On the Wulff Construction as a Problem of Equivalence of Statistical Ensembles

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In this note, the statistical mechanics of SOS (solid-on-solid) 1-dimensional models under the global constraint of having a specified area between the interface and the horizontal axis, is studied. We prove the existence of the thermodynamic limits and the equivalence of the corresponding statistical ensembles. This gives a simple alternative microscopic proof of the validity of Wulff construction for such models, first established in [1].

We consider the SOS model defined as follows: To each site i of the lattice $\mathbf{Z}$ an integer variable h_i is assigned which represents the height of the interface at this site. The energy $H_N(\mathbf{h})$ of a configuration $\mathbf{h} = \{h_0, h_1, ..., h_N\}$, in the box $0 \leq i \leq N$, of length N, is equal to the length of the corresponding interface

$$H_N(\mathbf{h}) = \sum_{i=1}^{N} (1 + |h_i - h_{i-1}|) \tag{1}$$

Its weight, at the inverse temperature β, is proportional to the Boltzmann factor $\exp[-\beta H(\mathbf{h})]$. More general Hamiltonians of the form $H = \sum P(|h_i - h_{i-1}|)$, where P is a strictly increasing function such that $P(x) \geq |x|$, when $x \to \infty$, can be treated in the same way. The proofs extend also to the case of continuous height variables.

We introduce the Gibbs ensemble which consits of all configurations, in the box of length N, with specified boundary conditions $h_0 = 0$ and $h_N = Y$.

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The associated partition function is given by

$$Z_1(N,Y) = \sum_{\mathbf{h}} e^{-\beta H(\mathbf{h})}\ \delta(h_0)\delta(h_N - Y) \tag{2}$$

where the sum runs over all configurations in the box and $\delta(t)$ is the dicrete Dirac delta ($\delta(t) = 1$ if $t = 0$ and $\delta(t) = 0$ otherwise). We define the corresponding free energy per site as the limit

$$\tau_p(y) = \lim_{N\to\infty} -\frac{1}{\beta N} \ln Z_1(N, yN) \tag{3}$$

where $y = -\tan\theta$, the slope of the interface, is a real number. This free energy is called the projected surface tension. The surface tension, which represents the interfacial free energy per unit length of the mean interface, is

$$\tau(\theta) = \cos\theta\ \tau_p(-\tan\theta) \tag{4}$$

We introduce also a second Gibbs ensemble, which is conjugate to the previous ensemble, and whose partition function, in the box of length N, is given by

$$Z_2(N,x) = \sum_{\mathbf{h}} e^{-\beta H(\mathbf{h})} e^{\beta x h_N}\ \delta(h_0) \tag{5}$$

where $x \in \mathbf{N}$ replaces as a thermodynamic parameter the slope y and $h_0 = 0$. We define the associated free energy as

$$\varphi(x) = \lim_{N\to\infty} -\frac{1}{\beta N} \ln Z_2(N,x) \tag{6}$$

Theorem 1. *Limits (3) and (6), which define the above free energies, exist. The first, τ_p, is a convex even function of y. The second, φ, is a concave even function of x. Moreover, τ_p and $-\varphi$ are conjugate convex functions, i.e., they are related by the Legendre transformations*

$$\begin{aligned} -\varphi(x) &= \sup_y\, [xy - \tau_p(y)] \\ \tau_p(y) &= \sup_x\, [xy + \varphi(x)] \end{aligned} \tag{7}$$

Proof. The validity of the above statements is well known. See for instance [2, 3] for a proof of these results in a more general setting. □

The convexity of τ_p is equivalent to the fact that the surface tension τ satisfies a stability condition called the triangular inequality [2, 3]. Relations (7) between the free energies express the thermodynamic equivalence of the two ensembles (2) and (5).

These relations imply that the curve $z = \varphi(x)$ gives, according to the Wulff construction or its modern equivalent the Andreev construction, the equilibrium shape of the crystal associated to our system [3].

The function $\varphi(x)$ defined by (6) is easily computed by summing a geometrical serie. One introduces the difference variables

$$n_i = h_{i-1} - h_i \tag{8}$$

for $i = 1, ..., N$, so that the partition function factorizes and one obtains

$$\varphi(x) = 1 - \beta^{-1} \ln \sum_{n \in \mathbf{Z}} e^{-\beta|n| + \beta x n} \tag{9}$$

The explicit form of this function is

$$\varphi(x) = 1 - \beta^{-1} \ln \frac{\sinh \beta}{\cosh \beta - \cosh \beta x} \tag{10}$$

if $-1 < x < 1$ and $\varphi(x) = -\infty$ otherwise.

