A novel method for evaluating the critical nucleus and the surface
tension in systems with first order phase transition

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Abstract

We introduce a novel method for calculating the size of the critical nucleus and the value of
the surface tension in systems with first order phase transition. The method is based on classical
nucleation theory, and it consists in studying the thermodynamics of a sphere of given radius
embedded in a frozen metastable surrounding. The frozen configuration creates a pinning field
on the surface of the free sphere. The pinning field forces the sphere to stay in the metastable
phase as long as its size is smaller than the critical nucleus. We test our method in two first-order
systems, both on a two-dimensional lattice: a system where the parameter tuning the transition is
the magnetic field, and a second system where the tuning parameter is the temperature. In both
cases the results are satisfying. Unlike previous techniques, our method does not require an infinite
volume limit to compute the surface tension, and it therefore gives reliable estimates even by using
relatively small systems. However, our method cannot be used at, or close to, the critical point,
i.e. at coexistence, where the critical nucleus becomes infinitely large.
I. INTRODUCTION

Whenever in a system there is coexistence of two (or more) thermodynamic phases, the crucial issue arises of how to compute the free energy cost associated to creating a surface among the different phases. This cost is the surface tension. The surface tension is relevant in the case of broken ergodicity at equilibrium, when the two phases have the same free energy density, as for example in the Ising model below $T_c$ at zero magnetic field: equilibrium droplet excitations of a phase within the dominating opposite phase, as well as off-equilibrium coarsening dynamics of competing domains, are all phenomena quantitatively ruled by the surface tension cost. The surface tension is in fact related to the prefactor of the square gradient term suppressing fluctuations of the order parameter in any field-theoretical approach to statistical physics.

Surface tension is also a key ingredient in nucleation theory, that is the theory of how metastable states decay when crossing a first order critical point. In this case the two phases do not have the same free-energy density. Rather, the metastable phase has higher free energy, and it decays by nucleating droplets of the stable phase. The thermodynamic advantage of a nucleus is proportional to its volume, while its cost is proportional to the surface. Therefore, nucleation is a competition between the bulk free energy difference and the surface tension between the two phases. As a consequence, computing the surface tension is essential also in this context.

Numerical determinations of the surface tension are not trivial. Leamy and coworkers compared two systems: one in which opposite boundary conditions give origin to an interface between two phases with the same free-energy, and a second one with uniform boundary conditions. They numerically evaluated the extra free-energy density profile of a dividing surface (essentially flat up to fluctuations) and the density variation across this surface. Some years later Binder presented a method suitable for studying the free-energy excess density near the critical point, where the correlation length is large and the excess free-energy is small and strongly fluctuating. Binder’s method therefore works well in a region where the Leamy method is not accurate. The main idea of this method is that in a broken symmetry phase, the (small) probability of having order parameter equal to zero is dominated by configurations with phase separation, where the surface tension contribution is the most relevant. Binder’s method, currently the standard for computing the surface
tension, is theoretically very well motivated and it shows a good agreement with experimental data, even compared with the results of some analytical approaches. However, this method requires the introduction of several fitting parameters, and, more importantly, the results depend on the infinite-size extrapolation.

Both these methods compute the surface tension between two phases of equal free-energy density. However in the context of first-order transition and nucleation theory, we deal with the free-energy cost of surfaces between a stable and a metastable phase. The theoretical context is therefore slightly different, as are the numerical methods to compute the surface tension. The transition path sampling (TPS) method, is based on the idea of sampling the distribution of paths in the phase space with a Monte-Carlo procedure analogous to the sampling of the canonical probability density of many-particle system. The TPS method can be used in the context of nucleation, but more generally it is a very useful tool for all dynamical problems dominated by rare events, as the dissociation of weak acid in water or protein folding. Due to its intrinsic generality, the TPS method is numerically heavier and somewhat less suited to the study of first order transitions, than a method directly inspired by nucleation theory. The aim of the present work is to introduce such a method.

The main idea of our method is to study the thermodynamics a sphere of radius $R$ embedded in a system frozen into a typical metastable configuration. The metastable surrounding produces a frozen pinning field (FPF) at the surface of the sphere, which biases the Gibbs distribution of the sphere. For small $R$ the sphere is kept in the metastable phase by the pinning field, whereas for large $R$ the free-energy gap drives the sphere to the stable phase. The value of $R$ where the probability for the sphere to be in the metastable phase is the same as in the stable one gives the critical nucleus, and from this the surface tension can easily be calculated. The FPF idea of using constrained systems to modify the Gibbs measure and magnify the effect of metastability, is well known in disordered systems, and in particular in spin-glasses. In fact, the FPF method was originally proposed for the study of glassy systems to test the Mosaic scenario.

In Sec. II we will make a short review of classic nucleation theory and explain the FPF method in general. As a warm-up exercise, in Sec. III we will study the method in absence of metastability, where it will turn out to be a tool for computing the correlation length of the system. In Sec. IV the FPF method is applied to the ferromagnetic Ising model.
\(d = 2\), with nonzero magnetic field. In this case there is a first-order phase transition driven by the field, and we will compute the surface tension at different values of the magnetic field and of the temperature. The obtained surface tension values will be compared with the exact Onsager results. In Sec. \(V\) we will consider a different first-order model, where the tuning parameter is temperature, rather than field. This case is interesting, since it mimics the liquid-crystal transition, and it allows to investigate the method in the case of a disorder-order phase transition.

