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Morphological thermodynamics of composite media

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Abstract

The homogeneous spatial domains of phases on a mesoscopic scale are a characteristic feature of many composite media such as complex fluids or porous materials. The thermodynamics and bulk properties of such composite media depend often on the morphology of its constituents, i.e., on the spatial structure of the homogeneous domains. Therefore, a statistical theory should include morphological descriptors to characterize the size, shape and connectivity of the aggregating mesophases. We propose a new model for studying composite media using morphological measures to describe the homogeneous spatial domains of the constituents. Under rather natural assumptions a general expression for the Hamiltonian can be given by extending the model of Widom and Rowlinson [B. Widom, J.S. Rowlinson, J. Chem. Phys. 52 (1970) 1670–1684] for penetrable spheres. The Hamiltonian includes energy contributions related to the volume, surface area, mean curvature, and Euler characteristic of the configuration generated by overlapping sets of arbitrary shapes. A general expression for the free energy of composite media is derived and we find that the Euler characteristic stabilizes a highly connected bicontinuous structure resembling the middle-phase in oil–water microemulsions for instance. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

As a rule, the bulk properties of a composite material depend on the chemistry and on the supramolecular morphology of its constituents. Therefore, the statistical theory should include geometrical as well as topological descriptors to characterize the size, shape and connectivity of the aggregating mesophases in such media [1,2]. In this paper we focus on the morphological aspects of two component media by employing the Minkowski functionals, known from integral geometry [3,4], as suitable descriptors of spatial patterns. In a d-dimensional ambient space, these functionals constitute a distinguished family of $d+1$ morphological measures which share the common features

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of being additive, motion-invariant and continuous. In $d=3$ they are related with familiar measures: covered volume, surface area, integral mean curvature and Euler characteristic.

For completeness we collect in Section 2 some requisites from integral geometry required to formulate our model. 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 bodies ('grains') embedded in the host component (II). The form of the grains is otherwise arbitrary; they may be balls, flat discs, thin sticks, etc. A typical configuration of randomly distributed discs is shown in Fig. 1.

(ii) The Boltzmann weights are specified by a potential energy which is a linear combination of Minkowski functionals on the configuration space of the grains.

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

The WR-model only accounts for the volume covered by spherical grains. In a mean-field approximation it shows a liquid–vapor transition whose existence for $d \geq 2$ has also been established rigorously. In Section 3 the WR-type mean-field approximation is applied to study the modifications caused by the surface area and curvature terms on the phase transition in the present model. We concentrate primarily on the effects due to the Euler characteristic X, which is both a geometrical and a topological invariant. Since X is related with the integral Gaussian curvature of the interface between the mesophases, it measures the bending energy arising from saddle-splay type interfacial

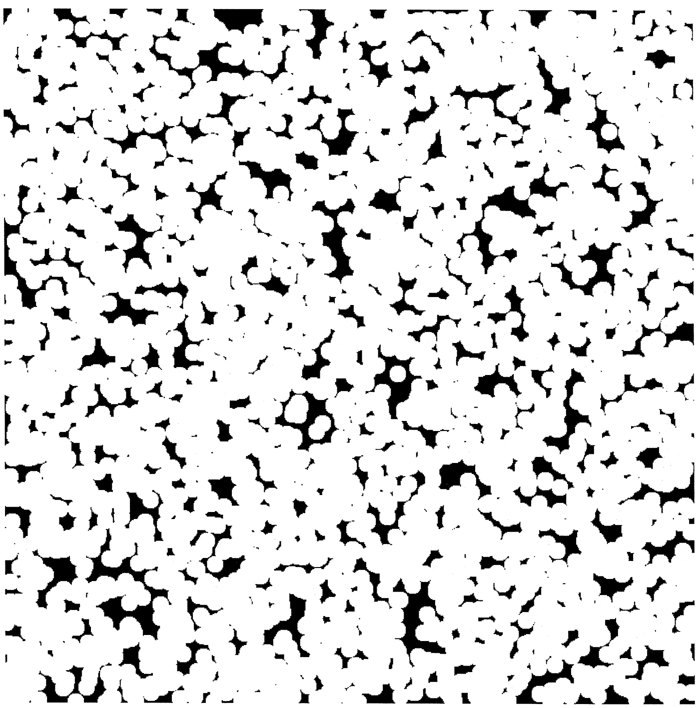

Fig. 1. Composite media such as porous materials and complex fluids can be modelled by overlapping balls distributed uniformly in space.

deformations. Moreover, the Euler characteristic has the attributes of a topological order parameter; configurations with $X>0$ consist typically of isolated grain clusters interdispersed in the host component, whereas multiply connected aggregates of grains yield $X<0$.

