^N) = \sum_{\alpha=0}^{d} \frac{\epsilon_\alpha}{w_\alpha} W_\alpha\left(\bigcup_{i=1}^{N} K_i\right) \tag{4}$$

with $w_\alpha := W_\alpha(K)$. For simplicity, the grains are assumed to be congruent bodies. This is the most general expression of an Hamiltonian obeying the morphological constraints (3). The configurational partition function is taken to be

$$\mathcal{Z}(T, V, N) = \frac{1}{N!\Lambda^{Nd}} \int \exp\left(-\beta\mathcal{H}\left(\bigcup_{i=1}^{N} K_i\right)\right) \prod_{j=1}^{N} \mathrm{d}K_j. \tag{5}$$

The integral denotes averages over the motions of the grains with $\mathrm{d}K$ being the invariant Haar measure on the group of motion normalized by $V = \int \mathrm{d}K$. The length Λ is a scale of resolution for the translational degrees of freedom of the grains. Apart from their convexity, the size and shape of the grains are not restricted and 'improper' bodies (e.g. sticks and discs in $\mathbb{E}^3$) are not excluded; a δ-dimensional convex set A with $\delta \leqslant d$ has $W_\alpha(A) = 0$ for $\alpha \leqslant d - \delta - 1$.

For penetrable spheres $K_i = B_r^d(x_i)$ and the choice $\epsilon_\alpha = 0$ for $1 \leqslant \alpha \leqslant d$ we recover the WR model $\mathcal{H}(K^N) = (\epsilon_0/v)W_0(x_1, \ldots, x_N)$, where $W_0(x_1, \ldots, x_N)$ is the volume covered by balls centred at the points $x_1, \ldots, x_N$ and $v = W_0(B_r^d)$.

With the area and curvature measures $W_\alpha, 1 \leqslant \alpha \leqslant d$, included in $\mathcal{H}$, equations (4) and (5) establish a model for random interfaces formed by the boundaries ∂K_N, with the surface tension ϵ_1 and curvature moduli $\epsilon_2, \ldots, \epsilon_d$.

Since the Minkowski functionals are well defined also for polyhedral bodies, there is a natural lattice version of our model which preserves its morphological features [2, 6]. Setting $\epsilon_2 = \epsilon_3 = 0$ one arrives, of course, at a conventional lattice gas model with nearest-neighbour interaction only.

Because of the proliferation of multibody interactions an exact evaluation of the partition function (5) for $d \geqslant 2$ appears to be unmanageable. Therefore, we look for an approximation which should keep the geometrical and topological aspects of the model intact. For this purpose we follow reference [5] by keeping only the first two terms in a high-temperature expansion of the free energy:

$$f(\rho, T) := \lim_{N,V\to\infty} \frac{1}{N}\beta F(T, V, N) = -\lim_{N,V\to\infty} \frac{1}{N} \log \mathcal{Z} = \log(\rho\Lambda^3/w_0) - 1 + \frac{\beta}{\rho}\langle\mathcal{H}\rangle. \tag{6}$$

The mean value $\langle\mathcal{H}\rangle = \sum_\alpha \epsilon_\alpha \langle W_\alpha\rangle / w_\alpha$ is obtained from the averages of the Minkowski functionals over an ensemble of randomly and independently distributed grains within the cube Ω. In the large-volume limit, $N, V \to \infty$, $N/V = n$, the averages $\bar{W}_\alpha := \langle W_\alpha\rangle/N$ are known exactly [7] and are given by

$$\begin{aligned} \bar{W}_0 &= \frac{v}{\rho}(1 - \mathrm{e}^{-\rho}) & \bar{W}_2 &= \frac{c}{3}\left(1 - \frac{\pi^2}{32}\frac{a^2}{cv}\rho\right)\mathrm{e}^{-\rho} \\ \bar{W}_1 &= \frac{a}{3}\mathrm{e}^{-\rho} & \bar{W}_3 &= \frac{4\pi}{3}\bar{\chi} = \frac{4\pi}{3}\left(1 - \frac{1}{4\pi}\frac{ac}{v}\rho + \frac{\pi}{384}\frac{a^3}{v^2}\rho^2\right)\mathrm{e}^{-\rho} \end{aligned} \tag{7}$$

for $d = 3$ (considered exclusively from now on). Here v, a and c denote volume, area and mean curvature of a single grain, $\rho = nv$ the density, and $\bar{\chi} = \langle X\rangle/N$ the mean Euler characteristic.