II. THE FROZEN PINNING FIELD METHOD

The frozen pinning field (FPF) method is inspired by homogeneous nucleation theory, originally introduced by Gibbs in 1948\textsuperscript{24}. A system in a metastable phase makes the transition via the formation of droplets (nuclei) of the stable phase. The free-energy cost, \(\Delta F(R)\), of a nucleus of linear size \(R\) is given by the balance between a volume gain, proportional to the bulk free-energy density difference between the two phases \(\delta f\), and a surface price, proportional to the surface tension \(\sigma\),

\[
\Delta F(R) = -V_d R^d \delta f + S_d R^{d-1} \sigma , \tag{1}
\]

where \(V_d\) and \(S_d\) are the volume and surface numerical prefactors related to the shape of the droplet in dimension \(d\). The critical nucleus size,

\[
\hat{R} = \left(\frac{d-1}{d V_d}\right) S_d \frac{\sigma}{\delta f} , \tag{2}
\]

that maximizes Eq. (1), distinguishes smaller unstable nuclei that will shrink, from bigger stable nuclei, which are thermodynamically favoured to grow. When the volume gain exceeds the surface cost, the nuclei become stable, and the system is heterogeneous. At that point growth can start, and it will eventually drive the whole system to the stable phase.

The calculation of \(\hat{R}\), and therefore of \(\sigma\), is typically done by calculating the time needed to form a critical nucleus, i.e. the nucleation time. From (1) we have that the barrier to nucleation is given by,

\[
\Delta F(\hat{R}) = A \frac{\sigma^{d-1}}{\delta f^d} , \tag{3}
\]

where \(A\) contains all geometrical factor. The nucleation time is simply the time needed to
cross this barrier, which, according to Arrhenius formula, is given by,

\[ \tau_N = \tau_0 \exp \left( \frac{\beta A \sigma^{d-1}}{\delta f^d} \right). \]  
(4)

In finite dimension this time is infinite only at the transition point, where \( \delta f = 0 \), and at zero temperature, where \( \beta = \infty \). Therefore, in finite dimension the decay time of a metastable state is always finite. For this reason, of course, giving a sharp theoretical definition of a metastable state in finite dimension is very difficult. In our work, we will simply give an operational definition of metastability. This can be done by comparing the nucleation time \( \tau_N \) with the equilibration time of the metastable phase, or relaxation time, \( \tau_R \). As long as,

\[ \tau_N \gg \tau_R, \]  
(5)

the metastable phase is operationally well defined, in the sense that it is possible to measure observables which are in local equilibrium, well before the metastable phase decays and becomes heterogeneous. By varying the external parameters, one may reach the kinetic spinodal point, defined by the relation,

\[ \tau_N \sim \tau_R \quad \text{kinetic spinodal}. \]  
(6)

Beyond this point the metastable phase is no longer well defined, since the time needed to relax any perturbation is of the same order as the time needed to form critical nuclei of the stable phase. In what follows we will always operate under the condition of equation (5). In the cases analyzed in the present paper the parameter tuning the first-order transition will be either the magnetic field \( h \), or the temperature \( T \). However, to fix ideas in the general discussion we will consider a 'thermal' setup, with a transition temperature \( T_c \) (where \( \delta f = 0 \)), below which one of the two phases becomes metastable, and a kinetic spinodal temperature \( T_{sp} \), below which the metastable phase becomes kinetically unstable. All our discussion will thus be staged for \( T_{sp} < T < T_c \). To avoid misunderstandings, we also note that throughout the paper we will consider a metastable phase to be in local equilibrium if one-time quantities (as the energy) do not depend on time, and if two-time quantities (as the correlation function) depend only on the difference of times (which ensures that the fluctuation dissipation theorem holds).

One could think that by measuring the nucleation time \( \tau_N \), it is possible to directly access the surface tension \( \sigma \), provided that the \( \delta f \) is known. However, this is practically very hard...
to do, and for many good reasons. First, determining the prefactor \( \tau_0 \) in \( [4] \) is far from trivial\(^{27}\). Nucleation is a dynamical aggregation process, and for this reason it is well known that \( \tau_0 \) is \textit{not} a constant. For example, in liquids it will strongly depend on the temperature, possibly through the diffusion constant \( D \). However, it is still not well established the exact form of the dependence of \( \tau_0 \) on the external parameters, like temperature, density, field, etc. Moreover, the result of classic nucleation theory is not the nucleation time, but rather the nucleation rate \textit{per unit volume}. This is obvious: larger systems have a larger probability to produce stable nuclei\(^{28}\). The consequence is that the prefactor \( \tau_0 \) contains also a volume factor, which may not be easy to determine. Secondly, the geometric factors \( V_d \) and \( S_d \), which enter in \( A \), are not known for general spontaneous droplets, which may have any sort of complicated shape. Note that these factors enter in the exponential, so they are not at all irrelevant. Third, the very calculation of the nucleation time is very difficult, and most of the times it is done inaccurately. A typical protocol is to fix the nucleation time as the time when the amount of stable phase (for example, the crystal) in the system reaches a certain arbitrary threshold. The problem is that by doing this one is mixing \textit{nucleation} and \textit{growth}, which, however, are different phenomena\(^{29}\). In fact, there may be cases when nucleation is very fast, but growth is exceedingly slow, due to the very small mobility of the system. Measuring a \textit{bona fide} nucleation time is extremely difficult, since it requires knowing the size of the critical nucleus. But if we knew it, we would have no need to find out the nucleation time to access the surface tension!