2. The morphological model

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 $K_i \subset \mathbb{E}^d$, $i=1,\ldots,N$ (see, for instance, the union of randomly distributed discs shown in Fig. 1). For simplicity, the grains are assumed to be congruent bodies. Let $\mathscr{G}$ denote the group of motions (translations and rotations) in the Euclidean space $\mathbb{E}^d$. The location and orientation of the grains are specified by the action of $g_i \in \mathscr{G}$ on a tripod fixed at the centroid of each grain K, $K_i = g_i K$. Thus, a configuration is given by

$$K^N = \bigcup_{i=1}^{N} g_i K. \tag{1}$$

The complement $\Omega \backslash K^N$ constitutes component (II). To avoid finite-size effects we assume periodic boundary conditions on $\partial\Omega$. In order to introduce morphological measures, it is convenient to proceed within a more general framework and to consider the class $\mathscr{R}$ of subsets of $\mathbb{E}^d$ which can be represented as a *finite* union of convex compact sets, with the empty set $\emptyset \in \mathscr{R}$.

Let us now define three general properties a functional $\mathscr{W}:\mathscr{R} \to \mathbb{R}$ should possess in order to be a morphological measure.

(i) Additivity: The functional of the union $A \cup B$ of two domains A, $B \in \mathscr{R}$ is the sum of the functional of the single domains subtracted by the intersection

$$\mathscr{W}(A \cup B) = \mathscr{W}(A) + \mathscr{W}(B) - \mathscr{W}(A \cap B). \tag{2}$$

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

(ii) Motion invariance: Let $\mathscr{G}$ be the group of motions, namely translations and rotations in $\mathbb{R}^d$. The transitive action of $g \in \mathscr{G}$ on a domain $A \in \mathscr{R}$ is denoted by gA. Then

$$\mathscr{W}(gA) = \mathscr{W}(A), \tag{3}$$

i.e., the morphological measure of a domain is independent of its location and orientation in space.

(iii) Continuity: If a sequence of convex sets $K_n \to K$ for $n \to \infty$, converges towards the convex set K (with convergence defined in terms of the Hausdorff metric for sets), then

$$\mathscr{W}(K_n) \to \mathscr{W}(K). \tag{4}$$

Intuitively, this continuity property expresses the fact that an approximation of a convex domain by convex polyhedra K_n, for example, also yields an approximation of $\mathscr{W}(K)$ by $\mathscr{W}(K_n)$. We emphasize that we require this condition only for the morphological measure of convex sets K and not for unions $A \in \mathscr{R}$.

In three-dimensional space we can easily give examples of morphological measures which obey the three conditions (i)–(iii): for instance, the volume V and the surface area S of a domain in three dimensions are continuous, motion-invariant and additive. In two dimensions we mention the area F and the boundary length U of a domain as morphological measures in the sense described above. Naturally the question arises if there are other measures which obey the conditions (i)–(iii) and if there is a systematic way to find such measures.

A remarkable theorem in integral geometry is the completeness of the Minkowski functionals [3]. The theorem asserts that any additive, motion-invariant and conditional continuous functional $\mathscr{W}(A)$ on subsets $A \subset \mathbb{R}^d$, $A \in \mathscr{R}$, i.e., each morphological measure is a linear combination of the $d+1$ Minkowski functionals,

$$\mathscr{W}(A) = \sum_{\nu=0}^{d} c_\nu W_\nu(A), \tag{5}$$

with real coefficients c_ν independent of A. The Minkowski functionals are familiar geometric quantities. In $d=3$ we have, for instance,

$$W_0 = \mathscr{V},\ 3W_1 = \mathscr{A},\ 3W_2 = \mathscr{C},\ 3W_3 = 4\pi X, \tag{6}$$

with the area $\mathscr{A}$ and integral mean curvature $\mathscr{C}$ of the surface exposed by a coverage with volume $\mathscr{V}$ and Euler characteristic X. Thus, every morphological measure $\mathscr{W}$ defined by the properties (i) – (iii) can be written in terms of Minkowski functionals W_ν, i.e., the $d+1$ Minkowski functionals are the complete set of morphological measures. The subsequent construction of our model rests on this theorem.