We next define two new Gibbs ensembles for the system under consideration. In the first of these ensembles we consider the configurations such that $h_N = 0$, which have a specified height at the origin $h_0 = M$ and which have a specified volume V between the interface and the horizontal axis, this volume being counted negatively for negative heights:

$$V = V(\mathbf{h}) \equiv \sum_{i=0}^{N} h_i \tag{11}$$

The corresponding partition function is

$$Z_3(N, V, M) = \sum_{\mathbf{h}} e^{-\beta H(\mathbf{h})} \ \delta(h_N) \delta(V(\mathbf{h}) - V) \delta(h_0 - M) \tag{12}$$

The second of these ensembles is the conjugate ensemble of the first one. Its partition function is given by

$$Z_4(N, u, \mu) = \sum_{\mathbf{h}} e^{-\beta H(\mathbf{h})} \ e^{\beta u(V(\mathbf{h})/N) + \beta \mu h_0} \ \delta(h_N) \tag{13}$$

where $u \in \mathbf{N}$ and $\mu \in \mathbf{N}$ are the conjugate variables. Our next step will be to prove the existence of the thermodynamic limit for these ensembles and their equivalence in this limit. We shall take $N = 2^n$, $n \in \mathbf{N}$. In (12), V and M must be understood as their integer part when they do not belong to $\mathbf{Z}$.

Theorem 2. *The following limits exist*

$$\begin{aligned} \psi_3(v,m) &= \lim_{N\to\infty} -\frac{1}{\beta N} \ln Z_3(N, vN^2, mN) \qquad (14) \\ \psi_4(u,\mu) &= \lim_{N\to\infty} -\frac{1}{\beta N} \ln Z_4(N, u, \mu) \qquad (15) \end{aligned}$$

They define the free energies per site associated to the considered ensembles as, respectively, convex and concave functions of their variables. Moreover, ψ_3 and $-\psi_4$ are conjugate convex functions:

$$\begin{aligned} -\psi_4(u,\mu) &= \sup_{v,m} \left[uv + \mu m - \psi_3(v,m)\right] \\ \psi_3(v,m) &= \sup_{u,\mu} \left[uv + \mu m + \psi_4(u,\mu)\right] \end{aligned} \qquad (16)$$

Proof. The crucial observation is the subadditivity property given in Lemma 1 below. Then we addapt known arguments [4, 5] in the theory of the thermodynamic limit. A more detailed discussion is given in the Appendix. □

Lemma 1. *The partition function Z_3 satisfies the subadditivity property*

$$Z_3(2N, 2(V'+V''), M'+M'') \geq Z_3(N, V', M')\ Z_3(N, V'', M'')\ e^{-2\beta|M''|/(2N-1)} \qquad (17)$$

Proof. In order to prove this property we associate a configuration $\mathbf{h}$ of the first system in the box of length $2N$, to a pair of configurations $\mathbf{h}'$ and $\mathbf{h}''$ of the system in a box of length N, as follows

$$\begin{aligned} h_{2i} &= h'_i + h''_i\ , \qquad i = 0, \ldots, N \\ h_{2i-1} &= h'_{i-1} + h''_i\ , \quad i = 1, \ldots, N \end{aligned} \qquad (18)$$

Then $h_{2N} = h'_N + h''_N = 0$, $h_0 = h'_0 + h''_0 = M' + M''$ and

$$\begin{aligned} V(\mathbf{h}) &= 2\sum_{i=1}^{N} h'_i + \sum_{i=0}^{N} h''_i + \sum_{i=1}^{N} h''_i \\ &= 2\left[V(\mathbf{h}') + V(\mathbf{h}'')\right] - M'' \end{aligned}$$

This shows that the configuration $\mathbf{h}$ belongs to $Z_3(2N, 2(V'+V'')-M'', M'+M'')$. Since $H_{2N}(\mathbf{h}) = H_N(\mathbf{h}') + H_N(\mathbf{h}'')$, because $n_{2i} = n'_i$ and $n_{2i-1} = n''_i$ for $i = 1, ..., N-1$, as follows from (18), we get

$$Z_3(N, V', M')\; Z_3(N, V'', M'') \leq Z_3(2N, 2(V'+V'') - M'', M' + M'')$$

Then we use the change of variables $\tilde{h}_i = h_i + [M''/(2N-1)]$ for $i = 1, \ldots, 2N-1$, $\tilde{h}_0 = h_0$, $\tilde{h}_{2N} = h_{2N} = 0$ which gives

$$Z_3(2N, V - M'', M) \leq e^{2\beta|M''|/(2N-1)}\; Z_3(2N, V, M)$$

to conclude the proof. □

The subadditivity property and thus also Theorem 2 are satisfied when the height variables h_i are restricted to take non negative values.