The FPF method avoids these problems, giving us direct access to the critical nucleus. The method can be used both in off-lattice and in lattice models, in any dimension. In the following work, however, we will apply it to systems whose degrees of freedom are spins on a 2d lattice, and thus we will use the familiar 'spin' terminology of statistical mechanics. The system is first prepared in a typical equilibrium configuration belonging to its metastable phase between \( T_{sp} \) and \( T_c \). All the spins outside a certain region (typically spherical) of size \( R \) are then \textit{frozen}. The frozen spins produce a pinning field on the border of the free sphere, which bias the thermodynamics of the sphere. With this setup, the 'bubble' becomes a sort of laboratory for studying nucleation in action: it can either remain in the metastable phase, with free energy density \( f_m \), or flip to the stable phase with free energy density \( f_s \), at the price of paying a surface energy due to the frozen pinning field. We can thus write
the partition function of the subsystem as the sum of two contributions,

\[ Z(R) = \exp \left( -\beta V_d R^d f_m \right) + \]
\[ + \exp \left( -\beta V_d R^d f_s - \beta S_d R^{d-1} \sigma \right) = \]
\[ = Z_0 \exp \left( -\beta V_d R^d f_m - \beta S_d R^{d-1} \sigma \right) , \tag{7} \]

where,

\[ Z_0 = \exp(\beta V_d R^d \delta f) + \exp(\beta S_d R^{d-1} \sigma) , \tag{8} \]

and \( \delta f = f_m - f_s \), is the bulk free energy density difference between the two phases. From the partition function we have that the probability for the bubble to be in the metastable phase is,

\[ P_m(R) = \frac{1}{Z_0} \exp \left( \beta S_d R^{d-1} \sigma \right) , \tag{9} \]

while the probability of finding it in the stable phase is,

\[ P_s(R) = \frac{1}{Z_0} \exp \left( \beta V_d R^d \delta f \right) . \tag{10} \]

Due to the nucleation trade-off explained above, for small \( R \) the bubble stays in the metastable phase, pinned there by the frozen field, whereas for large \( R \) it is thermodynamically more favourable to be in the stable phase. The sharp transition between the two states occurs when \( R \) is equal to to critical nucleus size \( R_c \), which is thus defined by the equation,

\[ P_m(R_c) = P_s(R_c) . \tag{11} \]

The value of the critical nucleus is equal to,

\[ R_c = \frac{\sigma}{\delta f} \frac{S_d}{V_d} . \tag{12} \]

The FPF method consists in measuring the critical nucleus \( R_c \) as the point where the two probabilities are the same. The bulk free energy density difference \( \delta f \) is normally quite easy to obtain (either numerically, or by an extrapolation of the free energy of the stable phase), and the numerical constants \( S_d \) and \( V_d \) are known from the outset, since they depend on the chosen shape of the bubble. As a result, the surface tension \( \sigma \) becomes available. Note that the critical nucleus size \( R_c \) is up to a numerical constant equal to the value \( \hat{R} \) that maximizes Eq. (1).
A possible objection is that this is just the same as considering the entire system and look for stable nuclei. After the discussion above, it should be clear that this is not the case. By considering the entire system, the surface tension can be obtained only on the basis of dynamical observations. The FPF method, instead, extracts information on the surface tension from static probabilities, without the need of any hypothesis on the unknown prefactor of the nucleation time.

We end this Section by noting that Gibbs’ nucleation theory is based on the assumption of sharp edges (or thin walls) separating two homogeneous phases. Nevertheless the theory is still valid as far as the critical nucleus is big enough to contain a homogeneous core. Several theories have been introduced to treat the case in which the nucleus is completely non-homogeneous, defining a local free-energy in a non-uniform system. The FPF method uses the simple scheme of nucleation theory, but, as we shall see in the following, it is also able to find out whether we really are in the validity range of this scheme, whether a homogeneous core exists, and, in the case where the edge is not sharp, to study the profile of the order parameter across the boundary.

III. THE PARAMAGNETIC ISING MODEL

The first system we consider is the Ising model in two dimensions,

\[ H = -J \sum_{\langle i,j \rangle} s_is_j, \tag{13} \]

with \( s_i = \pm 1 \) and the sum is over nearest-neighbours. Even though our main interest is to test the FPF method within the first-order transition induced by the presence of a magnetic field below \( T_c \), we will first study the method above \( T_c \), in the paramagnetic phase. This will be a useful warm-up exercise to get familiar with all features of the method not strictly related to the presence of a nucleation-driven transition. In the following we will take \( J = 1 \) with no loss of generality.