In order to set up a phenomenological model for the statistical morphology of a Gibbs ensemble of configurations such as K^N in (1), it is natural to adopt the properties (i)–(iii) as criteria for the choice of a potential energy $\mathscr{U}(K^N)$. Then, the theorem (Eq. (5)) forces $\mathscr{U}$ to take the form

$$\mathscr{U}(K^N) = \sum_{\alpha=0}^{d} \epsilon_\alpha \mathscr{U}_\alpha\left(\bigcup_{i=1}^{N} g_i K\right), \tag{7}$$

where we introduce the dimensionless functionals $\mathscr{U}_\alpha = W_\alpha / w_\alpha$, with $w_\alpha = W_\alpha(K)$ for a single grain K. We emphasize that the Hamiltonian (Eq. (7)) 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

$$\mathscr{Z}(T,V,N) = \frac{1}{N!\Lambda^{Nd}} \int \exp\left\{-\beta\mathscr{U}\left(\bigcup_{i=1}^{N} g_i K\right)\right\} \prod_{j=1}^{N} dg_j. \tag{8}$$

The integral denotes averages over the motions of the grains with dg being the invariant Haar measure on the group $\mathscr{G}$. The translational parts of the integrals are restricted to the cube Ω. The length Λ is a scale of resolution for the translational degrees of freedom of the grains.

We emphasize, that apart from their convexity, the size and shape of the grains is not restricted and 'improper' bodies are not excluded; a δ-dimensional convex set A with $\delta \le d$ has $W_\alpha(A) = 0$ for $\alpha \le d - \delta - 1$.

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 [6]. Consider, for example, a simple cubic lattice where the elementary cells are randomly occupied by the component (I) and with the configurational integral over $\mathscr{G}$ replaced by a sum over occupation numbers. The occupied (closed) cubes may intersect at common faces, edges or vertices, which are the supports of surface area, mean and Gaussian curvature, respectively. After setting, $\epsilon_2 = \epsilon_3 = 0$, one arrives, of course, at a conventional lattice gas model with nearest-neighbor interactions only.

3. Phase diagrams

Because of the proliferation of multi-body potentials, an exact evaluation of the partition function for $d \geq 2$ 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 Ref. [5] by keeping only the first two terms in a high-temperature expansion of the free energy. This procedure amounts to replacing the configurational integral in the partition function $\mathscr{Z}$ by

$$\exp\{-\beta\langle\mathscr{U}\rangle\} := \exp\left\{-\beta\int\mathscr{U}(K^N)\prod_i dg_i\right\}, \tag{9}$$

which yields a lower bound $Z \leq \mathscr{Z}$. Here, $\langle\mathscr{U}\rangle = \sum_\alpha \epsilon_\alpha \langle\mathscr{U}_\alpha\rangle$ is obtained from the averages $\langle\mathscr{U}_\alpha\rangle$ 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 $u_\alpha(\rho) := \langle\mathscr{U}_\alpha\rangle/N$ are known exactly [2,7] and are given for $d = 3$ (considered exclusively from now on) by

$$\begin{aligned}
u_0(\rho) &= \bar{v}/v = (1 - e^{-\rho})/\rho, \\
u_1(\rho) &= \bar{a}/a = e^{-\rho}, \\
u_2(\rho) &= \bar{c}/c = \left(1 - \frac{\pi^2}{32}\frac{a^2}{cv}\rho\right)e^{-\rho}, \\
u_3(\rho) &= \bar{\chi} = \left(1 - \frac{1}{4\pi}\frac{ac}{v}\rho + \frac{\pi}{384}\frac{a^3}{v^2}\rho^2\right)e^{-\rho},
\end{aligned} \tag{10}$$

with the notations $\langle\mathscr{V}\rangle = \bar{v}N$, $\langle\mathscr{A}\rangle = \bar{a}N$, $\langle\mathscr{C}\rangle = \bar{c}N$ and $\langle X\rangle = \bar{\chi}N$; furthermore, v, a and c denote volume, area and mean curvature of a single grain; finally, $\rho = nv$. The approximate free energy per grain,

