

Wulff shape for equilibrium phases

by

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Abstract

We use surface tension to distinguish between phases with isotropic internal structure from phases which are microscopically anisotropic. There are many interesting open problems, especially in two dimensions, and in phase coexistence.

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The sphere is the shape which minimizes the surface tension of a drop of fluid. On the molecular scale a fluid – gas or liquid – consists of an isotropic, disorderly configuration of particles. The Wulff shape traditionally plays the same minimum-surface-tension role, but for the orderly, anisotropic particle configurations of crystals. For an intuitive picture consider liquid oil filling a large cylinder with a movable piston at one end, so the oil can be subjected to a range of pressure. The cylinder should also be temperature controlled. Now imagine a drop of water was injected into the middle of the oil, the water and oil being immiscible. The water would quickly attain a spherical shape because of surface tension. (We are ignoring gravity.) Finally, by slowly varying the temperature and/or pressure of the oil we can change the water to ice, which is crystalline at the molecular scale. The external shape which the ice assumes is its polyhedral Wulff shape: the sphere of water becomes a polyhedron of ice. We emphasize that the boundary shape is therefore an indicator of the different internal structure between fluid water and solid ice. Indeed the existence of facets in crystals was the inspiration for Haüy to conjecture an atomic-like structure for matter back in the eighteenth century [H]. We will return to this point, which is the focus of this article.

Many years ago the mathematics of minimum-surface-tension surfaces was extended within the calculus of variations from Plateau’s problem, by Jean Taylor and others [T], to include a wide range of possible anisotropic formulas for surface tension, which one imagines are based on a supposed underlying structure, with crystalline structures being simple examples. However in physics ‘surface tension’, like ‘crystal’, is random at the molecular scale. We describe here an attempt to model minimum-surface-tension shapes in this more fundamental setting. Afterwards we contrast our approach with recent work on Wulff shapes in the Ising model, where the objective (and meaning) is quite different, based on different roles for randomness in the two settings.

Consider the pressure-temperature ensemble for N particles in \mathbb{R}^d , in a container of shape S , with potential energy function, for particles at x and y , given by:

$$v(x, y) = \begin{cases} +\infty, & \text{if } |x - y| < 1; \\ |x - y| - 3, & \text{if } 1 \leq |x - y| \leq 3; \\ 0, & \text{if } |x - y| > 3. \end{cases} \quad 1)$$

Usually one chooses some container shape such as a unit cube, and then the distribution is over the volume V and the $2N$ position-momentum coordinates of the N particles restricted to the container scaled to have volume V . The distribution depends on parameters T, P as follows.

Given a function f of $2m$ particle coordinates, $x_1, \dots, x_m, p_1, \dots, p_m$, $m < N$, the integral of f is:

$$\frac{1}{Z_N(P, T)} \int_{(VS)^N \times \mathbb{R}^{dN} \times \mathbb{R}^+} f(x_1, \dots, x_m, p_1, \dots, p_m) e^{-\beta E(x_1, \dots, x_N, p_1, \dots, p_N)} e^{-\beta PV} dx_1 \dots dx_N dp_1 \dots dp_N dV, \quad 2)$$

$$E(x_1, \dots, x_N, p_1, \dots, p_N) = \sum_{j=1}^N p_j^2/2 + \sum_{j,k=1}^N v(x_j, x_k), \quad 3)$$

$\beta = 1/(k_B T)$, and $Z_N(P, T)$ is the normalization constant:

$$Z_N(P, T) = \int_{(VS)^N \times \mathbb{R}^{dN} \times \mathbb{R}^+} e^{-\beta E(x_1, \dots, x_N, p_1, \dots, p_N)} e^{-\beta PV} dx_1 \dots dx_N dp_1 \dots dp_N dV. \quad 4)$$

Although it has not been proven, it is expected that in the limit of large N this standard formalism will exhibit the familiar thermodynamic phases as in Figure 1, at least for $d = 3$. We elaborate on that in the context of a new twist.