The main point of the FPF method is to control whether the free bubble changes phase or not. To this aim a convenient tool is to use the overlap \( Q \) between two different configurations of the bubble, let us call them \( \{ \rho_i \} e \{ \tau_i \} \),

\[ Q \equiv \frac{1}{n(R)} \sum_{i=1}^{n(R)} \rho_i \tau_i = \frac{1}{n(R)} \sum_{i=1}^{n(R)} q_i \tag{14} \]
where $n(R)$ indicates the number of spins in the bubble, $R$ represents the bubble’s size, and $q_i \equiv \rho_i \tau_i$. In the paramagnetic phase, there is no possibility for the bubble to flip to another states, and both $\{\rho_i\} e \{\tau_i\}$ will belong to the paramagnet. In $d = 2$, we can rewrite $Q$ as,

$$Q(R) = \frac{2}{R^2} \int_0^R dr \, r \, q(r),$$

(15)

where $q(r)$ is the radial overlap, i.e. the average overlap of a shell of spins of radius $r$ within the bubble. In presence of a single paramagnetic phase, it seems reasonable to assume that the radial overlap $q(r)$ decays exponentially off the border with characteristic length $\lambda$,

$$q(r) = q_0 \exp\left(-\frac{R - r}{\lambda}\right),$$

(16)

where $q_0$ is the value of the local overlap at the border, which varies with the temperature $T$. By plugging this form into (15) we get,

$$Q(R) = 2q_0 \frac{\lambda}{R} \left[1 - \frac{\lambda}{R} \left(1 - \exp\left(-\frac{R}{\lambda}\right)\right)\right].$$

(17)

The length $\lambda$ gives an estimate of the thickness of the layer directly influenced by the frozen pinning field at the border.

We performed Montecarlo simulations to study a bidimensional Ising square lattice (1000x1000) at several temperatures in the interval $T \in [1.015T_c : 1.039T_c]$, and at zero magnetic field. We freeze the system in an equilibrium configuration, and follow the evolution of a free bubble (a disc, in fact) of radius $R$. For every size $R$, we averaged over 200 independent pinning fields, and over 1000 Montecarlo sweeps for each pinning field. The function (17) provides a good fit to the $Q(R)$ values at the several temperatures considered. By using standard methods we have also computed the correlation length $\xi$ of the system, which is known to diverge as $(T - T_c)^{-1}$ in two dimensions. Both $\lambda$ and $\xi$ are plotted in Figure 1: one clearly sees that they are basically the same length-scale. Not surprisingly, the thickness of the superficial layer most influenced by the pinning field is the same as the correlation length.

IV. THE ISING MODEL IN A FIELD

The Ising models below $T_c$ has a first-order phase transition ruled by the magnetic field $h$, and a transition point at $h_c = 0$. At negative values of the field the ’up’ phase is metastable,
and it does eventually decay to the stable 'down' phase. We want to use the FPF method to evaluate the size of the critical nucleus and the value of the surface tension. In order to have a well-defined metastable phase we have to stay away from the kinetic spinodal, that is we have to choose a field whose absolute value is smaller than the kinetic spinodal $h_{sp}(T)$ at that particular temperature. On the other hand, the field cannot be too small: the free energy difference $\delta f$ which enter in eq.(14) is proportional to the field, so that when $|h|$ decreases, the nucleation time increases exponentially. Thus, when the field is too small, a fair sampling of the bubble’s phase space, obtained by letting it flip between the two phases a sufficiently large number of times, becomes impossible. If we call $h^*$ this minimal value of the field, we have to work in the window $h^* < |h| < h_{sp}$. We study the FPF method at temperature $T = 0.56T_c$, where we have found that the field interval $h \in [-0.35 : -0.23]$ satisfies these requirements.

In Figure 2 we see the time evolution of the overlap between the initial metastable configuration of the bubble and its configuration at time $t$. The size $R$ in this particular run was very close to the critical one, and a clear flip-flop between the stable and metastable phases can be seen. In Figure 3 we report the probability distribution of the overlap.

The average overlap $Q$ as a function of $R$ is reported in Figure 4 the sharp jump corresponding to the size of the critical nucleus $R_c$ is very clear. In order to be sure that we have sampled fairly the bubble’s phase space we initialize it both in the metastable and in the stable phase, and check that we get the same asymptotic results (see Fig. 4). This means that we correctly thermalized the bubble. From the Eqs. (9) and (10) we can write

$$Q(R) = P_m(R)q_{mm}(R) + P_s(R)q_{ms}(R),$$

(18)

where $q_{mm}$ and $q_{ms}$ are respectively the overlap of the metastable phase with itself (self-overlap), and with the stable one. These values, however, do not refer to the entire system, but are restricted to the bubble of radius $R$. We already know from the paramagnetic case that even with one single phase the average overlap $Q(R)$ does not decay sharply to its asymptotic value, but it rather has a slow power-low behaviour dependent on $R$. This is due to the presence of a layer influenced by the pinning field. For this reason we indicate a $R$ dependence into $q_{mm}$ and $q_{ms}$, which is particularly evident after the jump if Fig. 4: the overlap does not directly reach the asymptotic value between the metastable and stable phase ($Q = 1$). Rather, the sharp drop-off at $R_c$ becomes a smooth decay for $R > R_c$. 

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As we have said, this behaviour is the result of the finite interfacial thickness of the region between the two phases. As in the paramagnetic phase of the Ising model the presence of a transition region moves the mean global overlap value away from the value of a uniform subsystem.