Theorem 3. *The functions ψ_3 and ψ_4 can be expressed in terms of the functions φ and τ_p as follows*

$$\psi_3(v, m) = \frac{1}{u_0}\int_{\mu_0}^{\mu_0+u_0} \tau_p(\varphi'(x))dx \tag{19}$$

$$\psi_4(u, \mu) = \frac{1}{u}\int_0^u \varphi(x+\mu)dx \tag{20}$$

if u_0 and μ_0 satisfy

$$\frac{1}{u_0^2}\int_0^{u_0} \varphi(x+\mu_0)dx - \frac{1}{u_0}\varphi(\mu_0+u_0) = v \tag{21}$$

$$\frac{1}{u_0}[\varphi(\mu_0) - \varphi(\mu_0+u_0)] = m \tag{22}$$

Proof. We consider again the difference variables (8) and observe that

$$V(\mathbf{h}) = \sum_{i=0}^{N} h_i = \sum_{i=1}^{N} i n_i$$

therefore

$$Z_4(N, u, \mu) = \prod_{i=1}^{N}\Big(\sum_{n_i\in\mathbf{Z}} e^{-\beta|n_i|+\beta(u/N)in_i+\beta\mu n_i}\Big)$$

Taking expression (9) into account it follows

$$Z_4(N,u,\mu) = \exp\Big(-\beta \sum_{i=1}^{N} \varphi(\frac{u}{N} i + \mu)\Big)$$

and

$$\psi_4(u,\mu) = \lim_{N\to\infty} \frac{1}{N} \sum_{i=1}^{N} \varphi(\frac{u}{N} i + \mu) = \lim_{N\to\infty} \frac{1}{u} \sum_{i=1}^{N} \frac{u}{N} \varphi(\frac{u}{N} i + \mu)$$

which implies expression (20) in the Theorem.

The function ψ_3 is determined by the Legendre transform (16). The supremum over u, μ is obtained for the value u_0, μ_0 for which the partial derivatives of the right hand side are zero: $v + (\partial\psi_4/\partial u)(u_0,\mu_0) = 0,\ m + (\partial\psi_4/\partial\mu)(u_0,\mu_0) = 0$. That is, for u_0, μ_0 which satisfy (21) and (22).

Then, from (16), (20), (21) and (22), we get

$$\psi_3(v,m) = 2\psi_4(u_0,\mu_0) - \frac{1}{u_0}[(\mu_0+u_0)\varphi(\mu_0+u_0) - \mu_0\varphi(\mu_0)] \tag{23}$$

The right hand side of (23) represents twice the area of the sector OBC in Fig. 1 divided by u_0.

But, it is a known property in the Wulff construction, that twice this area is equal to the integral in (19). Indeed, by using the relation (7) under the form

$$\varphi(x) = x\varphi'(x) + \tau_p(\varphi'(x))$$

in (20) and integrating by parts $x\varphi'(x)$, we get

$$2\psi_4(u_0,\mu_0) = \frac{1}{u_0}\int_{\mu_0}^{\mu_0+u_0} \tau_p(\varphi'(x))dx + \frac{1}{u_0}[(\mu_0+u_0)\varphi(\mu_0+u_0) - \mu_0\varphi(\mu_0)]$$

which together with (23) implies the expression (19) in the Theorem. □

To interpret these relations, let us observe that the right hand side of (21) represents the area ABC, in Fig. 1, divided by $\overline{AC}^2$. Therefore, the values u_0, μ_0, which solve (21) and (22), are obtained when this area is equal to v, with the condition coming from (22), that the slope $\overline{AB}/\overline{AC}$, is equal to m. Then, according to (19), the free energy $\psi_3(v,m)$ is equal to the integral of the surface tension along the arc BC, of the curve $z=\varphi(x)$, divided by the same scaling factor $\overline{BC} = u_0$.