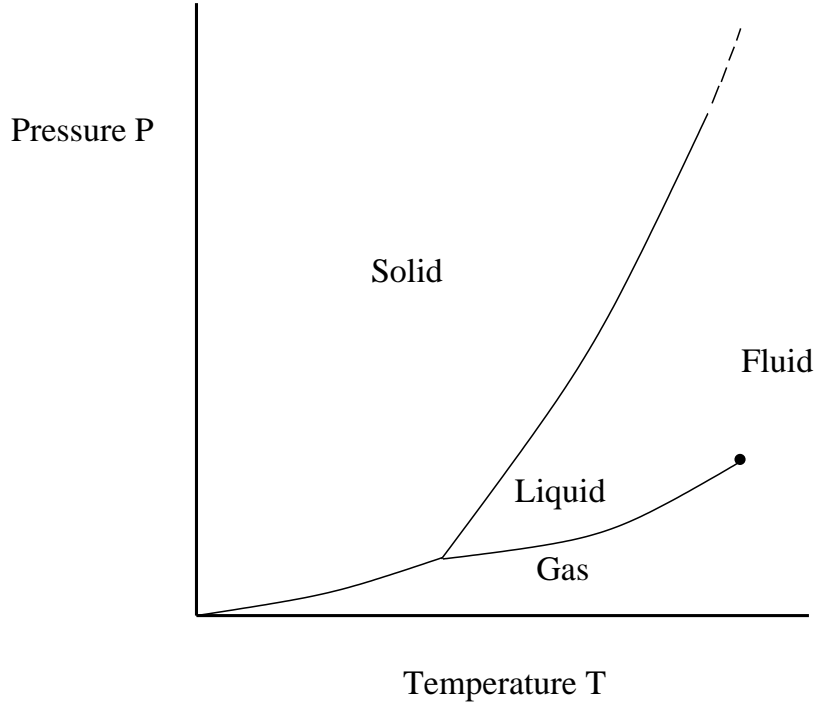


Figure 1. The phase diagram of a simple material.

As a new feature we propose to treat the (star-shaped, fixed volume) container shape S as a variable. For fixed S it is expected that for ‘most’ pairs (T, P) , i.e. except for phase coexistence on the phase transition curves in Figure 1, there is a unique Euclidean invariant weak-limit Gibbs probability measure as $N \rightarrow \infty$, which is *independent of S* . This is why S is not usually considered an interesting variable. However the phenomenon we wish to model is a surface effect, so it is necessary to analyze finite systems before taking any infinite system limit. (This approach is related to the one in [AR], which used a different surface effect.)

For each S the pressure-temperature ensemble defined by 2) is a probability distribution over particle configurations. If we think of S as a free surface, the minimization of (the dissipative) surface tension can be implemented by minimizing the average total energy of the configurations: particles away from the boundary obtain a certain negative potential energy from their surrounding particles, while those near the surface have a higher potential energy – losing the negative potential energy of missing neighbors – so minimizing the energy should tend to minimize surface area. This is the underlying nature of ‘surface tension’. Now this should lead to S being a sphere if most configurations are isotropic, as

in a fluid, but not if they are ordered, as in a crystal. This is the idea, but how does one implement a free surface?

If we model the surface as an interface between molecular water and molecular oil we would have to show that the interface becomes sharp under some scaling. Instead we will assume the interface is sharp (completely immiscible fluids) but flexible, responding to the random configuration of water molecules, i.e. negligible surface tension for the oil. It will still be difficult to obtain a well-defined optimal shape, as we shall see.