Unlike in the paramagnetic case, we now deal with the contact between two different phases, and one may therefore think that the interfacial thickness $\delta$ has an entirely different origin compared to the length $\lambda$ we obtained in the paramagnet. However, within Van der Waals theory of liquid-vapour coexistence, it has been demonstrated that $\delta$ diverges at the critical point with the same critical exponent as the bulk correlation length $\xi$, as we found in the paramagnetic phase. Using eq. (17), with $\delta$ in place of $\lambda$, one obtains that at large $R$ the overlap $Q(R)$, should decay as $Q(R) \sim \delta/R$. A careful study of our data for $Q(R)$, however, shows that it decays slightly faster than $1/R$. This suggests that also the width $\delta$ varies with $R$, decreasing with the surface curvature, and approaching an asymptotic value $\delta_\infty$ for very large $R$ (flat surface).

The critical nucleus size can be extracted from the probability distribution of the overlap, as the point where $P_m = P_s$, that is the size of the bubble spending half of its time in the metastable phase and half in the stable one. In particular, we can interpolate the value of $R_c$ (and calculate its error) from the two data immediately smaller and larger than the value $P(R) = 1/2$. The values of the critical nucleus obtained at $T = 0.56T_c$ are listed in Tab.1.

From classic nucleation theory, for a disc in two dimensions, we have,

$$R_c = \frac{2\sigma}{\delta f}.$$  \hspace{1cm} (19)

At our values of temperature and field one can prove that a very good approximation is,

$$\delta f \sim 2h,$$  \hspace{1cm} (20)

thus giving,

$$\sigma = R_c h,$$  \hspace{1cm} (21)

giving the values of surface tension $\sigma$ listed in the third column of Tab.1. As expected, the surface tension $\sigma$ very weakly depends on $h$. In fact, if we plot the critical nucleus size against the inverse of the field (Fig.5), we find a very good linear behaviour. A linear fit gives $\sigma = 1.94$, compatible with the values in Tab.1.
We now want to compare the FPF estimate of the surface tension with the exact result of Onsager\textsuperscript{34}: the expression of the surface tension for an interface parallel to the lattice axes in the two-dimensional Ising model at zero field is,

\[
\sigma_{\text{ONS}} = \{2J - k_B T \log[\coth(J/k_B T)]\} .
\]  

(22)

At our working temperature this relation gives,

\[
\sigma_{\text{ONS}} = 1.467 .
\]  

(23)

Before we can compare with our result, we have to make remarks. First, Onsager’s value holds at \( h = 0 \), whereas we are working at non-zero field, therefore we do not expect the two values to be identical. However, as already said, the dependence of \( \sigma \) on the field is weak: only close to the spinodal the surface tension is expected to abruptly decrease. Secondly, and more importantly, we computed the surface tension for a disc, whereas Onsager’s value refers to an interface parallel to the (square) lattice. In this latter case, the number of bonds is equal to the number of spins along the surface, whereas in the disc the average number of spins is equal to \( 2\pi R/l \) and the number of bonds is \( 8R/l \) (\( l \) is the lattice spacing). Therefore the surface tension for the straight surface must be smaller than that of the disc by a factor equal to the ratio between spins and bonds, i.e. \( \pi/4 \). These values are listed in the fourth column of Tab.1.

The agreement between our estimate and Onsager’s value is on average within 5%. Considered the remarks above about the fact that we are at non-zero value of the magnetic field, this result is encouraging. Note that to get this result we had to perform no infinite size extrapolation, and the computational time is therefore relatively limited. However, if we wanted to obtain the value of \( \sigma \) for \( h \to 0 \), in order to exactly check Onsager’s results, we would get larger and larger critical sizes \( R_c \), and this \textit{would} in fact require an infinite size limit. Considered that, as we have already said, the dependence of the surface tension of the field is very small, it is just a matter of convenience to perform or not this limit. On the other hand, if one needs the surface tension at \textit{finite} values of the field, then the value of \( R_c \) is finite, and the large \( N \) limit is not at all necessary.

To conclude this Section, we study the dependence of the critical nucleus size \( R_c \) on the temperature, at fixed magnetic field. We use the FPF method with magnetic field \( h = -0.25 \) and temperatures \( 0.56T_c \) and \( 0.64T_c \). The resulting values of the of the critical size at the
listed temperature are, $R_c(0.56T_c) = 7.83 \pm 0.06$ and $R_c(0.64T_c) = 7.24 \pm 0.01$. The increase of the temperature induces a slight decrease of the critical size $R_c$. Why is that? When the temperature is increased, we have a decrease of both $\sigma$ and $\delta f$. Yet, $\sigma$ variation with $T$ is almost linear according to Onsager equation, while at temperatures well below $T_c$ and weak magnetic field, the change of $\delta f$ is weak, since it is mainly given by the change in the magnetization $m$, which saturates rapidly to 1, far from $T_c$. Therefore the decrease of $\sigma$ is sharper than that of $\delta f$, and for this reason $R_c = \sigma/\delta f$ decreases when $T$ is increased far from $T_c$.