$$\lim_{N,V\to\infty}\frac{1}{N}\beta F(T,V,N) = -\lim_{N,V\to\infty}\frac{1}{N}\log Z =: f(\rho,T), \tag{11}$$

may be written as

$$\rho f(\rho,T) = \beta_0(1 - e^{-\rho}) + (f_1\rho - f_2\rho^2 + f_3\rho^3)e^{-\rho} + \rho\log(\rho\lambda^3) \tag{12}$$

where $\beta_\alpha = \epsilon_\alpha/k_B T$, $\lambda^3 = \Lambda^3/(ev)$ and

$$\begin{aligned}
f_1 &= \beta_1 + \beta_2 + \beta_3, \\
f_2 &= \frac{3\pi^2}{32}\Phi_1\beta_2 + 3\Phi_2\beta_3, \\
f_3 &= \frac{3\pi^2}{32}\Phi_3\beta_3.
\end{aligned} \tag{13}$$

The shape of the grains appears in the free energy in terms of the coefficients

$$\Phi_1 = \frac{a^2}{3vc}, \; \Phi_2 = \frac{ac}{12\pi v}, \; \Phi_3 = \frac{a^3}{36\pi v^2}. \tag{14}$$

For three-dimensional convex bodies these coefficients are bounded from below by the Minkowski inequalities $\Phi_j \geq 1$, $j = 1, 2, 3$, with the equality holding in the case of spheres. The expression, Eq. (11), for the free energy of a composite media in terms of morphological measures of the constituents is our main result. A general discussion of phase behavior in such media is now possible. Furthermore, it may be interesting to compare Eq. (11) with experimental data for systems where the conditions (2)–(4) are fulfilled.

We now look for phase transitions signalized by the occurrence of critical points. Within the present approximation, the values of ρ_c and T_c are found by solving

$$\frac{\partial p}{\partial \rho} = 0 = \frac{\partial^2 p}{\partial \rho^2}, \; \left.\frac{\partial^3 p}{\partial \rho^3}\right|_{\rho_c, T_c} > 0, \tag{15}$$

with the pressure

$$pv = \rho^2 \frac{\partial f}{\partial \rho}. \tag{16}$$

For a generic set of parameters in the free energy, $\partial^2 p / \partial \rho^2 = 0$ yields 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. However, let us first consider some special choices for these parameters.

The choice $\epsilon_\alpha = 0$, $\alpha \geq 1$, leads back to the original Widom–Rowlinson model with

$$f(\rho, T) = \beta_0 (1 - \mathrm{e}^{-\rho}) / \rho + \log(\rho \lambda^3). \tag{17}$$

having a single critical point at $\rho_c = v n_c = 1$, $k_B T_c = \epsilon / e$. We note that these values are independent of the grain shape which enters only in the expected mean curvature $u_2 = \bar{c}/c$ and Euler characteristic $u_3 = \bar{\chi}$; in the example of spheres one has $u_2(\rho_c) = (1 - 3\pi^2/32)/\mathrm{e} \approx 0.03$ and $\bar{\chi}(\rho_c) = -(2 - 3\pi^2/32)/\mathrm{e} \approx -0.39$. The dashed line shown in Fig. 2 indicates the location of the coexisting densities.

In the case $\epsilon_0 = \epsilon_2 = \epsilon_3 = 0$, the configurational energy is determined by the exposed area which may be viewed as a continuum analog of Peierls contours of an Ising lattice model. The free energy simplifies to

$$f(\rho, T) = \beta_1 \mathrm{e}^{-\rho} + \log(\rho \lambda^3). \tag{18}$$

There is a single critical point $\rho_c^+ = 2 + \sqrt{2}$, $k_B T_c^+ = \epsilon_1 \rho_c^+ (\rho_c^+ - 2) \mathrm{e}^{-\rho_c^+}$ for $\epsilon > 0$, with $\bar{\chi}(\rho_c^+) \approx 0.05$, and another one, $\rho_c^- = 2 - \sqrt{2}$, $k_B T_c^- = |\epsilon_1| \rho_c^- (2 - \rho_c^-) \mathrm{e}^{-\rho_c^-}$ for $\epsilon < 0$, with $\bar{\chi}(\rho_c^-) \approx -0.24$.