Consider the mean value $\langle E \rangle_T^P(S, N)$ of the total energy E for the system with N particles, where we emphasize its dependence on S and N . Let us define a topological space for S . Since we are only interested in star-shaped S , we model S by giving the radial coordinate ρ as a positive continuous function of ‘angle’ α , i.e. a point on the compact unit sphere S^d . More specifically, starting with the set of continuous functions on S^d with values $\rho(\alpha) \geq 1$, we then define the subset associated with volume 10 (computed in spherical coordinates from ρ), and finally define our space of shapes as the quotient \mathcal{S} of that space by Euclidean motions, in the quotient topology. For each point in \mathcal{S} we have defined in 2), using similarities VS of $S \in \mathcal{S}$, the family of pressure-temperature probability distributions, which are continuous in S in the weak topology. In particular $\langle E \rangle_T^P(S, N)$ is continuous in S . At this point we do not see an easy way to prove the existence of the minima we want, to eventually define a Wulff shape as a function of (T, P) . Technically we now do this by replacing \mathcal{S} by some convenient compact subset, containing at least the sphere and some appropriate polyhedra. (For instance Lipschitz continuous with fixed Lipschitz constant.) This is unsatisfying, but does not impede our main goal, as we shall see. Choosing such a subset we find that $\langle E \rangle_T^P(S, N)$ achieves a minimum at one or more $S = S_W(P, T, N)$. We denote by $S_W(P, T)$ any accumulation point, as $N \rightarrow \infty$, of these $S_W(P, T, N)$, and call it a Wulff shape for (T, P) .

For $d = 3$, large fixed N , any fixed $T > 0$ and S , and all large enough P (high density) i.e. above the solid/fluid transition in Figure 1, the pressure-temperature distribution is expected to concentrate on ‘crystal-like’ particle configurations, while for all small enough P (low density) i.e. below the transition, it is expected to concentrate on highly disordered configurations, with a sharp transition between the two regimes as $N \rightarrow \infty$, defining the transition curve. Therefore fixing T and large N , we expect for all large enough P that $S_W(P, T, N)$ would be approximately a polyhedral shape (cuboctahedron) which minimizes the boundary for densest packing of spheres [BoRa] (and $S_W(P, T)$ to be exactly this), while for all small enough P , we expect $S_W(P, T, N)$ to be approximately the sphere (and $S_W(P, T)$ to be exactly this), since it minimizes the energy due to particles near the surface. In both cases this is a surface effect.

Needless to say these conjectures are far from proven; after all, they imply a solid/fluid phase transition, something that has so far resisted proof in any reasonable model; see however [BLRW]. In fact one reason for taking this path is the hope that perhaps this could be a way to prove such a transition [AR]. Indeed, if one could simply prove that for some (P, T) the sphere gives a lower value to surface energy than some other shape, say a polyhedron, while for other (P, T) the polyhedron gives a lower value than the sphere, this would be of great interest, and we emphasize that this does not require proving the existence of optimal shapes.

We also note that in the above two paragraphs we assumed $d = 3$. The reason is

that for $d = 2$ it is known that you cannot have a crystal in the full sense of long-range positional order [Ri], the densest phase presumably only having orientational long-range order [BK]. It is therefore an interesting open problem to determine what the Wulff shape would be for high pressure in our model in $d = 2$. (The regular hexagon is a natural candidate, and was proven for $T = P = 0$ in [Ra].)

At this point one might naturally ask what happens to the Wulff shapes as one varies (T, P) through the phase transition curve separating the solid and fluid phases. In terms of the oil/water discussion above, for (T, P) actually on the curve separating the fluid and solid phases one has a mixture of liquid water and a chunk of ice coexisting together in the oil. (To fix the relative volume of each phase one needs to use a different ensemble than the one used here.) One could perhaps analyze the shape of the ice in contact with (perhaps surrounded by) water, but we emphasize that this is inherently different from the above analysis within the pure fluid and solid phases, and is precisely the problem we avoided by not modeling the oil at a molecular level. In particular one would have to address the question of whether it is appropriate to consider the interface between water and ice as well-defined, since we expect molecules to be constantly moving from one phase-region to the other. We avoided this by assuming (complete) immiscibility of the water and oil. This phenomenon has been the focus of a sequence of beautiful works in probability, as part of an emerging subfield called ‘limit shapes’: not however for the interface between ice and water, but for that between water and steam, in both of which the internal structure is isotropic. (For a useful introduction to limit shapes, including a review of work on Wulff shapes in the Ising model, see the Colloquium lectures of Okounkov [O].) Assuming the reader is somewhat familiar with the Ising model we give a very brief description of this work, with an emphasis on contrasting it with our modeling with Wulff shapes above.