From the value of $R_c$ at $T = 0.64T_c$ and from the corresponding $\delta f$, we get,

\[
\sigma = 1.810 \pm 0.003
\]  

and

\[
\sigma \cdot \pi/4 = 1.421.
\]  

Onsager’s surface tension at the same temperature is,

\[
\sigma_{\text{ONS}} = 1.29.
\]

At this temperature the agreement between the FPF surface tension and Onsager’s one is worse than the one at $T = 0.56T_c$, even though still within 10%.

We note that in all cases considered the FPF method gives a surface tension slightly larger than the exact zero-field result. Although the field is non-zero in our case, we believe the discrepancy mainly comes from a different effect, namely the fact that our method overestimates the size of the critical radius $R_c$ by an amount roughly equal to the interfacial thickness. The reason for this is quite simple: due to the frozen nature of the external environment, the order parameter can change its value only within the disc, and not in going through the disc. The intermediate value (zero, for the magnetization), which defines the bona fide border of the critical droplet, is therefore attained at the interior of the disc, and it is thus smaller than the one we measure, by an amount approximately equal to half of the interfacial thickness. Indeed, as we have seen, the discrepancy is larger at larger temperature, where one expects to have a thicker interface. Of course, such effect is negligible when the size $R_c$ of the bubble is much bigger than the interfacial thickness.
V. A MODEL WITH TEMPERATURE-DRIVEN FIRST-ORDER TRANSITION

The parameter tuning the first-order transition in the Ising model is the magnetic field, and both the stable and the metastable phases are ordered (ferromagnetic). Due to this, the frozen pinning field produced by the metastable configuration on the border of the bubble is quite similar to a standard magnetic field (up to thermal fluctuations), and this makes the setup of the FPF method somewhat predictable. In this section we will apply the FPF method to a model with a first-order transition driven by temperature, rather than magnetic field. In such a model we will consider a disordered (liquid-like) metastable phase, in contact with an ordered (crystal-like) stable phase. In this way we will test the FPF method in a far less trivial context than the Ising model.

The two-dimensional lattice model we consider is called CTLS (Coupled Two Levels System), and it was studied in\(^29,35\). The Hamiltonian of the model is,

\[ H = J \sum_{i=1}^{N} f_i (1 + \sigma_i) \]  \hfill (27)

where \( N \) is the number of spins and \( f_i \) indicates the product of the 4 nearest neighbour spins,

\[ f_i = \sigma_i^N \sigma_i^S \sigma_i^E \sigma_i^O, \]

where \( N \) stands for north, \( S \) for south, and so on. The CTLS has a crystalline ground-state (Fig.6), and the low temperature crystalline phase is separated by a high temperature disordered ‘liquid’ phase by a first-order transition at a melting temperature \( T_m = 1.30 J/k_B \). The multibody interaction in the Hamiltonian introduces frustration in the system, and due to this the CTLS exhibits a behaviour typical of supercooled and glassy systems\(^29\), with many disordered local minima of the energy. Below the melting temperature, the liquid enters a metastable region, which is bounded by a kinetic spinodal at a temperature \( T_{sp} \): below \( T_{sp} \) the relaxation time of the metastable liquid phase becomes larger than the crystal nucleation time. The metastable phase becomes therefore kinetically unstable below \( T_{sp} \). Our test of the FPF method will thus be performed for \( T_{sp} < T < T_m \).

We equilibrate the system in a metastable liquid configuration below \( T_m \), and we freeze all spins outside a disc of radius \( R \). In order to check what phase the disc is in, we must introduce a suitable order parameter. Following\(^29\) we define the local crystalline mass \( m_i \in [0 : 1] \). In the temperature range we will consider we have \( \langle m \rangle \sim 1 \) in the stable crystalline phase, and
$\langle m \rangle \sim 0.3$ in the metastable liquid phase. Therefore, the crystalline mass is a good order parameter to distinguish the liquid from the crystal phase. The average crystal mass of the disc,

$$M = \frac{1}{n(R)} \sum_{i=1}^{n(R)} m_i ,$$

(28)

where $n(R)$ is the number of spins within the disc, is plotted as a function of time for a particular value of $R$ in Figure 7. This value of $R$ is quite close to the critical nucleus. Even though the jumps between stable and metastable phases are less clear-cut than in the Ising case, the histogram still shows a very evident bimodal distribution of the order parameter (Figure 8). The two peaks correspond to the probabilities of the liquid (LQ) and crystalline (CR) phases. By changing the radius $R$ of the bubble the balance between the two phases changes according to nucleation’s prediction. The critical nucleus size $R_c$ corresponds to the point where the two peaks have the same weight. In the inset of Figure 8 we plot the probability $P_{CR}$, i.e. the weight of the crystalline peak, as a function of $R$.

As we did in the Ising model we can now obtain the value of the critical nucleus: $R_c = 27.4 \pm 0.4$ at $T = 0.931T_m$ and $R_c = 28.8 \pm 0.5$ at $T = 0.938T_m$. Using the liquid-crystal bulk free energy difference $\delta f(T)$ calculated in 29, it is finally possible to find the corresponding surface tension values: $\sigma(0.931T_m) = 0.262 \pm 0.004$ and $\sigma(0.938T_m) = 0.250 \pm 0.004$. As in the Ising model, the surface tension is very weakly dependent on the parameter driving the transition (the temperature, in this case), provided that we are far enough from the spinodal point.