We conclude that, for large N, the configurations of the SOS model, with a prescribed area vN^2, follow a well defined mean profile, the macroscopic profile given by the Wulff construction, with very small fluctuations. This follows from the fact that the probability of the configurations which deviate macroscopically from the mean profile is zero in the thermodynamic limit. The free energy associated to the configurations which satisfy the conditions above, and moreover, are constrained to pass through a given point not belonging to the mean profile, can be computed with the help of Theorem 3. The corresponding probabilities decay exponentially as $N \to \infty$, as a concequence of the usual large deviations theory in statistical mechanics [6].

Appendix

We give here a more detailed discussion of the proof of Theorem 2. We define:

$$f_n(v, m) = -\frac{1}{\beta 2^n} \ln Z_3(2^n, 2^{2n}v, 2^n m)$$

For v and m of the form $2^{-q}p$, the subadditivity property with $N = 2^n$, $V' = V'' = vN^2$ and $M' = M'' = mN$ implies that f_n is a decreasing sequence: $f_{n+1}(v, m) \leq f_n(v, m)$. Since this sequence is

bounded from below its limit exits when n tends to infinity and coincide with

$$\psi_3(v, m) = \inf_N \left[-\frac{1}{\beta N} \ln Z_3(N, vN^2, mN) \right] \tag{24}$$

Indeed

$$Z_3(N, V, M) \leq \sum_{\mathbf{h}} e^{-\beta H(\mathbf{h})} \delta(h_N)$$

The right hand side of the above expression is easily computed by inroducing the difference variables (8) and we get that f_n is bounded from below by $1 + (1/\beta) \ln \tanh(\beta/2)$. Let us notice that one can obtain a lower bound to $Z_3(N, vN^2, mN)$ by restricting the summation to the configuration such that $(N-1)h_i = vN^2 - mN$ for $i = 1, \ldots, N-1$. This gives that f_n is bounded from above by $1 + |v - m| + |v|$.

To prove that ψ_3 is convex, we notice that the subadditivity inequality (17) with $N = 2^n$, $V' = v_1 N^2$, $V'' = v_2 N^2$ and $M' = M'' = mN^2$ gives:

$$\psi_3\Big(\frac{1}{2}(v_1 + v_2), m\Big) \leq \frac{1}{2}\psi_3(v_1, m) + \frac{1}{2}\psi_3(v_2, m)$$

which applied iteratively implies:

$$\psi_3\Big(\alpha v_1 + (1-\alpha)v_2, m\Big) \leq \alpha\psi_3(v_1, m) + (1-\alpha)\psi_3(v_2, m)$$

for α of the form $2^{-q}p$ and $0 \leq \alpha \leq 1$. For such α we obtain analogously

$$\psi_3\Big(v, \alpha m_1 + (1-\alpha)m_2\Big) \leq \alpha\psi_3(v, m_1) + (1-\alpha)\psi_3(v, m_2)$$

by applying the subadditivity inequality (17) with $N = 2^n$, $M' = m_1 N^2$, $M'' = m_2 N^2$ and $V' = V'' = vN^2$. Since ψ_3 is bounded, it follows, cf. [4], that ψ_3 can be extended to a convex Lipshitz continuous function of the real variables v and m.

To prove the the existence of the limit (15) and relations (16), we introduce

$$Z_4^+(N, u, \mu) = \sup_{V, M \in \mathbf{Z}} \Big[e^{\beta u(V/N) + \beta\mu M}\ Z_3(N, V, M)\Big]$$

and proceed, as in the Appendix of [5], to study the thermodynamic limit for this quantity. We introduce the convex function

$$\psi_4^*(u, \mu) = \sup_{v,m}\ [uv + \mu m - \psi_3(v, m)]$$

According to (24), we have

$$e^{\beta u(V/N) + \beta\mu M}\ Z_3(N, V, M) \leq e^{\beta N[uv + \mu m - \psi_3(v,m)]}$$

for all $V, M \in \mathbf{Z}$, so that

$$Z_4^+(N, u, \mu)\ \leq\ e^{\beta N \psi_4^*(u,\mu)} \tag{25}$$

On the other hand for any $\delta > 0$ and sufficiently large N one can find, $V = vN^2$ and $M = mN$ such that