The ferromagnetic Ising model on the square lattice can be presented (in the so-called grand canonical ensemble) in terms of a two parameter family of probability distributions, the parameters being temperature $T > 0$ and a constant external magnetic field B . It exhibits one phase, with a transition across a segment of the line $B = 0$ as indicated in Figure 2.

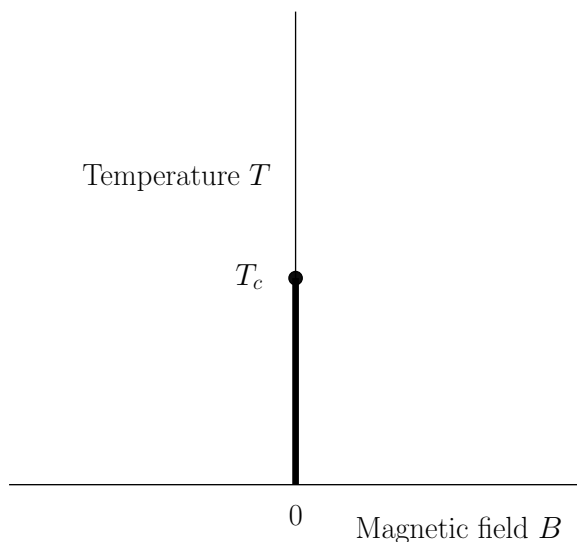


Figure 2. The phase diagram of the Ising model.

As we have done for the particle model with interaction 1), the Ising model is usually presented first for a finite system, and then one takes an infinite system limit. If one introduces a fixed boundary for the finite system model using a star-shaped curve S as done above for models based on 1), one sees that for $B \neq 0$ the Wulff shape based on minimizing energy is a square. The case $B = 0$ is more complicated and includes the temperature interval $[0, T_c)$, below the critical point, where the limiting probability measure is not unique and represents coexistence of states rich in spin up with states rich in spin down. When $B < 0$ one only gets the spin up type and when $B > 0$ one only gets the spin down type, and as noted above each has a square Wulff shape. One might imagine this perseveres in coexistence where both types of states are present, but careful analysis shows that the situation is more complicated [O].

Our reason for bringing up this work on the Ising model is to avoid confusion between the Ising work on the shape of interfaces, for thermodynamic parameters representing coexistence (or a ‘mixed phase’), from our modeling of minimum surface energy in a pure ‘solid’ phase with anisotropic internal structure; the analyses are focused on different problems but both use the term Wulff shape. If we view the Ising model as a lattice gas following Lee-Yang [LY], the work on Ising Wulff shape could naturally be interpreted as an analysis of the interface between water and steam (both having the same isotropic Wulff shape), in particular the scaling appropriate to making the interface sharp, while ours does not seriously attempt to determine well-defined optimal surfaces, and instead tries to analyze the difference between the internal structure of water and ice, each in its isolated state. Our motivation is that the transition between water and steam is generally considered well understood (away from the critical point!) as a transition between high density and low density states of a single fluid phase, while the transition between ice and water is not well understood. Following Landau the solid/fluid transition is usually associated with a change of symmetry in structure at the molecular level, and this is used in attempts to understand the level of continuity of the transition (see [RRS]). This paper is an attempt to use surface tension to distinguish such phases.

In conclusion the main question we pose, for dimensions $d = 2, 3$, is:

For the model of particles interacting through 1) is surface tension lower (i.e. is the average energy lower) for a polyhedron than the sphere for fixed temperature and all sufficiently high pressure? This is particularly interesting in dimension 2 since one still expects an ordered state in that regime [BK] even though it cannot be a true crystal in the sense of positional long-range order [Ri].

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