We note from the distribution of $M$ that even for $R > R_c$, the position of the (unique) crystalline peak is quite far from its equilibrium value $M \sim 1$. This is also clear from the average value of $M$ as a function of $R$ in Figure 9. If we assume that the radial order parameter $m(r)$ goes exponentially fast to 1 off the border,

$$m(r) = 1 - (1 - m_0) \exp(-r/\delta) ,$$

(29)

then, as we have seen in Section III, the large $R$ behaviour of $M(R)$ is,

$$M(R) \sim 1 - \delta/R$$

(30)

Therefore, the reason why the behaviour of $M(R)$ in Figure 9 is so smooth, is because the interfacial thickness $\delta$ is quite large in the CTLS. This suggests to check just the center of the bubble, rather than the entire disc, in order to get rid of the border effects and only
monitor the inner thermodynamics of the disc. More precisely, we can average the order parameter over a small circle of fixed radius \( \alpha \) around the center, and study the core order parameter \( M_0(R) \). A simple calculation gives,

\[
M_0(R) = 1 - 2(1 - m_0) \int_0^\alpha \! dr \, r e^{-\frac{R-r}{\delta}} \\
= 1 - \mathcal{M} e^{-\frac{R}{\delta}}
\]

with

\[
\mathcal{M} = \frac{2\delta}{\alpha} (1 - m_0) \left\{ 1 - \frac{\delta}{\alpha} \left[ 1 - e^{-\frac{\alpha}{\delta}} \right] \right\}.
\]

At fixed \( \alpha \), \( M_0(R) \) increase exponentially fast in \( R \), and due to this the jump at \( R_c \) of \( M_0(R) \) is much sharper than the one of \( M(R) \) (see Figure 9). Therefore, as a way to check whether the bubble exposed to the frozen pinning field has switched state or not, the core order parameter \( M_0(R) \) is certainly a better choice than \( M(R) \).

According to equation (31), \( \log\left[(1 - M_0(R))/\mathcal{M}\right] \) must be a linear function of \( (\alpha - R)/\delta \). This is very well verified by our data, and a linear interpolation gives an estimate of the interfacial thickness, \( \delta = 8.6 \pm 0.6 \). This shows that in the CTLS \( \delta \) is much larger than in the Ising model. It becomes therefore interesting to study the profile of the order parameter \( m(r) \) across the interface. According to Cahn and Hilliard, the order parameter across the liquid-vapour interface can be described by an hyperbolic-tangent of width \( \delta \). We can make a similar fit in our case for the crystal mass,

\[
m(r) = \frac{1}{2} \left[ 1 + m_0 + (1 - m_0) \tanh \left( -\frac{R-r}{\delta} \right) \right].
\]

This functional form works well only for large bubbles (large \( R \), Figure 10). The reason for this is that for \( R < R_c + 2\delta \), the transition region is forced into a region sharper than the natural one and it cannot take the profile that it would have in a spontaneously formed nucleus. The interfacial thickness \( \delta \) from equation (34) is \( \delta = 11 \pm 2 \), compatible with the one form eq. (31).

Finally, we want to understand more carefully what is the effect of the frozen pinning field produced by the metastable liquid surrounding the bubble. From the profile of the order parameter in Figure 11, it is clear that there is a wide region close to the border where the configuration is no longer crystalline, and it is becoming liquid. The interesting fact is that this intermediate liquid configuration is anyway very different from the initial liquid.
configuration the bubble was in. This can be seen by measuring the radial overlap $q(r)$ between the asymptotic configuration and the initial configuration of the disc (Figure 11). The overlap is very close to zero within the disc, telling us that the bubble has abandoned its initial liquid configuration. What is interesting is that $q(r) \sim 0$ even in the intermediate crossover region: this region is therefore almost liquid, but a different liquid configuration from the initial one. In other words, what we see here is that the frozen pinning field is attracting the sphere toward the liquid phase, rather than just toward the liquid configuration in which the system was frozen. Given that two different configurations of the same liquid phase have almost zero overlap, then $q \sim 0$ even in the region where $m$ is rapidly decreasing. This phenomenon was impossible to see in the Ising model, since in that case the pinning metastable phase had a very small entropy, and there was little difference between configurations belonging to the same phase.

VI. THE PROBLEM OF THE EQUILIBRIUM SHAPE

The problem of what is the equilibrium shape (ES) of the critical nucleus is a very old and, in general, very difficult one. When the system is isotropic, the surface tension is independent of the orientation, and it is easy to demonstrate that the ES is a sphere. However, in non-isotropic systems the situation is not as simple as that. Within the FPF method the droplet’s shape is imposed from the outset, and it is therefore reasonable to ask to what extent the surface tension obtained from the FPF depends on the imposed shape. As we are going to explain, there are in fact two distinct issues related to this point.