For two-dimensional grains with $v = 0$ the free energy reduces to

$$f(n, T) = \beta_0 + f_1 + \phi_2 n + \phi_3 n^2 + \log(n \Lambda^3 / \mathrm{e}) \tag{19}$$

where $\phi_j = f_j(v = 1)$, $j = 2, 3$, and $p = n^2 \partial f / \partial n$. A critical point occurs at $n_c = \phi_2 / 6\phi_3$, $k_B T_c = 6\phi_3 n_c^2$. Consider, for instance, two-dimensional discs with radius r. The area and the mean curvature are obtained from those of a cylinder, $a = 2\pi r^2 (1 + h/r)$, $c = \pi^2 r (1 + h/\pi r)$, when $h \to 0$. In

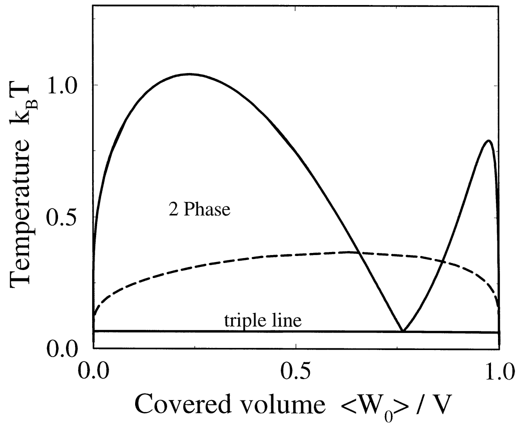

Fig. 2. A typical phase diagrams for penetrable spheres in three dimensions: the dashed line indicates the two-phase coexistence region of the Widom–Rowlinson model with $\epsilon_0 = 1$, $\epsilon_1 = \epsilon_2 = \epsilon_3 = 0$. The solid lines show the influence of the Euler characteristic, i.e., the two-phase region for $\epsilon_0 = 1$, $\epsilon_1 = 0$, $\epsilon_2 = 0.4$, and $\epsilon_3 = 0.83$. Two critical points occur at $\rho_c^{(1)} = 0.27$, $k_B T_c^{(1)} = 1.04$ and $\rho_c^{(2)} = 3.72$, $k_B T_c^{(2)} = 0.79$, and a triple line at $k_B T_{tr} = 0.066$ where three phases are in thermodynamic equilibrium. The middle phase at $\langle W_0 \rangle / V \approx 0.75$ is stabilized by the Euler characteristic χ in the Hamiltonian (Eq. (7)), i.e., highly connected configurations result in a large Boltzmann factor.

addition, we set $\epsilon_2 = 0$ to focus on the Euler characteristic; then $n_c = 16c/(\pi a)^2 = 4/(\pi^2 r^3)$, $k_B T_c = 2\epsilon_3$ and $\bar{\chi}(n_c) = 1 - 10c^2/(3\pi^3 a) = -2/3$.

The three particular examples, Eqs. (17)–(19), of the general expression, Eq. (11), for the free energy exhibit only one critical point, i.e., one two-phase coexistence. Our main result is the existence of a second critical point and a three-phase coexistence, i.e., a triple point for a nonvanishing term $\epsilon_3 \neq 0$. A typical phase diagram for penetrable spheres is shown in Fig. 2. The topology of the phase diagram changes qualitatively if the Hamiltonian contains a term proportional to the Euler characteristic X of the configuration. The stabilized 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, for instance, the experimentally observed phase behavior and spatial structure of a middle phase microemulsion. The temperature of the triple line can tend to zero yielding two separated two-phase regions with a phase at medium densities even at $T = 0$.

4. Conclusion

In this paper we derived a general expression for the free energy of composite media in terms of morphological measures of the constituents. We introduced penetrable grains to describe the homogeneous spatial domains of the constituents and we applied integral geometry in order to propose a potential energy of the configurations. The thermodynamics of such composite materials are then given in terms of additive, morphological measures of its constituents. Depending on the relative strength of the energies related to the volume, surface area, mean curvature, and Euler characteristic of the domains we find qualitative different phase diagrams and spatial structures. Monte-Carlo simulations of the model and also applications to colloidal systems are work in progress.

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