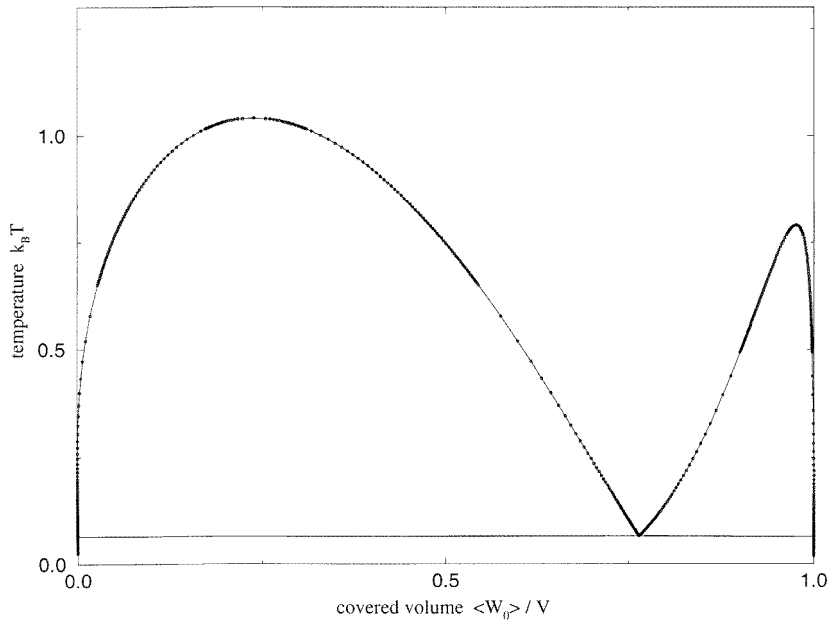

Figure 1. The phase diagram for penetrable spheres in three dimensions with $\epsilon_0 = 1$, $\epsilon_1 = 0$, $\epsilon_2 = 0.4$, and $\epsilon_3 = 0.83$. The middle phase at $\langle W_0\rangle/V \approx 0.75$ is stabilized by the Euler characteristic in the Hamiltonian (4), i.e., highly connected configurations get a large Boltzmann factor. The temperature $k_BT_{tr} = 0.066$ of the triple line can tend to zero yielding two separated two-phase regions with a phase at medium densities even at $T = 0$.

We now look for phase transitions signalled by the occurrence of critical points. Within the present approximation, the values of ρ_c and T_c are found by solving $\partial_\rho p = 0$, $\partial_\rho^2 p = 0$, and $\partial_\rho^3 p|_{\rho_c,T_c} > 0$ with the pressure $pv = k_B T \rho^2 \partial_\rho f$. For a generic set of parameters in the free energy, these equations yield a fourth-order polynomial equation for the possible values of the critical density ρ_c. Consequently, we expect to find in general two critical points. The choice $\epsilon_\alpha = 0, \alpha \geqslant 1$, leads back to the original Widom–Rowlinson model, having a single critical point at $\rho_c = vn_c = 1$, $k_B T_c = \epsilon_0/e$ and $\bar{\chi}(\rho_c) \approx -0.39$. We note that these values are independent of the grain shape.

In the case where $\epsilon_0 = \epsilon_2 = \epsilon_3 = 0$, and $\epsilon_1 > 0$ the configurational energy is determined by the exposed area with surface tension ϵ_1 which may be viewed as a continuum analogue of Peierls contours of an Ising lattice model. There is a single critical point $\rho_c = 2 + \sqrt{2}$, $k_B T_c = \epsilon_1 \rho_c (\rho_c - 2) \mathrm{e}^{-\rho_c}$ with $\bar{\chi}(\rho_c) \approx 0.05$.

Our main result is the existence of a second critical point and a three-phase coexistence for a nonvanishing term $\epsilon_3 \neq 0$, i.e., if the Hamiltonian contains a term proportional to the Euler characteristic X of the configuration. A typical phase diagram for penetrable spheres is shown in figure 1 with the critical points $\rho_c^{(1)} = 0.27$, $k_B T_c^{(1)} = 1.04$ and $\rho_c^{(2)} = 3.72$, $k_B T_c^{(2)} = 0.79$. The middle phase is characterized by a negative mean Euler characteristic $\bar{\chi} < 0$ indicating a highly connected bicontinuous structure between the densities of the critical points. This resembles the experimentally observed phase behaviour and spatial structure of a middle-phase microemulsion.

In this paper we propose a new model for complex fluids using morphological measures to describe homogeneous spatial domains generated by penetrable grains. The study of the structure and physical properties of the various phases by renormalization group techniques and Monte Carlo simulations as well as further applications on porous media is work in progress.

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