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Surface free energy of a finite system without interfaces at low temperatures

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ABSTRACT

We derive the specific surface free energy for a rather general system at low temperatures that can be rewritten as a gas of non-interacting contours (polymers). To this end, we use a standard cluster expansion series for the system's partition function. A specific regime of 'weak' boundary conditions is assumed to ensure that no interfaces or large droplets occur in the system. We illustrate the general results, using a simple lattice–gas model.

1. Introduction

When working with a finite system, effects of the system's surroundings must be inevitably taken into account. Periodic boundary conditions are not appropriate to circumvent this problem whenever surface effects play a critical role in a given case, such as in the description of current spikes at electrode–electrolyte interfaces [1–3]. Moreover, specific fixed boundary conditions are imposed to investigate systems in which macroscopic interfaces and/or large droplets occur, including the studies of surface tension and equilibrium crystal shapes [4–15], wetting [16], or vapor–liquid coexistence [17]. In such situations it is important to have good control over surface contributions to the system's free energy, $F = -k_B T \ln Z$.

To this end, very specialized and sophisticated methods have been usually employed, yielding results restricted to particular situations or models. Nevertheless, in a simple case when boundary conditions are sufficiently 'weak' not to strongly prefer any of the phases in the system, no large interfaces occur, and a bulk-surface expression

$$F = f_b L^d + f_s 2d L^{d-1} + O\left(L^{d-2}\right) \tag{1}$$

was established for a wide range of lattice–gas models in a cubic volume $V = L^d$ of dimension $d \geqslant 2$ [18]. The expression works for the systems at low temperatures and with a single stable phase (near coexistence of several phases a combination of bulk-surface expressions for each phase is needed to get F).

Moreover, the bulk and surface specific free energies f_b and f_s were shown to be close to their ground-state (zero-temperature) values, $f_b = e_b + \varphi_b$ and $f_s = e_s + \varphi_s$, where the terms φ_b and φ_s represent thermal perturbations of the ground state and are of order $\exp(-c/k_B T) \ll 1$ [18]. In some situations such estimates need not be sufficient and it is desirable to have an explicit formula from which φ_b and φ_s can be evaluated. A low-temperature cluster expansion series for f_b is well known [19–22]. On the other hand, such a series for f_s has been provided only for a large q-state Potts model [23]. Using similar arguments, in this Letter we extend the result to other models, obtaining a slightly simpler form of the series. We illustrate application of the series using a simple example.

2. The system

We will consider a system in a volume $V = L^d$ represented by a rectangular array of sites from a cubic or square lattice ($d = 2, 3$). Modifications of the results to other volumes of a parallelogram shape, other lattices, or higher dimensions are straightforward. The system will be given in a geometric fashion as a 'gas' of non-interacting objects called contours (or polymers) [24,25]. Rather canonic definitions of contours may be found, for example, in [24, 26,18]. A notorious example are the Ising contours from the Peierls argument [27,28] (see Fig. 1 below). To have a specific example in mind, let us consider here the contours that are connected unions of 'cells' (i.e., unit cubes and any of their two-dimensional faces or

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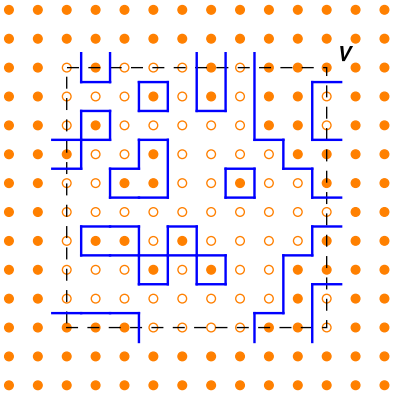

Fig. 1. The contours corresponding to a microstate in the volume $V = 10 \times 10$ (the dashed square) under fixed boundary conditions ($n_x = 1$ outside V). Vacant (occupied) sites are depicted as circles (disks).

one-dimensional edges) [18]. The length, $\Lambda(\gamma)$, of a contour γ will be the number of cells in γ. Its volume, $W(\gamma)$, is γ plus the unit cubes in all finite components of the complement to γ. We shall denote the volume and its size by an identical symbol.

Rather than via its Hamiltonian, the system in V is introduced via its partition function as [19–21]

$$Z_V = e^{-E_V/k_BT}\left[1 + \sum_{N=1,2,\ldots} \sum_{\{\gamma_1,\ldots,\gamma_N\}} \prod_{j=1}^{N} w(\gamma_j)\right], \tag{2}$$

where E_V is the energy of the ground-state in V and the second summation is over all collections of N contours that lie in V and are mutually non-intersecting. Contours usually represent thermal perturbations of a microstate over the ground state. Hence, in the absence of interfaces and large droplets, the contour weights w should be decaying with their size. Namely, an exponential decay with the contour length (called the Peierls condition) will be assumed, $|w(\gamma)| \leqslant \exp[-c\Lambda(\gamma)/k_BT]$ for some constant $c > 0$. Any lattice model with a translation invariant and finite-ranged m-potential and a finite number of ground states can be rewritten as a contour model (2) for which the Peierls condition is satisfied at low temperatures [29,30].