First of all, irrespective of nucleation and of the shape of the critical droplet, there is the problem that in non-isotropic systems the surface tension depends on the orientation of the surface itself. This is what happens typically on a lattice. In the Ising case, studied above, we get different values of the tension when the surface is parallel to the axes, diagonal, or circular. However, as we have seen, knowledge of the symmetry of the lattice allows us to relate all these values one to another by simple numerical factors (respectively $\sqrt{2}$ and $4/\pi$). This is something that can in principle be done for every system whose symmetries we have enough knowledge about. If, on the other hand, we have no a priori knowledge about interfacial orientations, the best we can do is to apply the FPF method using any convenient shape, and get an effective surface tension function of the (possibly many) elementary values,
σ₁, σ₂, ⋯

A second, distinct, problem is the one of the optimal equilibrium shape (ES) of the critical nucleus, also known as Wulff’s shape\(^{36}\). What happens if the shape imposed by the FPF method is very different from the ES? Imagine a system where the ES is very anisotropic, for example a long rectangle, with critical values of the sides \(L_1 \gg L_2\), and assume that we use a disc of radius \(R\) within the FPF method. One may argue that as long as \(2R < L_1\) the critical (rectangular) droplet cannot be formed, and therefore the disc does not change state, whereas for \(R > L_1\) we will observe the formation of rectangular nuclei within the disc. This is, however, not the case: in the Ising model, where the ES is much more similar to a square than a disc at low temperatures\(^{37}\), we never observe the formation of squares within the imposed disc (unless the disc is really much larger than the critical nucleus, such that the disc itself becomes an independent sub-system); on the contrary, when a change of state takes place, it is always the entire disc that participates to it. This means that the whole FPF shape switches state whenever the balance between area and surface of that particular shape becomes convenient. We believe this is due to a sort of nucleation ‘pressure’ within the imposed shape. It is clear, however, that this point needs further clarification.

VII. CONCLUSIONS

We described a novel method for the determination of the critical nucleus size, and of the surface tension between stable and metastable phases in systems with first-order phase transition. The main idea of the method is to stabilize the metastable phase of the system by freezing it outside a bubble of radius \(R\). By studying the thermodynamics of the bubble as a function of \(R\), we unveil the balance between the surface tension contribution, forcing the bubble to stay in the metastable phase by means of the frozen pinning field, and the free energy difference drive to switch to the stable phase. The critical radius \(R_c\) is defined as the point where these two contributions are equal. What we observe is therefore a sort of first-order transition as a function of the parameter \(R\), the size of the bubble.

We note that compared to other methods, the FPF method does not resort to a dynamical study of the nucleation events happening spontaneously in the system. Due to this, the FPF method avoids all the pitfalls related to the dynamical prefactor of the nucleation time, and to finding an accurate way to distinguish nucleation from growth. Moreover, our method
does not need a $N \to \infty$ extrapolation to produce a result, unless one needs to use it at the coexistence point, where there is no free energy difference between the two phases, and $R_c \to \infty$.

We used the FPF method to compute the surface tension in the two-dimensional Ising model in a field, where we get a result fairly consistent with Onsager exact calculation. Secondly, we analyzed a model (the CTLS) where a liquid-crystal first order transition driven by temperature exists. In this case, despite the fact that the metastable phase (the liquid) is disordered, we still find a very sharp bimodal probability distribution of the order parameter, and thus the determination of the critical nucleus and of the surface tension is very easy to do. In this model, the interface between the ordered and the disordered phase is far from being thin, stretching the very validity of Gibbs’ nucleation theory. Moreover, we saw in a clear way that the effect of the disordered (liquid) frozen pinning field is to attract the bubble to the disordered phase, and not simply the initial disordered configuration.

We believe the FPF method could be of some help also in other systems, including off-lattice systems. The fact that it can only be used away from the coexistence point should not be a major problem. The main aim of the method is to compute the surface tension, but this quantity is typically very weakly dependent on the parameter tuning the first-order transition, provided that we are not close to the spinodal point, where anyway the metastable phase is ill-defined.

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This work was directly inspired by the theoretical experiment proposed to test the mosaic scenario in supercooled liquids by G. Biroli and J.P. Bouchaud in\textsuperscript{21}. This experiment was later implemented numerically in a glassy system by T.S. Grigera, P. Verrochio and A.C. in\textsuperscript{23}. We thank all of them for their feedback. We also thank G. Parisi for many important suggestions, and I. Giardina, V. Lecomte, and E. Marinari for interesting discussions.

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### TABLE I: The critical sizes $R_c$, the corresponding surface tension values $\sigma$ at several magnetic field values $h$ and temperature $T = 0.56T_c$.

| $h$ | $R_c \pm \Delta R_c$ | $\sigma \pm \Delta \sigma$ | $\sigma \cdot \pi/4$ |
|-----|----------------------|--------------------------|------------------|
| 0.23 | 8.50 ± 0.06          | 1.96 ± 0.01              | 1.54             |
| 0.25 | 7.83 ± 0.06          | 1.96 ± 0.02              | 1.54             |
| 0.27 | 7.27 ± 0.01          | 1.963 ± 0.003            | 1.542            |
| 0.29 | 6.87 ± 0.04          | 1.99 ± 0.01              | 1.564            |
| 0.31 | 6.28 ± 0.01          | 1.945 ± 0.004            | 1.528            |
| 0.33 | 6.2 ± 0.1            | 2.05 ± 0.04              | 1.61             |
| 0.35 | 5.51 ± 0.01          | 1.928 ± 0.005            | 1.514            |