$$\begin{aligned} e^{\beta u(V/N) + \beta\mu M}\ Z_3(N, V, M) &= e^{\beta N[uv + \mu m - \psi_3(v,m)]}\ e^{\beta N \psi_3(v,m)}\ Z_3(N, V, M) \\ &\geq e^{\beta N[\psi_4^*(u,\mu) - \delta]} \end{aligned}$$

and therefore

$$Z_4^+(N,u,\mu) \;\geq\; e^{\beta N[\psi_4^*(u,\mu)-\delta]} \tag{26}$$

Inequalities (25) and (26) imply that

$$\lim_{N\to\infty} -\frac{1}{\beta N}\;\ln Z_4^+(N,u,\mu) \;=\; -\psi_4^*(u,\mu) \tag{27}$$

We shall now prove that the thermodynamic limit (15) exits and gives the same quantity following the argument of Theorem 2 in [5]. First, we notice that

$$Z_4(N,u,\mu) = \sum_{V,M\in\mathbf{Z}} e^{\beta u(V/N)+\beta\mu M}\; Z_3(N,V,M)$$

which implies

$$Z_4^+(N,u,\mu) \leq Z_4(N,u,\mu) \tag{28}$$

Moreover, the inequality

$$Z_3(N,V,M) \leq e^{-\beta\bar{u}(V/N)-\beta\bar{\mu}M}\; Z_4^+(N,\bar{u},\bar{\mu})$$

used with $\bar{u}=u'$ and $\bar{u}=u''$, $\bar{\mu}=\mu'$ and $\bar{\mu}=\mu''$ gives for any $u''<u<u'$ and any $\mu''<\mu<\mu'$:

$$\begin{aligned} Z_4(N,u,\mu) \;&\leq\; Z^*\sum_{V\geq 0} e^{\beta(u-u')(V/N)}\sum_{M\geq 0} e^{\beta(\mu-\mu')M} \\ &+\; Z^*\sum_{V\leq 0} e^{\beta(u''-u)(V/N)}\sum_{M\geq 0} e^{\beta(\mu-\mu')M} \\ &+\; Z^*\sum_{V\geq 0} e^{\beta(u-u')(V/N)}\sum_{M\leq 0} e^{\beta(\mu''-\mu)M} \\ &+\; Z^*\sum_{V\leq 0} e^{\beta(u''-u)(V/N)}\sum_{M\leq 0} e^{\beta(\mu''-\mu)M} \\ &\leq\; \frac{4Z^*}{(1-e^{-\beta(\Delta u/N)})(1-e^{-\beta(\Delta\mu)})} \end{aligned} \tag{29}$$

where

$$\begin{aligned} Z^* &= \sup\{Z_4^+(N,u',\mu'), Z_4^+(N,u',\mu''), Z_4^+(N,u'',\mu'), Z_4^+(N,u'',\mu'')\} \\ \Delta u &= \min\{u'-u, u-u''\} > 0 \\ \Delta u &= \min\{\mu'-\mu, \mu-\mu''\} > 0 \end{aligned}$$

By referring to (27), and to the continuity of ψ_4^*, the
inequalities (28) and (29) imply (15) and (16).

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References

[1] J. De Coninck, F. Dunlop, and V. Rivasseau, On the microscopic validity of the Wulff construction and of the generalized Young equation, *Commun. Math. Phys.* **121**, 401–419 (1989).

[2] R. L. Dobrushin, R. Kotecký and S. B. Shlosman, "Wulff Construction: A Global Shape from Local Interactions," Am. Math. Soc., Providence, RI (1992).

[3] A. Messager, S. Miracle-Solé and J. Ruiz, Convexity properties of the surface tension and equilibrium crystals, *J. Stat. Phys.* **67**, 449–470 (1992).

[4] D. Ruelle, " Statistical Mechanics: Rigorous Results," Benjamin, New York Amsterdam (1969).

[5] L. Galgani, L. Manzoni, and A. Scotti, Asymptotic equivalence of equilibrium ensembles of classical statistical mechanics, *J. Math. Phys.* **12**, 933–935 (1971).

[6] D. Ruelle, "Hasard et Chaos" (chap. 19), Odile Jacob, Paris (1991). O. Landford, Entropy and equilibrium states in classical statistical mechanics, *in*: "Statistical Mechanics and Mathematical Problems," A. Lenard, ed., Springer, Berlin (1973).

Figure Captions

Figure 1. Graphical interpretation of Theorem 3.