The free energy $F_V = -k_BT \ln Z_V$ of system (2) may be expressed as a cluster expansion series [19–22]

$$F_V = E_V - k_BT \sum_K \Phi(K). \tag{3}$$

The summation is over all clusters K, i.e., collections of contours that cannot be split into two parts such that every contour from one part would intersect no contours from the other one [19]. Due to the Peierls condition, the series in Eq. (3) quickly converges: not only that the weights of clusters decrease exponentially with their length $\Lambda(K) = \sum_{\gamma\in K} \Lambda(\gamma)$, but it is even true that

$$\sum_{K \text{ contains } x} e^{b\Lambda(K)/k_BT} \left|\Phi(K)\right| \leqslant 1 \tag{4}$$

for any fixed lattice site x and a constant $0 < b < c$. [A cluster K contains a site x whenever x lies in its volume $W(K) = \bigcup_{\gamma\in K} W(\gamma)$.] Consequently, the dominant contributions to F_V come from the clusters of small sizes, i.e., the clusters of a few small contours. The weight of a cluster containing just one contour is [19]

$$\Phi\big(\{\gamma\}\big) = \ln\big[1 + w(\gamma)\big] \approx w(\gamma). \tag{5}$$

An expression for the weight of a cluster containing any number of contours is given by Eq. (3) in [19].

There are two types of contours: those not intersecting the boundary of V of any size L (the bulk contours) and the remaining (boundary) contours. Using the bulk contours, it is easy to get the bulk contributions to the series in Eq. (3). Namely, the specific bulk free energy is [19–22]

$$f_b = e_b + \varphi_b \quad \text{with } \varphi_b = -k_BT \sum_{K_b \text{ contains } x} \frac{\Phi(K_b)}{W(K_b)}, \tag{6}$$

where the sum is over the bulk clusters K_b (those composed of the bulk contours). Here it is needed that the bulk contours have translation invariant weights. Note that the leading term in φ_b corresponds to the cluster K_b containing only the bulk contour, γ_b^0, of the smallest length, Λ_0. Thus, $\varphi_b \approx -k_BT\, w(\gamma_b^0)/W(\gamma_b^0)$. In addition, Eq. (4) yields

$$|\varphi_b| \leqslant k_BT e^{-c\Lambda_0/2k_BT}. \tag{7}$$

Remark 2.1. If there are several phases in a given system, each phase is associated with one contour partition function (2), and the Peierls condition can be satisfied only for those phases that are stable in the system [18]. For example, for a system with two possible phases the condition holds for both phases at or near the coexistence of these phases, while farther away from the coexistence only one of the two phases is stable and the condition holds for this phase and fails for the other one.

3. Surface free energy: General results

To express the surface contributions to the free energy, we need to consider the boundary contours. Namely, the contours whose intersection with the boundary of V lies within a single $(d-1)$-dimensional face, p, of V. Since face p may move as V increases, let us fix a $(d-1)$-dimensional plane of sites, P, parallel to p and consider the contours, γ_P, that are translations (perpendicular to P) of the boundary contours intersecting only face p by the distance between p and P.

We shall now show that the specific surface free energy of the system from Eq. (2) may be expressed as

$$f_s = e_s + \varphi_s \quad \text{with } \varphi_s = \varphi_{sP} - \varphi_{sb} - \varphi_b. \tag{8}$$

The first term in φ_s corresponds to the clusters, K_P, composed of the contours γ_P attached to plane P,

$$\varphi_{sP} = -k_BT \sum_{K_P \text{ contains } y} \frac{\Phi(K_P)}{\Omega(K_P)}, \tag{9}$$

where y is a fixed site from P and $\Omega(K)$ is the number of sites from P contained in K. The second term corresponds to the bulk clusters that intersect P,

$$\varphi_{sb} = -k_BT \sum_{K_b \text{ contains } y} \frac{W_b(K_b)}{W(K_b)} \frac{\Phi(K_b)}{\Omega(K_b)}, \tag{10}$$

where $W_b(K_b)$ is the number of sites from the bulk, V_b, of V contained in K_b (so, V_b is the volume V with the boundary sites excluded). In deriving Eq. (9) it is needed that the weights of contours γ_P are invariant under translations parallel to the plane P and lattice rotations around the center of V.

To verify Eq. (8), we combine Eqs. (3) and (6) to get $F_V = E_V + \varphi_b V_b + k_BT X_V$ with $V_b = (L-2)^d$ and

$$X_V = \sum_{K_b \text{ intersects bd } V} \frac{W_b(K_b)}{W(K_b)} \Phi(K_b) - \sum_{K \text{ intersects bd } V} \Phi(K), \tag{11}$$

where $\text{bd}\, V = V \backslash V_b$ stands for the boundary of V. The total contribution to X_V from the clusters intersecting only one face of V